Thermal stability of atomic Ag/Au and Au/Ag interfaces on a Ru(001) substrate

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THERMAL STABILITY OF ATOMIC Ag/Au AND Au/Ag INTERFACES ON A Ru(001) SUBSTRATE

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The thermally activated intermixing in Ag/Au and Au/Ag bilayers supported on a Ru(001) substrate has been studied using the PAX-technique (photoemission of adsorbed xenon). It is found that the Ag/Au interface (on Ru) is thermally more stable than the Au/Ag interface. In the first case Ag atoms do not penetrate into the Au underlayer at 275 K, while in the second case Au atoms do penetrate into the Ag underlayer at this temperature. These investigations also represent a very successful model study which may be carried over the other metal/metal combinations.

1. Introduction

Epitaxial metal monolayers recently attract increasing attention because of their potential technological importance. For instance, epitaxial monolayers of a magnetic material on a non-magnetic substrate like Fe/Cu(100) [1], Fe/Au(100) [2] may exhibit new magnetic behavior due to an altered geometrical structure and their electronic interaction with the substrate. Furthermore, the magnetic moment of e.g. thin Gd films deposited on Fe is found to couple antiparallel to that of the substrate [3]. These magnetic properties together with the advantages of thin films like miniaturization and low material consumption make these structures potentially useful for magnetic storage devices. But beyond the mere geometrical and electronical structure of these epitaxial metal/metal interfaces it is also their stability against temperature effects which is of great importance for the design and the technological application of such layered structures. Analytically it is not trivial to demonstrate (or exclude) the onset of site-exchange processes and intermixing across

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and atomically sharp interface between two metals. In the present paper we demonstrate that the high surface- and site-specificity of the PAX-technique (photoemission of adsorbed xenon) [4] can be taken advantage of to study this problem very successfully. Here we give a full description of model studies, in which we have investigated the thermally activated site exchange between atoms across atomically sharp Ag/Au and Au/Ag interfaces supported on a Ru(001) substrate. Part of this work has been written up in a previous short account [5]. Of course, these investigations with the silver-gold system must be regarded as a test study with obvious model character for other metal/metal systems. The results once again prove the surface analytical power of the PAX-technique on the nanometer-scale.

2. Experimental

Since the UHV system in which the experiments were carried out has been described in great detail in earlier publications (e.g. refs. [6]) we emphasize here only those technical details which are relevant in the present context. Most importantly, the substrate, a Ru(001) single crystal, was suspended between two thin parallel tungsten wires and connected with a closed-loop helium refrigerator via a gold-plated flexible copper braid [7]. This mounting enabled cooling to < 50 K as well as resistive heating to ~ 1500 K. The temperature was measured with a NiCr-Ni thermocouple spot-welded directly to the backside of the crystal and served to control the temperature rise in a linear fashion using a feedback circuit [8]. This, in turn, enabled the detection of thermal desorption spectra (TDS) of both adsorbed xenon and the deposited metals, silver and/or gold [9,10], by means of a quadrupole mass-spectrometer.

The surface cleanliness and the crystallographic perfectness of both the Ru(001) substrate as well as of the initially deposited Au or Ag monolayer were verified with Auger electron spectroscopy (AES, CMA) and low energy electron diffraction (LEED), respectively. The cleaning procedure of Ru has been described in great detail in ref. [6]. UV (HeI) excited photoemission spectra of xenon adsorbed at 60 K on the differently prepared surfaces were monitored with a hemispherical electron energy analyzer and stored, analyzed and plotted by means of PDP-computer.

The atomically sharp interfaces between Ag on Au and Au on Ag, respectively, were formed by first preparing just one complete, well annealed monolayer of Au or Ag on the clean and perfect Ru(001) surface, and then depositing at 60 K a submonolayer amount of the other metal on top. At this low substrate temperature no intermixing and significant atom mobility is expected. Both metals were evaporated from little resistively heated tungsten baskets, and during deposition the pressure remained in the low 10^{-10} Torr

range. The Ag and Au coverages, θ , were best determined by the thermal desorption traces of both metals recorded after completion of each experiment. These traces are also a better indicator for the completeness of the respective underlayer [9] than AES, LEED or the confidence in a constant (calibrated) evaporation rate. Both Au and Ag do not form alloys with Ru [5,9–11]; the Ru surface acts as an infinite diffusion barrier. Hence, after desorption of the respective Ag + Au overlayer the Ru surface was clean and ready for the next experiment.

