RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 3 15 JULY 1991-I

Ultrathin films of Rh on Au{001} and Rh on Ag{001}: Growth mode and magnetism

H. Li, S. C. Wu,* D. Tian, Y. S. Li, J. Quinn, and F. Jona
College of Engineering and Applied Science, State University of New York, Stony Brook, New York 11794

(Received 15 April 1991)

Deposition of minute amounts of Rh on a clean and reconstructed Au{001} surface destroys the reconstruction and yields a 1×1 structure. Prolonged deposition produces epitaxial but not pseudomorphic films of Rh with the bulk equilibrium fcc structure. Deposition of Rh on a clean Ag{001} surface produces overlayers which are partially covered by or intermixed with Ag, but which are pseudomorphic with the Ag{001} substrate. Photoemission experiments in the very early stages of overlayer growth reveal a 4.1 ± 0.3 eV splitting of the 4*s* levels of Rh, which is not observed in thick Rh films. The 4*s* splitting is explained by the presence of a magnetic moment on the Rh atoms and is related to recent theoretical predictions of ferromagnetism in a monolayer of Rh on either Ag{001} or Au{001}.

Recent theoretical studies have produced interesting predictions about possible magnetism of 4*d* overlayers on nonmagnetic substrates. Thus Zhu, Bylander, and Kleinman[1] (ZBK), using a scalar-relativistic norm-conserving pseudopotential and a Gaussian-orbital expansion, have calculated the magnetic moment of a free-standing Rh monolayer to be 1.56 μ_B and that of an epitaxial monolayer of Rh on Au{001} to be 1.09 μ_B. Eriksson, Albers, and Boring,[2] doing *ab initio*, spin-polarized, electronic-structure calculations within the framework of the local-spin-density approximation, have presented theoretical evidence for ferromagnetism of monoatomic overlayers of Rh or Ru on Ag{001}.

The present paper describes experimental efforts directed at testing the theoretical predictions of Rh on Au{001} and Rh on Ag{001}. The tools used in these experiments were low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and ultraviolet photoemission spectroscopy (UPS). LEED was used for investigations of the atomic structure and of the growth mode of the overlayers; AES was used for determinations of surface composition and coverage; UPS was used for tests of the presence of magnetic moments through studies of possible splitting of the 4*s* core levels. The experiments were done on beamline *U7B* of the National Synchrotron Light Source at the Brookhaven National Laboratory.

The substrates were prepared according to conventional procedures, i.e., they were oriented along a ⟨001⟩ direction to within ±0.5°, lapped and mechanically polished with abrasives of decreasing particle sizes (1, 0.3, and 0.05 μm). Prior to introduction into the experimental chamber the Au{001} sample was electrolytically polished to remove the damage caused by the abrasives. The base pressure in the chamber was about 1×10^{-10} Torr and cleaning *in situ* involved argon-ion bombardments (5×10^{-5} Torr, 400 eV, 10 μA) followed by anneals at about 500 °C (for Au) and 600 °C (for Ag). The Rh source consisted of a 0.25-mm Rh wire wrapped around a *W* spiral that was electrically heated. The distance between source and substrates was about 25 cm.

The surface coverage was determined from the ratio $R = I_{\mathrm{Rh}(300)}/I_{\mathrm{Au}(239)}$ or $R = I_{\mathrm{Rh}(300)}/I_{\mathrm{Ag}(356)}$ between the intensity of the Rh AES line at 300 eV and the intensities of the Au or Ag AES lines at 239 and 356 eV, respectively, with the formula

$$R = R_0 \frac{1 - e^{-d/\lambda_{300}}}{e^{-d/\lambda_{230\ \mathrm{or}\ 356}}}, \tag{1}$$

where $R_0 = I^{\infty}_{\mathrm{Rh}(300)}/I^{\infty}_{\mathrm{Au}(239)} = 17.5$ or $R_0 = I^{\infty}_{\mathrm{Rh}(300)}/I^{\infty}_{\mathrm{Ag}(356)} = 0.625$ (Ref. 3); I^{∞} denotes the intensity of the AES line from a very thick sample of Rh at 300 eV or Au at 239 eV or Ag at 356 eV; the λ's are the inelastic mean-free paths of electrons with 300, 239, or 356 eV energy traveling in Rh ($\lambda_{239} = 8.32$ Å, $\lambda_{300} = 9.40$ Å, $\lambda_{356} = 10.20$ Å, data calculated from the formula given by Seah and Dench[4]); and d is the thickness of a film of Rh assumed to be uniform over the substrate surface. Taking $d \approx 2$ Å, we will quote surface coverages below in units of layer equivalents (abbreviated LE), with the understanding that 1 LE is the amount of adsorbate that produces the same value of R as would be produced by a uniform monolayer of the adsorbate on the substrate surface.

