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SITE-EXCHANGE PROCESSES ACROSS AN ATOMIC 
Ag/Au INTERFACE

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The thermally activated intermixing between Ag submonolayer deposits and a complete Au monolayer supported on a Ru(001) substrate was studied using the PAX (photoemission of adsorbed xenon) technique. At 275 K 2D Ag islands exist on the Au monolayer. At 350 K Ag–Au atom exchange occurs only within the area of the previous Ag islands. Only at even higher temperatures a homogeneous AgAu alloy double layer is formed. This study may, of course, serve as model for other metal/metal combinations.

1. Introduction

Beyond the geometrical and electronical structure of epitaxial metal/metal interfaces it is also their thermal stability which is of great significance for the design and the technological application of layered structures. In the present paper we present a model study, in which we have investigated the thermally activated site exchange between atoms across an atomically sharp Ag/Au interface using the PAX-technique (photoemission of adsorbed xenon) [1]. In a previous short account [2] we have qualitatively shown that a Ag/Au interface (supported on a Ru(001) substrate) is more stable against thermal treatment than a Au/Ag interface. Here we demonstrate that a careful quantitative analysis of PAX-data can provide even more detailed insight in the temperature induced interaction mechanism between the Au underlayer and a Ag submonolayer on top. The studies once again prove the surface analytical power of the PAX-technique on the nanometer scale and may, of course, be carried over to other metal-on-metal systems.

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2. Experimental

The experiments were carried out in a UHV system which has been described in detail in earlier publications [3]. Most importantly, the sample, a Ru(001) single crystal, could be cooled to 50 K by means of a cryo-head as well as heated by means of resistive heating. The temperature was measured with a thermocouple spot-welded directly to the backside of the crystal. The surface cleanliness and crystallographic perfectness of both the Ru(001) substrate as well as the Au monolayer were verified with AES and LEED, respectively. The cleaning procedure for Ru has been described in ref. [3]. UV(He I)-photoemission spectra of xenon adsorbed at 60 K on the differently prepared surfaces were monitored with a hemispherical electron energy analyzer.

The atomically sharp interface between Au and Ag was formed by first preparing just one complete, well annealed monolayer of Au on the clean and perfect Ru(001) surface, and then depositing at 60 K 0.5 monolayers of Ag ontop. Both metals were evaporated from little resistively heated tungsten baskets. The Ag and Au coverages were determined by the thermal desorption traces of both metals recorded after completion of the experiment. Both Au and Ag do not form alloys with Ru [4]; the Ru surface acts as an infinite diffusion barrier.

3. Results and discussion

As has been shown earlier [5], at monolayer (ML) saturation Au forms a compressed, (111)-like layer of mono-atomic thickness on Ru(001). This layer is completely stable against penetration of Ag atoms up to ~ 300 K [2]. Fig. 1a shows a set of 5p_{3/2,1/2} UPS spectra (from here on called “PAX-spectra”) of Xe adsorbed at 60 K on the perfect Au monolayer on Ru(001). The Xe 5p_{1/2} signal is located at 6.8 eV below $E_F$ (vertical line); the 5p_{3/2} signal is split into two components with the magnetic quantum numbers $m_j = \pm 3/2$ at ~ 5.1 eV and $m_j = \pm 1/2$ at ~ 5.6 eV [6]. For comparison fig. 1b shows the corresponding set of PAX-spectra from a perfect monolayer of Ag on Ru(001). In this case the electron binding energies of the three peaks are 7.55 eV (5p_{1/2}, vertical line); ~ 5.8 eV (5p_{3/2}, $m_j = \pm 3/2$) and ~ 6.3 eV (5p_{3/2}, $m_j = 1/2$). Note that the 5p_{1/2} signal is shifted by $\Delta E_B^F = 7.55 - 6.8$ eV = 0.75 eV with respect to the Xe 5p spectra from the Au monolayer, which is mainly due to the work function difference between the two surfaces: $\Delta \phi = \phi_{MLAg} - \phi_{MLAu} = 0.85$ eV [2]. This correlation $E_B^F = -\Delta \phi$, in fact, is the basis of the PAX-technique because it persists on heterogeneous surfaces [1]. The highest spectra in figs. 1a and 1b correspond to a complete Xe monolayer and the
sharpness of their $5p_{1/2}$ signals as well as the clear splitting of their $5p_{3/2}$ signals [6] is best prove by itself for the prefectness of both metal monolayers.