3. Results and discussion

3.1. Properties of adsorbed xenon

The first few figures are to recall the principles of the PAX-technique (photoemission of adsorbed xenon). As an overview fig. 1 shows the HeI (21.22 eV) excited angle-integrated UV-photoemission valence band spectrum of a clean Ru(001) surface covered with one monolayer (ML) of xenon. Near the onset of electron emission at E_F the spectrum shows some structure from the Ru valence band; the two sharp and very intense peaks between 5 and 7 eV below E_F arise from the $5p_{3/2}$ and $5p_{1/2}$ photoemission final states of the adsorbed Xe atoms, and the very intense emission around 15 eV is due to

Fig. 1. UV photoemission spectrum of a xenon covered Ru(001) surface excited with HeI radiation of 21.22 eV photon energy. The two sharp and intense signals between 5 and 7 eV below E_F arise from the $5p_{3/2}$ and the $5p_{1/2}$ photoemission final states of adsorbed Xe. The dashed line indicates the substrate background emission.

Fig. 2. $5p_{3/2,1/2}$ UPS spectra of increasing coverages of Xe on (a) one complete monolayer of gold on Ru(001) and (b) one complete monolayer of silver on Ru(001). The substrate background emission (see fig. 1) has been subtracted from each spectrum. The highest spectrum in both panels corresponds to Xe monolayer saturation.

emission of secondary electrons near threshold. The dashed line indicates the substrate induced background emission under the Xe $5p_{3/2,1/2}$ emission. This background is subtracted in all other Xe $5p_{3/2,1/2}$ spectra shown throughout this paper.

Fig. 2 shows sets of Xe $5p_{3/2,1/2}$ spectra on an expanded energy scale (henceforth called “PAX-spectra”) for increasing coverages of Xe adsorbed on (a) a complete and well annealed monolayer of gold on Ru(001) and (b) a complete and well annealed monolayer of silver on Ru(001). In both panels the highest spectrum corresponds to a saturated Xe monolayer. The double peak structure of the $5p_{3/2}$ signal (at lower binding energy) arises mainly from lateral interactions between the adsorbed Xe atoms and the formation of a two-dimensional (2D) electronic band structure within ordered, densely packed 2D Xe islands at submonolayer coverages or in the saturated Xe monolayer [12–14]. Such 2D solid Xe islands of monatomic thickness are only formed on homogeneous, perfectly flat surface patches of sufficient size. Surface defects and adatoms prevent the necessary ordering within the Xe layer. Without discussing this phenomenon any further, in this paper we will use the occurrence of a split $5p_{3/2}$ signal simply as a fingerprint for the existence of sufficiently large perfect patches on the respective surface, and, hence, as an

analytical tool for the demonstration of structural order and chemical homogeneity at the surface.

By contrast, the $5p_{1/2}$ signal (at higher electron binding energy; vertical lines in figs. 2a and 2b) is a single, sharp peak well separated from the $5p_{3/2}$ signal. The width of the $5p_{1/2}$ peaks is also an indicator for the perfectness of the surface: the more perfect the surface the narrower is the $5p_{1/2}$ peak as will

Fig. 3. $\text{Xe}(5p_{3/2,1/2})$ reference spectra from Xe monolayer adsorption on the various indicated single crystal surfaces. Note the different energy positions.