We describe experiments and observations on the two substrates separately, first for Rh overlayers on Au{001} and then for Rh overlayers on Ag{001}.

Rh ON Au{001}

The LEED pattern of clean Au{001} reflected the well-known reconstruction labeled 5×20, or more precisely denoted $\left(\begin{smallmatrix} 14 & 1 \\ -1 & 5 \end{smallmatrix}\right)$, in terms of the bulk basis vectors. With the sample at room temperature, this pattern exhibited a high signal-to-background ratio only at low electron energies and could, in fact, be observed only for incident-electron energies smaller than about 200 eV. Above 200 eV the diffraction beams were practically indistinguishable over a large background. Immediately after deposition of Rh, for surface coverages estimated to be about 0.1 or 0.2 LE, the LEED pattern became 1×1 with markedly larger signal-to-background ratio and diffracted beams clearly distinguishable up to energies of about 400 eV. Figure 1 depicts AES scans of a clean Au{001}-5×20 surface and of a Rh-induced Au{001}-1×1 surface. A quan-

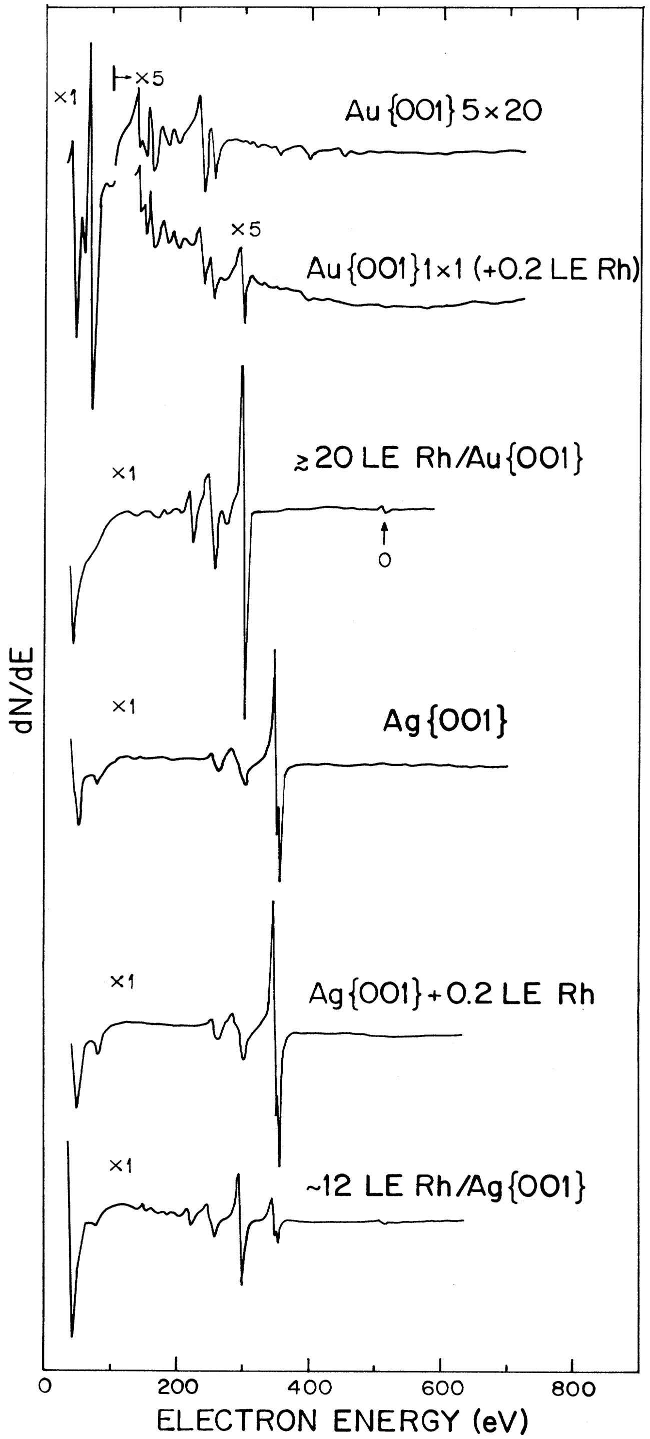

FIG. 1. AES scans of Au{001} and Ag{001} surfaces and of Rh overlayers as discussed in the text.

titative LEED intensity analysis of the Au{001}-1×1 structure (to be reported elsewhere) shows that the atomic arrangement was that of a nonreconstructed and relaxed {001} surface.

