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Mechanism of two-dimensional AgAu alloy formation on Ru(001)^{a)}

K. Markert, P. Dolle,^{b)} J. W. Niemantsverdriet,^{c)} and K. Wandelt

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faraday Weg 4-6, 1000 Berlin 33, West Germany

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Using the photoemission of adsorbed xenon technique we demonstrate that the two-dimensional alloy formation between ordered Ag islands on Ru(001) and Au atoms deposited on top of these islands proceeds via a two-step mechanism: The Au atoms do not penetrate the Ag layer directly, but first migrate from the islands onto the Ru substrate, from where they then "attack" the Ag islands to form a two-dimensional AgAu alloy.

I. INTRODUCTION

Nucleation and growth phenomena play a decisive role in the formation of epitaxial overlayers of one metal on top of another metal. Thin metal films evaporated in UHV onto single-crystal metal surfaces constitute important model systems for the investigation of the various parameters (relative bond energies, lattice mismatch, temperature, etc.) which control these phenomena. Immiscibility of the deposited and the substrate metal is a crucial prerequisite in order to arrive at conclusive results. Many data exist therefore for Cu, Ag, and Au on Ru or W,¹⁻¹⁰ as obtained with various surface sensitive techniques such as Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and thermal desorption spectroscopy (TDS), work function measurements and photoemission of adsorbed xenon (PAX).¹¹ Based on the known properties of submonolayer films of Ag (Refs. 2 and 12) and Au (Refs. 12 and 13) on Ru(001) we extended our interest to the problem of two-dimensional (2D) alloy formation between these two metals on Ru(001). In this paper we describe PAX results which provide evidence that the 2D alloy formation between Ag islands on Ru(001) and codeposited Au is not a direct but a two-step mechanism: In the first step Au atoms diffuse from the Ag islands onto the Ru(001) substrate and only in the second step lateral interalloying proceeds from the edges of the Ag islands.

II. EXPERIMENTAL

The experiments were carried out in a UHV system equipped with AES, LEED, ultraviolet photoemission spectroscopy (UPS), and TDS. High-purity Au and Ag were evaporated by resistive heating from a tungsten wire onto a Ru(001) surface, which, after careful cleaning by successive cycles of sputtering at 1100 K and roasting in oxygen,¹⁴ gave no more TDS spectrum of recombination CO after oxygen adsorption; showed no trace of other contaminants in AES; and produced an excellent LEED pattern. During metal evaporation the background pressure remained below 5×10^{-10} Torr and the Ru substrate was held at 60 K by means of a closed-loop He refrigerator.¹⁵ Also after deposition AES indicated no trace of contamination. The Ag and/or Au coverage was controlled by a shutter in front of the metal sources, and was determined after each experiment from the intensity (area) under the thermal desorption peaks of both metals calibrated against that of the respective

complete monolayer.¹⁶ After each deposition at 60 K the surface was characterized with UPS, $\Delta\phi$, and PAX (see below), annealed at a desired temperature, and then characterized again at 60 K. At last, the metals were desorbed in order to determine the metal coverages as described above and to begin a new experiment with the same substrate.