become obvious from this paper. More important, however, is the position of the $5p_{1/2}$ signal on the energy axis with respect to the Fermi level, $E_B^F(5p_{1/2})$. On the Au monolayer (fig. 2a) this binding energy is $E_B^F(5p_{1/2}) = 6.8$ eV, while on the Ag monolayer (fig. 2b) a value of $E_B^F(5p_{1/2}) = 7.55$ eV is found. Both values are also very similar to those found on a bulk Au(111) and a bulk Ag(111) surface, respectively, as shown in fig. 3. The difference $\Delta E_B^F(5p_{1/2}) = 7.55 - 6.8$ eV = 0.75 eV is due to the work function difference between these two surfaces: $\Delta\phi = \phi_{MLAu} - \phi_{MLAg} = 5.6 - 4.75$ eV = 0.85 eV [4,5]. This correlation $\Delta E_B^F \approx -\Delta\phi$ has been shown to hold for many pairs of different homogeneous surfaces [4] and constitutes the basis of the PAX-techniques, because it persists also for different *sites* on heterogeneous surfaces. It enables not only a distinction of Xe atoms adsorbed on Ag- and Au-patches of a surface containing *both* metals, but also of Xe atoms adsorbed at “mixed” surface sites being in contact with both Ag and Au atoms. These “mixed” sites can be of variable composition (Ag:Au ratio) and structure (Ag and Au forming a perfect alloy plane (see figs. 3, 6, and 7); Ag adsorbed *on* Au; Au adsorbed *on* Ag, etc.). Careful reference studies with differently prepared binary Ag + Au surfaces have shown, that $E_B^F(5p_{1/2})$ of Xe atoms adsorbed at all these various “mixed” sites ranges from 7.0 to 7.35 eV, hence, falls between the positions of Xe on pure Au and Xe on pure Ag [15]. This becomes evident from the spectrum of Xe adsorbed on a bulk $Ag_{0.5}Au_{0.5}(111)$ alloy surface compared to the pure metal cases as shown in fig. 3.

Consequently from a heterogeneous surface containing pure Ag-patches, pure Au-patches as well as “mixed” sites, and which is covered with a complete monolayer of Xe, the measured PAX-spectrum is a superposition of $5p_{3/2,1/2}$ spectra, each of which is characteristic for one kind of surface site. The partial spectra are shifted with respect to each other by the difference in “local work function” between inequivalent sites. In order to decompose such an integral spectrum each partial contribution is represented by a set of three Lorentzian lines as depicted in fig. 4. As mentioned above the $5p_{3/2}$ peak is split into the two photoemission final states $5p_{3/2}$ ($m_j = \pm 3/2$) and $5p_{3/2}$ ($m_j = \pm 1/2$), while the $5p_{1/2}$ -peak represents a single final state, $5p_{1/2}$ ($m_j = \pm 1/2$) [13]. The relative intensities and energy separations of the three states are given by the photoemission properties of adsorbed Xe, and therefore are essentially kept constant during the decomposition of a complex integral spectrum into partial PAX-spectra per kind of surface site. Hence, the intensity and the energy position of each partial PAX-spectrum as a whole (consisting of the three Lorentzians as shown in fig. 4) are basically the only variable fit-parameters (see below for more details). The intensity, e.g. of the $5p_{1/2}$ -peak, then is a measure of the relative abundance of the corresponding kind of surface site. The energy position E_B^F of the $5p_{1/2}$ peak, which is more accurate to determine than those of the $5p_{3/2}$ -signals, provides a determination of the local work function at the respective surface site (patch) [4].

Fig. 4. Experimental $5p_{3/2,1/2}$ UPS spectrum (upper trace) of one complete monolayer of xenon adsorbed on an Ag(111) single crystal surface. The fit curve 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 adsorbed Xe. n, l, j, m_j = quantum numbers. The sharp $5p_{1/2}$ peak is best used for the distinction of different coexisting Xe adsorption states on a heterogeneous surface.

The partial intensity per Xe adsorption state is only a meaningful measure of the relative site concentration if the surface is covered with a *complete* Xe monolayer of uniform atomic density. The completeness of the first Xe monolayer can easily be verified by means of TDS; Xe atoms in the second layer desorb at significantly lower temperatures (e.g. ref. [16]). Also fig. 5 shows that the Xe $5p_{1/2}$ intensity, as determined from a fit-procedure described above, abruptly saturates after an exposure of 11 L Xe to the Ru(001) surface covered with one complete monolayer of Ag. Furthermore, the linear relationship between intensity and exposure indicates a constant Xe sticking coefficient up to saturation of the first Xe monolayer at 11 L^{#1}. On flat surfaces the packing density of the adsorbed Xe atoms in a complete monolayer is always similar to a Xe(111) plane, more or less independent of the

^{#1} The exposures in terms of 1 L = 10^{-6} Torr·s given throughout this paper are not corrected for the ion gauge factor for Xe.