With prolonged deposition of Rh the LEED pattern remained 1×1, but the background increased, the intensity-versus-energy [so-called I(V)] spectra exhibited small and progressive changes, and the diffracted beams began to split. Figure 2 shows a sequence of profiles taken along a ⟨11⟩ line in reciprocal space with incident-electron energy of 146.5 eV and for increasing Rh coverage. We note that the 11 beams, initially single as due to the Au{001}-1×1 surface, split into two when the Rh coverage reached above 2 LE and finally became single again when the Rh film grew very thick (more than 20 LE). Measurements show that the inner set of beams corresponds to the in-plane lattice constant of Au{001}-1×1 (2.88 Å), while the outer set corresponds to a lattice constant about 7% smaller, suggesting that it stems from Rh islands with their own equilibrium in-plane lattice constant (2.69 Å).

The I(V) spectra measured on a thick Rh film (greater than 20 LE, AES spectrum depicted in Fig. 1) proved to be essentially the same as those measured on a bulk Rh{001} sample (not shown), showing again that the Rh film grew with its own equilibrium in-plane lattice constant.

Thus the growth process of Rh on Au{001} as revealed by LEED involved, at least in the later stages, epitaxial but not pseudomorphic islands. The high background in the LEED pattern indicated the presence of defects and misfit dislocations, as would be expected in a case of incommensurate epitaxial growth. Whether layer-by-layer growth occurred at the submonolayer or monolayer level is not known at this time. The present study provides no evidence for layer-by-layer growth in the very early stages, but cannot exclude the presence of a few separated, mostly monoatomic, islands of Rh on the Au{001} surface.

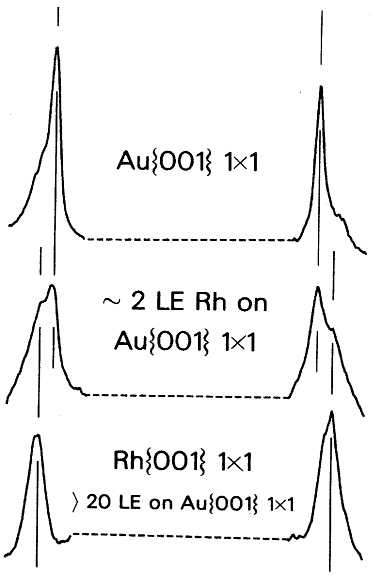

FIG. 2. Profiles of the 11 beams at 146.5 eV for (top panel) Au1×1 (with Rh), (middle panel), 2-LE–3-LE film of Rh on Au{001} (the splitting results from bulk Rh islands with the Rh equilibrium structure on the bare Au{001} substrate) and (bottom panel) thick (> 20 LE) epitaxial Rh{001} film.

Photoemission from the 4*s* levels of Rh was investigated with photon energies ranging from 105 to 165 eV. Figure 3 depicts the electron-distribution curve measured on a 20-LE Rh film grown on Au{001}. We note the presence of an emission peak at 81.4 eV, due to the Rh 4*s* level, and of emission peaks at 74.1, 83.7, and 87.6 eV, due to the Au $5p_{1/2}$, $4f_{7/2}$, and $4f_{5/2}$ levels, respectively. It is obvious that the presence of the Au core levels due to Au substrate makes it practically impossible to detect any eventual splitting of the Rh 4*s* levels.

Rh ON Ag{001}

The Ag{001} surface is not reconstructed—the LEED pattern of the clean surface was a sharp low-background 1 × 1 pattern. Deposition of Rh on this surface caused increase of the background but no change on either the geometry of the pattern or the energy dependence of the diffracted intensities. For Rh coverages between 0.2 and about 20 LE (see Fig. 1) the LEED spectra remained 1 × 1 with an increased background.