Fig. 2 shows a fit of the Xe monolayer spectrum for a Ag(111) surface using three Lorentzian lines for the three photoemission peaks of adsorbed Xe as mentioned above, namely the $5p_{3/2}(m_f = \pm 3/2)$, the $5p_{3/2}(m_f = \pm 1/2)$ and the $5p_{1/2}(m_f = +1/2)$ photoionization states [6]. Note that the $5p_{1/2}$ peak position is the same as on the monolayer of Ag on Ru. This is in agreement with the fact that both surfaces have the same (macroscopic) work function. Such fits as shown in fig. 2 will serve throughout this paper to decompose the PAX-spectra from different, coexisting Xe adsorption states on the binary surfaces discussed below. The relative energy separations and intensities within each set of three Lorentzian lines (since dictated by the Xe photoionization process) are essentially constant, so that the energy position and the intensity of each set as a whole are the only variables. The position and the intensity of e.g. the $5p_{1/2}$ peak are then a measure of the local work function and the relative concentration of each kind of Xe adsorption site, respectively.

Fig. 3 shows PAX-spectra monitored from four differently treated binary Au + Ag films. Starting from a perfect Au monolayer on Ru(001) as characterized in fig. 1a, this Au film was then covered with 0.5 ML Ag at 60 K. The corresponding PAX-spectra are shown in fig. 3a. At Xe monolayer saturation (at 60 K) the highest spectrum clearly shows two $5p_{1/2}$ signals (vertical lines) exactly in the positions as on pure Au and pure Ag. The two peaks appear only broader because extra intensity between these two lines
Fig. 2. Decomposition of an experimental $5p_{3/2,1/2}$ spectrum of one monolayer of Xe on Ag(111) into three Lorentzian lines corresponding to the photo-ionization final states $5p_{3/2}(m_j = \pm 3/2)$, $5p_{1/2}(m_j = \pm 1/2)$ and $5p_{1/2}(m_j = \pm 1/2)$.

becomes obvious at lower Xe coverages (arrow). This intermediate peak corresponds to Xe atoms adsorbed at “mixed” surface sites being in contact with both Au and Ag atoms. These “mixed” sites can be of variable composition (Au:Ag ratio) and structure (Ag and Au forming a perfect alloy plane, Ag adsorbed on Au, or Au adsorbed on Ag) [2]. As careful reference studies with differently prepared binary Ag + Au surfaces have shown, all these various “mixed” sites correspond to Xe5$5p_{1/2}$ positions ranging from 7.0 to $\sim$ 7.35 eV [2], hence, to positions between Xe on pure Au and Xe on pure Ag. As mentioned before (and shown here) below 300 K Ag does not penetrate into the Au underlayer. Furthermore, at 60 K adsorbed Ag atoms are rather immobile, so that their statistical distribution across the Au surface will create a lot of “mixed” Ag/Au sites, which (since the Ag atoms remain on the surface) are also step-like or high-coordination sites. Hence, these sites are occupied first by coadsorbed Xe atoms and therefore show up first in fig. 3a (arrow). A small hard sphere model of this surface topography is sketched in fig. 4 (60 K). If this surface is held at room temperature (275 K) for 10 min and then cooled back to 60 K the PAX spectra from fig. 3b are obtained. The major difference compared to fig. 3a is the strong reduction of the intermediate intensity (arrow) which indicates a substantial reduction of “mixed” Ag/Au sites, but also excludes AgAu alloy formation yet, because Xe5$5p_{1/2}$ emission from AgAu alloy surfaces occurs also between 7.0 and 7.3 eV (see fig.
Fig. 3. Xe5p_{3/2} \ (= PAX) spectra from Au+Ag layers on Ru(001) treated under different temperature conditions (see text). The two vertical lines mark the 5p_{3/2} electron binding energies of Xe adsorbed on a pure Au- (6.8 eV) and a pure Ag-monolayer (7.55 eV) on Ru(001), respectively.