III. RESULTS AND DISCUSSION

In this paper we emphasize the PAX results which provide deep insight into the atomic distribution of both metal species after the chosen deposition and annealing conditions. As described in a number of earlier papers^{11,17-20} photoemission of adsorbed xenon is a local work function probe on an atomic scale. The binding energy E_B^F of core and valence electrons (with respect to E_F) of Xe atoms adsorbed at low temperatures (≤ 60 K), e.g., $E_B^F(5p_{3/2,1/2})$, are determined by the electrostatic surface potential at the site of adsorption. On a homogeneous single-crystal surface one therefore finds only one single $5p_{1/2}$ binding energy, which, however, is displaced by $\Delta\phi = -\Delta E_B^F(5p_{1/2})$ from the position measured on another homogeneous metal substrate, $\Delta\phi$ being the work function difference between both surfaces. This manifests itself again in Fig. 1, which displays Xe($5p_{3/2,1/2}$) UPS (He I) spectra from Xe monolayers adsorbed on a perfect Ru(001) surface as well as on well-ordered^{12,13} complete monolayers of Ag and Au on Ru(001). The work functions of these three surfaces as determined *in situ* from the low-kinetic-energy cutoff of the UPS spectra are $\phi_{Ru} = 5.6$ eV, $\phi_{ML Ag} = 4.7$ eV, and $\phi_{ML Au} = 5.60$ eV with an accuracy of ± 0.05 eV. The corresponding $E_B^F(5p_{1/2})$ values are 6.72, 7.55, and 6.80 eV on Ru(001), Ag and Au (see Table I), in agreement with the above correlation between E_B^F and $\Delta\phi$. Note also that the narrow width of the $5p_{1/2}$ signal [full width at half-maximum (FWHM) 0.33 eV] is indicative of the homogeneity of all three surfaces. Peak position and width are obtained from a fit of the experimental spectrum with the usual three Lorentzian lines, one for the $5p_{1/2}$ and two for the $5p_{3/2}$ spin-orbit component^{11,18,19} as exemplified in Fig. 1 for the Xe/1 ML Ag case. The splitting of the $5p_{3/2}$ peak arises mainly from the formation of a 2D electronic band structure within a close-packed Xe layer.²¹ In turn, the absence of any $5p_{3/2}$ splitting (or at least broadening) is indicative of isolated Xe atoms.²² We will make diagnostic use of this fact.

For later calibration purposes Fig. 1 also shows a

FIG. 1. Xe($5p_{3/2,1/2}$) UPS (He I) spectra of a complete monolayer of xenon adsorbed at 60 K on Ru(001), an ordered monolayer of Au on Ru(001), a bulk AgAu alloy surface, and an ordered monolayer of Ag on Ru(001). The latter spectrum is decomposed into the usual three component peaks, one Lorentzian for the $5p_{1/2}$ and two Lorentzians for the $5p_{3/2}$ spin-orbit state.

Xe($5p_{3/2,1/2}$) monolayer spectrum from a AgAu alloy surface, which was prepared by codeposition of equal amounts of Ag and Au (equivalent to more than 40 monolayers) and careful annealing at 800 K (just below the onset of Ag desorption) for 30 min followed by slow cooling. Although the surface of this alloy contains two different species, PAX cannot distinguish between the different atomic surface sites of this *ideal* mixture: One obtains only *one* narrow $5p_{1/2}$ peak (FWHM = 0.35 eV) independent of Xe coverage at $E_B^F(5p_{1/2}) = 7.25$ eV, which is still of great diagnostic value.

In order to study the 2D AgAu alloy formation we have first deposited 0.27 monolayers of Ag (as determined from TDS after the experiment) on the Ru(001) surface at 60 K and then annealed it 15 min at 525 K. As shown with LEED¹² and PAX² this procedure yields monoatomically thick Ag islands of a (111)-like structure. Corresponding PAX spectra are shown in Figs. 2(a) and 2(b). At Xe monolayer saturation [Fig. 2(b)] the two $5p_{1/2}$ signals at 6.7 and 7.6 eV correspond to Xe emission from Ru and Ag patches, respectively.² The two arrows indicate that the $5p_{3/2}$ peak of the Xe(Ag) state is again split due to the formation of a 2D Xe band structure,²¹ which is only conceivable, if the Ag islands are not too small and completely flat. Spectrum (a) in Fig. 2 was measured after an exposure of only 3-L Xe to the Ag/Ru surface, and is to show that only the Ru sites at

FIG. 2. Xe($5p_{3/2,1/2}$) spectra from saturated monolayers (~ 14 L) of Xe on (b) a 0.27-ML Ag/Ru(001) surface annealed for 15 min at 525 K; (c) the Ag/Ru(001) surface from (b) covered with 0.12 ML of Au at 60 K; (d) the surface from (c) after mild annealing at 270 K for 15 min; and (e) same surface as (c) (except with relatively more Au) after annealing at 525 K for 10 min. The drastic spectral changes can be correlated with different distributions of Xe adsorption sites on the differently prepared surfaces as sketched in the models and described in the text. Spectrum (a) corresponds to a low Xe coverage (3 L) on the 0.27-ML Ag/Ru(001) surface, showing the selective initial population of Ru sites and Ag/Ru boundary sites (steps).