Fig. 5. Plot of the partial $5p_{1/2}$ intensity resulting from a fit as shown in fig. 4 as a function of Xe exposure to an Ag(111) surface at 60 K. The linear rise suggests a constant sticking coefficient up to Xe monolayer saturation at 11 L (1 langmuir (L) = 10^{-6} Torr · s¹).

surface periodicity. Structural surface imperfections, however, prevent perfect ordering within the Xe overlayer, because defects are sites of higher coordination and, hence, of higher adsorption energy. They are preferred adsorption sites and therefore act as heterogeneous nucleation centers. The resultant disorder in the Xe overlayer may lead to a moderate scatter in the monolayer capacity (Xe atoms/cm²), which, however, may be roughly estimated from Xe TDS spectra.

3.2. Characterization of (Ag + Au)-films on Ru(001)

3.2.1. PAX-spectra – qualitative aspects

With the adsorption and photoemission properties of Xe in mind we can now turn to a discussion of the PAX-spectra obtained from differently prepared and treated binary (Ag + Au)-layers on Ru(001). We begin with a series of experiments, in which the Ru(001) surface was first covered with a complete well annealed monolayer of Ag, which then was covered with 0.3 ML Au at 60 K and heated to successively increasing temperatures for 10 min each time. Fig. 6 displays four sets of PAX-spectra. The spectra from fig. 6a, were obtained after the 0.3 ML Au/1 ML Ag overlayer (“/” stands for “on”) was warmed up to 275 K for 10 min and then recooled to 60 K. Note the lack of any $5p_{1/2}$ -intensity at $E_B^F = 6.8$ eV (vertical line) which excludes unambiguously the existence of pure Au-sites (patches) on the surface. The single $5p_{1/2}$ peak is at most somewhat asymmetric and its position shifts from 7.1 eV at

Fig. 6. Xe(5p_{3/2,1/2}) (= PAX) spectra for different coverages of Xe adsorbed at 60 K on a complete monolayer of Ag (on a Ru(001) substrate) which was covered with 0.3 ML Au at 60 K following by annealing for 10 min at (a) 275, (b) 350 K, (c) 420 K, and (d) 760 K. Note the spectral changes as a function of annealing treatment in particular at low Xe coverages, which are related to structural transformations at the surface. The highest spectrum in each panel corresponds to a saturated Xe monolayer.

low Xe coverage to 7.45 eV at Xe monolayer saturation (highest spectrum). The evolution of this peak asymmetry (arrow) at intermediate Xe coverage suggests the growth of new Xe states at the higher binding energy side, which

leads to the overall shift of the peak maximum. The $5p_{3/2}$ peak splits only visible at higher Xe coverages. Since the total coverage of $\theta_{\text{Ag}} + \theta_{\text{Au}} = 1.3$ ML implies only a fractional second layer, the surface will comprise step-sites, namely the boundary-sites of islands or small 2D clusters. These step-sites are “decorated” first by Xe atoms and prevent the formation of 2D Xe islands, which explains the poor splitting of the $5p_{3/2}$ peak at lower Xe coverages. Furthermore, these step-sites obviously involve Au atoms as suggested by the low binding energy E_{B}^{F} of the $5p_{1/2}$ signal. Only with increasing Xe coverage the remaining pure Ag-patches from the original Ag monolayer are populated causing the $5p_{3/2}$ splitting and the $5p_{1/2}$ shift to higher binding energies.

Further annealing of the 0.3 ML Au/1 ML Ag film for 10 min at 350 K (fig. 6b) and 420 K (fig. 6c), respectively, causes only minor changes of the resultant PAX-spectra. The $5p_{1/2}$ peak sharpens up; at low Xe coverages ($E_{\text{B}}^{\text{F}}(5p_{1/2})$ is higher than in fig. 6a, and the $5p_{3/2}$ signals begin to split at lower Xe coverages. All three trends support a progressive homogenization of the surface sites populated first by Xe (low coverages) as well as a growth of the metal islands in the second layer. Even annealing at 760 K for 10 min (fig. 6d) causes hardly any further change, except one important detail: At Xe monolayer saturation (highest spectrum) the $5p_{1/2}$ peak exhibits a well resolved shoulder (arrow) near the binding energy characteristic of Xe on pure Ag. Qualitatively, the PAX-spectra from figs. 6a–6d support the notion that already at 275 K the Au atoms (originally deposited on top of a complete Ag monolayer) have started to penetrate into the Ag underlayer, because no $\text{Xe}(5p_{1/2})$ peak from pure Au-sites is observed. An equivalent number of Ag atoms is displaced into the second layer thereby producing a rough surface with high-coordination (step-) sites. With increasing annealing temperature more Au atoms are dissolved homogeneously in the first layer (in contact with Ru) and more Ag atoms form increasingly growing Ag islands in the second layer.