4, last line) as has been tested with bulk AgAu alloy samples. At Xe monolayer saturation the two 5p_{3/2} signals from Xe on Ag-sites and Xe on Au-sites are therefore better resolved and sharpened. The Xe(Ag) signal has undergone a small shift to lower binding energies, because it corresponds to Ag on Au and not to Ag on Ru. This shift is consistent with the fact, that one complete monolayer of Au increases the work function of Ru(001) by ~ 100 meV [1b]. The PAX-spectra from fig. 3b suggest the formation of extended Ag islands on the Au underlayer. The remnant intensity from “mixed” sites (arrow) arises from the boundaries of these larger Ag islands (see model in fig. 4, 275 K).
Fig. 4. 5p$_{1/2}$ electron binding energies (black bars) and relative intensities (percentages) of different coexisting Xe adsorption states on the differently treated Au + Ag layers on Ru(001); see fig. 3. These data support the small structure models shown on the right-hand side (see text).

Further annealing of this Ag/Au double layer at 350 K for 10 min and recouling leads to the PAX-spectra shown in fig. 3c. The Xe(Au) 5p$_{1/2}$ peak is still in the same position (6.8 eV). The second peak, however, is no longer near the Xe(Ag) position, but has now shifted to 7.3 eV, which is suggestive of "mixed" sites. These mixed sites, however, are no longer high-coordination sites near Ag atoms on the Au underlayer, because these sites are now populated only at high Xe coverages in contrast to the behavior reflected in fig. 3a. Hence, we are bound to conclude that the peak at 7.3 eV in fig. 3c arises from Xe atoms on flat AgAu alloy patches surrounded by unperturbed pure Au regions. Only annealing at even higher temperature, e.g. 760 K (see fig. 3d), causes the Xe(Au) signal to disappear suggesting homogeneous AgAu alloy formation throughout the whole double-layer.

These qualitative conclusions drawn from a simple visual inspection of the PAX-spectra shown in figs. 3a–3d can be even more refined on the basis of a careful quantitative decomposition of each spectrum. As mentioned earlier each individual Xe adsorption state is represented by a set of three Lorentzian lines as shown in fig. 2. For each surface preparation the PAX-spectra are analyzed in the order of increasing Xe coverage, which minimizes the number of Xe adsorption states to be considered at low coverages. As the Xe coverage increases additional Xe states are added. (For more details of the fit procedure the reader must be referred to ref. [1].) Only the results of the finally obtained best fits of the Xe monolayer PAX-spectra of the differently prepared surfaces are compiled in fig. 4 (actual fits can be seen in ref. [2]). At the top the electron binding energy scale is divided into three regimes, namely two vertical lines at 6.8 and ~7.6 eV indicating the position of the Xe 5p$_{1/2}$ signal on a pure Au and pure Ag monolayer on Ru(001), respectively, and a broad regime
between 7.0 and ~7.4 eV which encompasses the Xe 5p\(_{1/2}\) positions of all kinds of “mixed” sites including a substitutional bulk AgAu alloy surface (see lowest line). The black bars mark the Xe 5p\(_{1/2}\) positions as they came out from the decomposition of the experimental Xe monolayer spectra. The corresponding percentages denote the relative intensity of each state (with an estimated relative uncertainty of 5%). We do not claim to know the exact origin of each state within the energy regime of the “mixed” sites (they were simply needed in order to account for the broad emission at these energies (see e.g. fig. 3a)), but we do claim to be able to distinguish quantitatively between Au-, “mixed”- and Ag-sites on the various surfaces. A careful inspection of the numbers in fig. 4 then reveals two very interesting details. Firstly, upon annealing from 60 to 275 K the relative intensity of the Xe(Ag) state increases from 45% to 54%, the latter being in good agreement with the actual coverage as determined by Ag-TDS after the experiment. This increase may be indicative of the existence of small Ag clusters at 60 K which spread out upon warming to 275 K as depicted in the small atomistic models. Secondly, annealing from 275 to 350 K does not change the intensity of the Xe(Au) state (34%), while on the other hand the Xe(Ag) vanishes. This is a strong indication that the initial AgAu alloy formation proceeds via site-exchange only within the area of the original Ag islands which were produced atop of the underlayer at 275 K. This suggests also, that the activation energy for this site-exchange normal to the surface is smaller than the 2D heat of sublimation of the Ag islands on Au. Only very high temperature treatment leads to a homogenization of the AgAu alloy parallel to the surface.

These results once again demonstrate what kind of detailed informations can be obtained by means of the PAX-method in order to characterize the structure and structural transformations at heterogeneous surfaces on an atomic scale.

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