6.73 eV and the Ag/Ru boundary sites at 7.25 eV are populated before Ag sites become covered at higher Xe coverages. This example once again illustrates the two spectroscopic observables underlying the PAX technique: E_{ad} controls the selective and, hence, successive population of different surface sites; and $E_B^F(5p_{3/2,1/2})$, which is sensitive to the local work function. In particular, the high-coordination (step-like) island boundaries populate first, because $E_{ad}(\text{Ag/Ru}) \approx E_{ad}(\text{Ru}) > E_{ad}(\text{Ag})$. Correspondingly the same sequence was found with a partly Au covered Ru(001) surface.¹³ $E_B^F(5p_{3/2,1/2})$ can be determined for various specific surface sites using appropriate model systems as demonstrated for the pure metal and alloy surfaces in Fig. 1 as well as for the three possible sites on the binary Ag/Ru surface.² Table I summarizes average $E_B^F(5p_{1/2})$ values, which can serve as spectroscopic standards (Au/Ag denotes Au on top of Ag, while AgAu stands for the substitutional alloy).

TABLE I. Empirical standard $5p_{1/2}$ electron binding energies of Xe atoms adsorbed at the different surface sites. "/" stands for "on top of"; AgAu denotes the substitutional alloy.

	Ru(001)	1 ML Au/Ru	Au/Ru	Au/Ag	AgAu	Ag/Ru	1 ML Ag/Ru
$E_B^f(5p_{1/2})$ (eV)	6.7	6.8	6.85	7.1	7.25	7.3	7.55

A fit to the Xe monolayer spectrum from the 0.27-ML Ag/Ru surface [Fig. 2(b)] yields 58% pure Ru sites, 11% Ag/Ru boundary sites, and 31% Ag sites; the latter value is in good agreement with the TDS derived Ag coverage and proves the monoatomic thickness of the Ag islands. [For the sake of clarity curves (a) and (b) in Fig. 2 show only the $5p_{1/2}$ components together with the total fit of the respective experimental spectrum.] Assuming circular Ag islands these relative site concentrations are compatible with an average island diameter of $44 \text{ \AA}^2$.

Next we have deposited 0.12-ML Au onto the thus characterized Ag/Ru(001) surface held at 60 K. At this low temperature Au will be atomically dispersed over the whole surface. Hence, 7% ($= 58\% \times 0.12$), 1% ($= 11\% \times 0.12$), and 4% ($= 31\% \times 0.12$) of a monolayer of Au will not only cover up the same amount of Ru, Ag/Ru, and Ag sites, respectively, but will also create a sphere of new "mixed" sites around each Au atom, namely, Au/Ru, Au/(Ag/Ru), and Au/Ag sites. As a consequence, we expect qualitatively a strong suppression of the Xe(Ru) and Xe(Ag) intensities, but a corresponding increase of Xe($5p$) emission from all kinds of mixed sites. This is exactly what is seen in Fig. 2(c). Most obvious is the lack of any resolved Xe(Ag) signal. Also the Xe(Ru) intensity has decreased, in particular, when considering that the new Xe(Au)- and Xe(Au/Ru)-emission lines now contribute at approximately the same electron binding energy (see Table I). On the other hand, strong intensity builds up between the original Xe(Ag) and Xe(Ru) signals, arising from all possible mixed sites mentioned above. The existence and successive population of at least five different sites on this highly dispersed ternary surface become immediately evident from the corresponding difference spectra for successive Xe exposures as shown in Fig. 3. The broad signal denoted as state 1 coincides with the position of Xe(Au/Ru) and/or Xe(Ru), in agreement with the fact that these sites populate first. We have not yet attempted any specific assignment of the other states (nor in Fig. 4) which requires additional calibration work.

Based on these difference spectra which accentuate the sequence of population, the standard energy positions given in Table I as well as the site-specific order of E_{ad} we have tried to decompose the PAX spectra from this nonannealed Au/Ag/Ru surface at different Xe coverages and arrive at a rough estimate for the relative abundance of the various sites as given in Table II. As expected the Xe(Ag) and Xe(Ru) states are strongly suppressed, while the mixed sites dominate.

