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Miscibility between monolayer gold and silver layers

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Photoemission of Adsorbed Xenon (PAX) as a local work function probe is used to study the intermixing between successively deposited monolayers of Au and Ag on Ru(001) on an atomic level. Remarkable differences in the kinetics and in the final equilibrium Ag- and Au-distribution are found depending on whether Au or Ag is deposited first.

1. Introduction

The quasi-two-dimensional (2D) properties of supported monolayer (ML) metal films have attracted much interest recently, because both their geometrical and electronic structure may deviate from those of a lattice layer of the same material in three-dimensional form, due to interactions with the substrate. As a consequence these films may exhibit modified chemical, catalytical and 'electrical' properties. In model studies these monolayer films are usually prepared by deposition from the vapour phase. The existence of such films, however, may be a more general phenomenon as a consequence of segregation effects at surfaces of multi-component materials.

We have extended our interest also to the investigation of 2D binary alloy films. In this case the distribution of both components is a further very important parameter beyond the mere knowledge of concentration, geometrical and electronic structure. As demonstrated in several earlier papers¹⁻⁴, PAX (Photoemission of Adsorbed Xenon) may provide this kind of information. The basis of PAX^{1,3} is the fact that the electron binding energies E_B^F (with respect to the substrate Fermi level) of Xe electrons vary linearly with the local work function of the immediate adsorption site of a Xe atom. Figure 1 [and Figure 2(a1)] displays an experimental Xe $5p_{3/2,1/2}$ spectrum of a complete Xe monolayer (from here on called PAX-spectrum) adsorbed at 60 K on a well annealed epitaxial monolayer of gold on a Ru(001) substrate. The spectrum consists of three (Lorentzian) lines arising from the $5p_{3/2}(m_j = \pm 3/2)$, $5p_{3/2}(m_j = \pm 1/2)$ and $5p_{1/2}(m_j = \pm 1/2)$ final states of photoionized Xe atoms. On this Au monolayer $E_B^F(5p_{1/2}) = 6.8$ eV. Figure 2(b1) shows the PAX-spectrum from a complete epitaxial monolayer of silver on Ru(001); in this case $E_B^F(5p_{1/2}) = 7.55$ eV. The difference $\Delta E_B^F = 7.55$ eV - 6.8 eV = 0.75 eV is mainly due to the difference in work

Figure 1. Experimental $5p_{3/2,1/2}$ uv-photoemission spectrum (data points) of one complete monolayer of Xenon adsorbed on an epitaxial monolayer of gold on Ru(001). The full line through the data points corresponds to the best fit with three Lorentzian functions representing the $5p_{3/2}(m_j = \pm 3/2)$, $5p_{3/2}(m_j = \pm 1/2)$ and $5p_{1/2}(m_j = \pm 1/2)$ final states of photoionized Xe. n, l, j, m_j = quantum numbers. The sharp Xe($5p_{1/2}$) peak is best used for the distinction of different Xe adsorption sites.

function between these two surfaces: $\Delta\phi = \phi_{MLAu} - \phi_{MLAg} = 5.6$ eV - 4.75 eV = 0.85 eV^{3,4}. This close correlation between ΔE_B^F and $\Delta\phi$ persists between different sites on heterogeneous surfaces. It enables an identification not only of Xe atoms adsorbed on Ag- and Au-patches of an overlayer containing both metals, but also of Xe atoms adsorbed at AgAu alloy- or at Ag- and Au-island boundary-sites²⁻⁴. The distinction is easiest with the $5p_{1/2}$ signal and therefore Table 1 summarizes $E_B^F(5p_{1/2})$ -values for Xe atoms being bound to the indicated sites, as measured in careful

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Figure 2. PAX (Photoemission of Adsorbed Xenon) spectra of complete Xe monolayers (ML) adsorbed on: (a1) a complete epitaxial monolayer of gold on Ru(001); (a2) the surface from (a1) additionally covered with 0.5 ML silver and warmed to 273 K for 10 min; (a3) the surface from (a2) further annealed at 773 K for 10 min; (b1) a complete epitaxial monolayer of silver on Ru(001); (b2) the surface from (b1) additionally covered with 0.3 ML gold and warmed to 273 K for 10 min; (b3) the surface from (b2) further heated to 773 K for 10 min. The strong spectral changes are indicative of the structural changes in the Ag₂Au-films as illustrated in Figure 4.

calibration experiments. In a previous paper⁴ we have studied the formation of 2D AgAu alloys on Ru(001) in the submonolayer regime. Here we take advantage of the site-specificity of PAX in order to follow the kinetics of the intermixing between a complete monolayer of Au (or Ag) and submonolayer amounts of Ag (Au) deposited onto it. Note that both metals do not alloy with Ru. (Experimental details can be found in refs 2 and 4.)