This observation is easily explained by the assumption of growth either of a pseudomorphic (and therefore strained) overlayer of Rh and/or of a mixture of Rh and Ag with the in-plane lattice constant of Ag. Since Rh and Ag, with atomic numbers 45 and 47, respectively, have very similar ion cores, LEED cannot distinguish between them if they have the same atomic structure. Hence, the increase in Rh concentration on the Ag surface upon prolonged Rh deposition could only be monitored with AES, not with LEED. But even after long exposures of the substrate to the Rh source (exposures which, according to estimates made from the deposition rate as determined in the Rh-Au experiments, should have produced Rh films of more than 20 LE) the Ag signal was still large in the AES scans (see Fig. 1). There are two explanations for these results: (1) experiments and calculations by the Iowa group[5] have shown that while the formation of a Rh monolayer on an Ag surface may be possible, the Rh layer is then immediately covered by a layer of Ag, even at room temperature; (2) the sensitivity of AES is much larger for Ag than for Au (Ref. 3), so that even small amounts of interdiffusion that would be difficult to detect

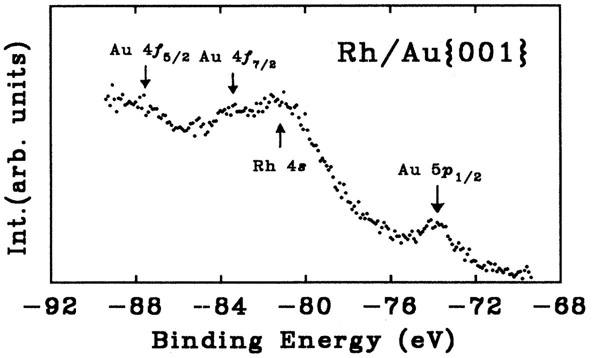

FIG. 3. Electron-distribution curves from a thick Rh film on Au{001} of the Rh 4*s* and the Au 4*p* and 4*f* levels (photon energy 168 eV).

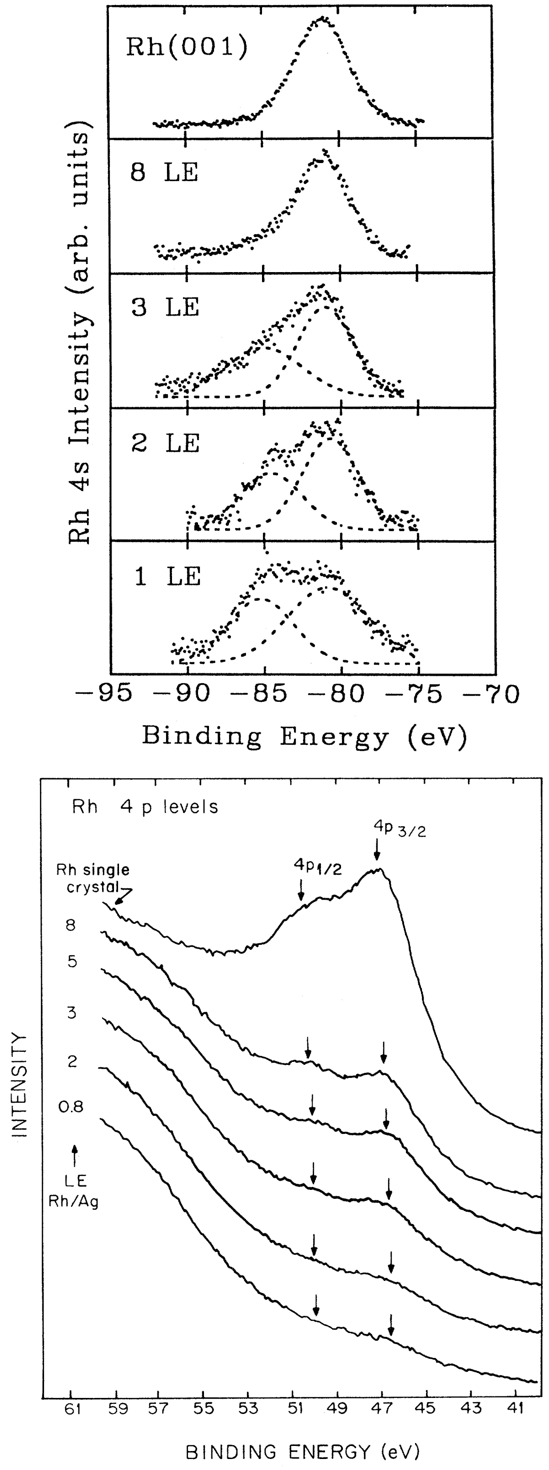

FIG. 4. Top panels: Rh 4*s* levels for increasing Rh coverage, given on the left-hand side in LE. The experimental data (black dots, after background subtraction) were fitted with two Gaussians (dashed curves). The splitting is obvious at low Rh coverages (lower three panels), but is not visible in thick Rh films, which produce curves indistinguishable from those of single-crystal Rh (top panel). The photon energy is 165 eV. Bottom panel: Rh 4*p* levels for increasing Rh (background not subtracted). The photon energy is 110 eV.

in the case of Au are easily seen in the case of Ag.