In the next step we have annealed the Au/Ag/Ru surface for 10 min at 270 K and then characterized with PAX again.

The corresponding Xe monolayer spectrum is shown in Fig. 2(d). Most obvious is the full recovery of the Xe(Ag) $5p_{1/2}$ emission peak, which is accompanied by a corresponding filling between the Xe(Ru) peaks due to the Xe(Ag) $5p_{3/2}$ signal (arrow). But also the valley between the Xe(Ru) and Xe(Ag) $5p_{1/2}$ signals is partly filled with intensity indicating still more mixed sites than on the original Ag/Ru surface [Fig. 2(b)]. The corresponding PAX difference spectra are displayed in Fig. 4. Again at least five different Xe states can be distinguished, but their relative intensities are significantly different than in Fig. 3 from the nonannealed surface. A similar decomposition as in the previous case yields relative concentrations as given in Table II. The fraction of all mixed sites is reduced from 60% to 30% while Xe(Ag) and Xe(Ru + Au) are strongly increased. In particular, the Xe(Ag) intensity has the same value as on the initial Ag/Ru surface. As a consequence, the Ag is not yet converted into alloy, but the Au atoms must have diffused from the Ag islands onto the Ru substrate instead of penetrating the Ag layer directly. This result is easy to conceive for both structural and energetic reasons: (a) The even slightly compressed (111)-like structure of the Ag islands¹² makes a perpendicular penetration of Au atoms difficult. (b) The

FIG. 3. Xe($5p_{3/2,1/2}$) difference spectra from the 0.27 ML Ag/Ru(001) + 0.12 ML Au, 60 K surface [see Fig. 2(c)] for increasing Xe uptake. The numbers emphasize only the successive population of the various possible surface sites. We have not yet attempted any firm assignment of these states (see the text).

TABLE II. Relative abundance (% ML) of surface sites on the differently pretreated Ag/Ru(001) and Au,Ag/Ru(001) surfaces as obtained from the respective partial Xe($5p_{1/2}$) intensities (see the text).

	Ru	Au	Au/Ru	Mixed sites		
				Au/Ag AgAu	Ag/Ru	Ag
Initial surface [Fig. 2(b)]	58				11	31
Au not annealed	— 20 —		30	— 30 —		20
Au 270 K annealed	— 40 —		10	— 20 —		30

surface free energy of silver is significantly smaller than that of gold.²³ (c) The Au–Ru bond is stronger than the Au–Ag bond as deduced from TDS.¹⁶ Of course, it can be expected that the two competing processes, the direct penetration into the islands and the diffusion from the islands, may depend on the island size. In the present case the islands are obviously small enough so that migration from the Ag islands dominates.

We refrain here from a detailed discussion of the other intensities [but Xe(Ag)] on this surface annealed at 270 K. Instead, we show in Fig. 2(e) the Xe monolayer spectrum which was obtained after the Au,Ag/Ru surface was annealed for 10 min at 525 K. The appearance of the spectrum has drastically changed; there is only one, though broadened, $5p_{1/2}$ signal with the same peak position as found on the bulk AgAu alloy (see Fig. 1 and Table I). In particular, there is no more Xe(Ag) emission, but there is still indication for remnant (but not resolved) intensity of Xe on free Ru and island boundary sites (together ~30%) within the

low-binding-energy edge of the leading $5p_{1/2}$ signal. It is clear, that the last temperature treatment has led to the formation of a submonolayer of AgAu alloy.

In summary, the sequence of PAX spectra (taken at Xe monolayer saturation) in Fig. 2 supports a two-step mechanism of 2D alloy formation between ordered Ag islands on Ru(001) and Au atoms deposited on top of these islands: First the gold atoms diffuse across the island edges from the Ag onto the Ru, from where they then “attack” the Ag islands to form a 2D AgAu alloy. These steps are illustrated by small models in Fig. 2, and are consistent with structural and energetic considerations as described above.