Table 1. Empirical standard $5p_{1/2}$ electron binding energies of Xe atoms being adsorbed at the indicated surface sites (● = gold, ○ = silver). '/' stands for 'on top of'; AgAu denotes the substitutional alloy

	1ML Au	Ag/Au	AgAu	Au/Ag	1ML Ag
$E_B^F(5p_{1/2})$	6.8 eV	~7.1 eV	7.3 eV	~7.1 eV	7.55 eV

2. Results and discussion

As mentioned before Figure 2(a1) displays the PAX-spectrum of a complete monolayer of Xe adsorbed on one complete, well-annealed epitaxial monolayer of Au on Ru(001). This Au monolayer was then covered with 0.5 ML Ag (as determined with TDS after the PAX measurements⁴) at 60 K followed by warming up to 273 K for 10 min. The corresponding PAX-spectrum [taken again at 60 K and shown in Figure 2(a2)] has drastically changed and now shows two dominant $5p_{1/2}$ peaks close to the positions of Xe on Au[Xe(Au)] and Xe on Ag[Xe(Ag)]. We have decomposed spectrum 2(a2) into three subspectra, each consisting of three Lorentzians as defined in Figure 1. For details of the fit procedure

we must refer the reader to our earlier papers²⁻⁴; we like to stress, however, that the positions and widths of the relevant $5p_{1/2}$ and most other Lorentzians are known from calibration experiments (see e.g. Table 1) and that often only the intensity of each subspectrum as a whole is varied. The best fit, together with the three components of spectrum 2(a2) is shown in Figure 3(a). The assignment of the three subspectra is straightforward and given in the figure. The relative intensities of the three $5p_{1/2}$ Lorentzians are a measure of the relative abundance of the corresponding kind of surface site. The fact that 35% of the Xe atoms indicate the existence of pure Au-sites ($E_B^F(5p_{1/2}) = 6.85$ eV) proves unambiguously that Au and Ag have not yet formed an alloy after annealing at 273 K. In turn, the relative intensity of the Xe(Ag) state ($E_B^F(5p_{1/2}) = 7.46$ eV) is 55% (in agreement with the amount of Ag deposited) and suggests the existence of extended Ag-islands on top of the undisturbed Au-monolayer. Only the small (10%) state with $E_B^F(5p_{1/2}) = 7.2$ eV corresponds to Ag/Au sites at the boundary of the Ag islands and/or incipient formation of AgAu-alloy sites (see Table 1).

Figure 3. (a) Decomposition of spectrum 2 from Figure 2(a) into three subspectra consisting of Lorentzian functions as defined in Figure 1. The full line through the data points is the sum of the three subspectra, which correspond to Xe atoms being adsorbed on pure Au-sites, on AgAu-alloy- and/or Ag/Au-step-sites and on pure Ag-sites. The percentages give the relative abundance of each kind of these surface sites. The lowest trace is the difference between the experimental and the total fit curve and illustrates the quality of the fit. (b) Decomposition of spectrum 2 from Figure 2(b) into three subspectra in analogy to Figure 3(a).

Further annealing of this Ag/Au double-layer at 773 K for 10 min results in the PAX-spectrum 2(a3), which is now clearly indicative of complete alloy formation between Ag and Au^{3,4}. The slightly larger width of the $5p_{1/2}$ signal (compared to spectrum 2(a1)) is due to the binary nature of the new surface as well as to steps around the alloy islands in the incomplete second layer.

In a second experiment we started with a complete, well-annealed epitaxial monolayer of Ag on the Ru(001) substrate; the corresponding PAX-spectrum is shown in Figure 2(b1). This Ag monolayer was covered with 0.3 ML Au at 60 K and then again held at 273 K for 10 min. The resulting PAX-spectrum 2(b2) shows definitely no peak at 6.8 eV characteristic of Xe on pure Au-sites (see arrow). Instead, the $5p_{1/2}$ peak is shifted to lower binding energy and broadened compared to spectrum 2(b1). On the basis of

the known peak positions as given in Table 1, spectrum 2(b2) can be fitted with two Xe subspectra characteristic of Xe on AgAu alloy-sites (70%) and Xe on pure Ag-sites (30%) as shown in Figure 3(b). Further annealing of this surface at 773 K for 10 min leads to spectrum 2(b3). The $5p_{1/2}$ peak position has not changed; the two subspectra [see Figure 3(b)] have only sharpened due to more complete healing of surface defects, making the Xe(Ag)-state now appear as a clear shoulder. The relative intensity of the Xe(Ag) peak is still 30% which corresponds to the amount of 0.3 ML Au originally deposited. This strongly suggests that the adsorbed Au atoms have completely penetrated the Ag layer, thereby displacing an equivalent number of Ag-atoms into the second layer where they form monoatomically thick pure Ag-islands.

Figure 4. Illustration of the structural changes in Ag/Au- (Ag on Au, 1. experiment) and Au/Ag- (Au on Ag, 2. experiment) double layers following different temperature treatments as suggested by the PAX spectra from Figures 2(a) and 2(b).

A summary of the structural changes in both experiments is illustrated with small models in Figure 4. In the first experiment (Au underlayer) Ag does not penetrate the Au layer below 273 K and the final equilibrium state (obtained after annealing at 773 K)

is a more or less uniform AgAu alloy in both layers. Conversely, in the second experiment the Au atoms exchange site with underlying Ag atoms already at 273 K, and the final state is a monolayer of a 0.7Ag0.3Au alloy covered with pure, monoatomically thick Ag-islands. This remarkable difference is easily conceivable when we consider the following energy terms involved: (1) The adsorption energy of Au on Ru(001) is significantly higher than that of Ag⁵. (2) The surface free energy of Ag is lower than that of Au. (3) The lateral interaction energy between adsorbed Ag atoms [on Ru(001)] is attractive while that between adsorbed Au atoms [on Ru(001)] is found to be repulsive⁵. (4) The formation of an AgAu alloy is slightly exothermic. Hence, the first two energy terms favour Au atoms to be in contact with Ru. A balance of the latter two, depending on the total Au coverage appears to control whether all gold atoms are in the first layer or distributed throughout both layers. The activation energy for Ag atoms to penetrate a perfect Au monolayer on Ru(001) is obviously higher than for the reverse process. The present study appears to be another example showing the great usefulness of PAX to investigate such atomic surface processes.

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