We conclude therefore, from the combined LEED and AES studies, that, whether or not limited Rh-Au interdiffusion occurred in the early stages, thicker (≥ 5 LE) Rh-only films did grow on Au{001} (as demonstrated by LEED, see Fig. 2 and the related discussion), but did *not* grow on Ag{001}. The thickest overlayers prepared in the Rh-Ag system were mixtures of Rh and Ag (our substrates were not intentionally heated during Rh deposition, but were also not cooled). However, we can tell from the LEED patterns that the Rh-Ag overlayers, although with steps and defects (high LEED background), were predominantly pseudomorphic with the Ag{001} substrate.

At least partial pseudomorphism was therefore expected even in the very early stages of growth—a necessary condition for the onset of magnetism in the Rh overlayer. The UPS experiments were aimed at the study of the Rh 4*s* level as a function of surface coverage. Figure 4 (top panels) shows the evolution of electron-distribution curves in the energy range of the 4*s* levels with increasing amounts of Rh. In the very early stages a splitting of the 4*s* levels is clearly visible, the splitting amounting to 4.1 ± 0.3 eV, while for thicker Rh films (either on Ag{001} or on Au{001}) or for a bulk Rh{001} sample the splitting could not be observed.

There are two possible explanations for a splitting of the 4*s* levels. One is that the Rh atoms may be absorbed on two different sites on the Ag{001} surface. While we cannot exclude this possibility with certainty, we consider it very unlikely; different surroundings of the Rh atoms would indeed produce shifts in the 4*s* levels, but in this case the 4*p* levels should show the same structure, and Fig. 4 (bottom panel) shows that no splitting of the $4p_{3/2}$ (47.2 eV) and $4p_{1/2}$ (50.2 eV) levels of Rh was detectable in our experiments. The second explanation, more probable in view of the theoretical predictions mentioned above, is that, as a consequence of the pseudomorphism which expands the natural Rh spacing, the Rh atoms have acquired a magnetic moment. We were unable to find in the literature detailed studies of the 4*s* levels of the 4*d* transition metals, and we have no way to correlate the observed splitting with the magnitude of magnetic moment. We can therefore not test the value of 1.09 μ_B predicted by ZBK for a monolayer of Rh on Au{001}.

CONCLUSION

We have shown that deposition of Rh on Au{001} eliminates the 5×20 reconstruction of the clean surface already at the tenths of a monolayer level, and that thick Rh films are epitaxial but not pseudomorphic with the Au{001} substrate. The present work cannot establish whether in the very early stages of overlayer growth the Rh film is indeed pseudomorphic with the substrate. If so, then it is very probable that the Rh atoms would be found to have a magnetic moment. Our attempts at proving this fact by looking for a split in the 4*s* levels were thwarted by the presence of strong photoemission from the 4*f* levels of Au. Other experimental techniques, such as inverse or spin-polarized photoemission, may be more successful in testing this case.

We have also shown that growth of overlayers of Rh on Ag{001}, while suffering from easy interdiffusion of Ag in and onto Rh, does produce pseudomorphic, albeit mixed, overlayers. In the very stages of growth a marked splitting of the Rh 4*s* levels is observed, which suggests the presence of a magnetic moment in the Rh atoms as predicted by theoretical calculations.[1,2] The splitting is no longer observed in thicker Rh films, whether grown on Ag{001} or on Au{001}.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation and to the U.S. Department of Energy for partial support of this work with Grants No. DMR-8921123 and No. DE-FG02-86ER45239, respectively. One of us (S.C.W.) is also indebted to the Science and Technology Commission of the People's Republic of China for partial support through Grant No. 19074004.

---

[*] On leave from the Physics Department, Peking University, Bejing, People's Republic of China.

[1] Ming J. Zhu, D. M. Bylander, and Leonard Kleinman, Phys. Rev. B **43**, 4007 (1991).

[2] Olle Eriksson, R. C. Albers, and A. M. Boring, Phys. Rev. Lett. **66**, 1350 (1991).

[3] L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber, *Handbook of Auger Electron Spectroscopy* (Physical Electronic Industries, Inc., Eden Praier, MN, 1978).

[4] M. P. Seah and W. A. Dench, Surf. Interface Anal. **1**, 2 (1979).

[5] P. J. Schmitz, W.-Y. Leung, G. W. Graham, and P. A. Thiel, Phys. Rev. B **40**, 11 477 (1989); T. J. Raeker, D. E. Sanders, and A. E. DePristo, J. Vac. Sci. Technol. A **8**, 3531 (1990); Bull. Am. Phys. Soc. **36** (3), B12 6 (1991).