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FIG. 4. Xe($5p_{3/2,1/2}$) difference spectra from the 0.27 ML Ag/Ru(001) + 0.12 ML Au, 270 K surface [see Fig. 2(d)] for increasing Xe uptake. The numbers emphasize only the successive population of the various possible surface sites. Note the distinct differences from Fig. 3.

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^{b1} Permanent address: Laboratoire de Recherches sur les Interactions Gaz-Solides, CNRS, Villers-Les-Nancy, France.

^{c1} Permanent address: Laboratory of Inorganic Chemistry, University of Technology, Eindhoven, The Netherlands.

¹ K. Christmann, G. Ertl, and H. Shimizu, *Thin Solid Films* **57**, 247 (1979); *J. Catal.* **61**, 397 (1980).

² A. Jablonski, S. Eder, and K. Wandelt, *Appl. Surf. Sci.* **22/23**, 309 (1985).

³ K. Wandelt, in *Proceedings of the 1985 Symposium on Surface Science*, Obertraun, Austria, 1985, p. 255.

⁴ C. Harendt, K. Christmann, W. Hirschwald, and J. C. Vickerman, *Surf. Sci.* **165**, 413 (1986).

⁵ E. Bauer, F. Bonczek, H. Poppa, and G. Todd, *Surf. Sci.* **53**, 87 (1975).

⁶ E. Bauer, H. Poppa, G. Todd, and P. R. Davis, *J. Appl. Phys.* **48**, 3773 (1977).

⁷ J. Kolaczekiewicz and E. Bauer, *Surf. Sci.* **144**, 477 (1984).

⁸ G. D. T. Spiller, P. Akhter, and J. A. Venables, *Surf. Sci.* **131**, 517 (1983).

⁹ J. E. Houston, C. H. F. Peden, D. S. Blair, and D. W. Goodman, *Surf. Sci.* **167**, 427 (1986).

¹⁰ J. E. Houston, C. H. F. Peden, P. J. Feibelman, and D. R. Hamann, *Phys. Rev. Lett.* **56**, 375 (1986).

¹¹ K. Wandelt, *J. Vac. Sci. Technol. A* **2**, 802 (1984).

¹² B. Konrad, F. J. Himpsel, W. Steinmann, and K. Wandelt, in *Proceedings of the International Seminar on Surface Structure Determination by LEED and Other Methods*, University of Erlangen, Nürnberg, FRG,

- 1985, p. 109 and in preparation.
- ¹³J. W. Niemantsverdriet, P. Dolle, K. Markert, A. Jablonski, and K. Wandelt (in preparation).
- ¹⁴K. Wandelt, J. Huise, and J. Küppers, *Surf. Sci.* **104**, 212 (1981).
- ¹⁵K. Wandelt, S. Daiser, R. Miranda, and H.-J. Forth, *J. Phys. E* **17**, 22 (1984).
- ¹⁶J. W. Niemantsverdriet, P. Dolle, K. Markert, and K. Wandelt, *J. Vac. Sci. Technol. A* **5**, 875 (1987).
- ¹⁷J. Küppers, K. Wandelt, and G. Ertl, *Phys. Rev. Lett.* **43**, 928 (1979).
- ¹⁸K. Wandelt and J. Huise, *J. Chem. Phys.* **80**, 1340 (1984).
- ¹⁹J. Behm, C. R. Brundle, and K. Wandelt, *J. Chem. Phys.* **85**, 1061 (1986).
- ²⁰K. Wandelt, in *Nichtkonventionelle Mikroanalyse*, edited by O. Brümmer (Martin-Luther-Universität, Halle/Wittenberg, 1986/8), (022) pp. 29–51.
- ²¹(a) K. Horn, M. Scheffler, and A. M. Bradshaw, *Phys. Rev. Lett.* **44**, 822 (1978); (b) M. Scheffler, K. Horn, A. M. Bradshaw, and K. Kambe, *Surf. Sci.* **80**, 69 (1986).
- ²²A. Jablonski, S. Eder, K. Markert, and K. Wandelt, *J. Vac. Sci. Technol. A* **4**, 1510 (1986).
- ²³G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell University, Ithaca, 1981).