Before we draw even more detailed conclusions from a careful quantitative decomposition of the spectra shown in figs. 6a–6d, we shall first describe the PAX-spectra observed from a second series of experiments in which the order of Ag and Au deposition was reversed. First a complete and well annealed Au monolayer was prepared onto which 0.5 ML Ag were deposited at 60 K. At this low substrate temperature the Ag atoms are basically immobile and remain statistically distributed across the Au underlayer, thereby producing a large number of high-coordination sites around them. The resultant PAX-spectra are displayed in fig. 7a. The initial $5p_{1/2}$ peak is rather broad and grows *between* the positions of Xe on pure Au or pure Ag, respectively (vertical lines), which is characteristic of “mixed” sites. These sites correspond to the high-coordination, next-nearest neighbor sites of the Ag atoms because they are populated first (low Xe coverage). At intermediate Xe coverage a $5p_{1/2}$ peak suddenly emerges at 6.8 eV characteristic for Xe on pure Au while the

Fig. 7. Xe($5p_{3/2,1/2}$) (=PAX) spectra for different coverages of Xe adsorbed at 60 K on a complete monolayer of Au (on a Ru(001) substrate) which was covered with 0.5 ML Ag at 60 K (panel (a)) followed by annealing for 10 min at (b) 275 K, (c) 350 K and (d) 760 K. Note the strong spectral changes of the $5p_{1/2}$ signal as a function of annealing temperature for both low and high Xe coverages. These changes are indicative of thermally activated structural and chemical redistributions at the surface. The highest spectrum in each panel corresponds to Xe monolayer saturation.

original intensity from “mixed” sites remains visible as a shoulder. Further increase of the Xe coverage causes the appearance of a second $5p_{1/2}$ peak in the position for Xe on pure Ag with $E_B^F = 7.55$ eV. At no stage in fig. 7a the

$5p_{3/2}$ peak shows any splitting. (The $5p_{3/2}$ double peak structure at high Xe coverages is not due to an m_j -splitting but arises from Xe on Au- and Ag-sites, respectively, as does the $5p_{1/2}$ double peak structure.) Warming this 0.5 ML Ag/1 ML Au film to 275 K for 10 min results in the PAX-spectra from fig. 7b. There is only very little intensity from “mixed” sites left (arrow). Instead, a rather sharp $5p_{1/2}$ peak first grows at 6.8 eV (Xe on Au) followed by a second also rather sharp $5p_{1/2}$ peak at 7.5 eV (Xe on Ag). The $5p_{3/2}$ peak begins to show indication of a double peak structure (shoulder at low binding energies). These spectra from fig. 7b are in marked contrast to those shown in fig. 6a. Both figures relate to films which were annealed at 275 K. In the first case (0.3 ML Au/1 ML Ag) this temperature is enough to activate penetration of Au atoms into the Ag underlayer. In the second case (0.5 ML Ag/1 ML Au), however, the Ag atoms do not yet exchange site with Au atoms from the first layer, but rather coalesce and form extended 2D Ag islands on the Au underlayer as suggested by the negligible number of (“mixed”) boundary sites (arrow) as well as the improved order in the Xe overlayer ($5p_{3/2}$ splitting).

Further annealing of the 0.5 ML Ag/1 ML Au system at 350 K leaves the $5p_{1/2}$ peak at 6.8 eV (Xe on Au) unaffected (fig. 7c). The second $5p_{1/2}$ signal now peaks at 7.3 eV, and can no longer be assigned to Xe on pure Ag islands but corresponds to a large number of “mixed” sites, which, however, are now populated at higher Xe coverages, in contrast to the “mixed” sites ($6.8 \text{ eV} < E_B^F(5p_{1/2}) < 7.5 \text{ eV}$) in fig. 7a. Therefore we assign the “mixed” sites from fig. 7c to *flat* alloy-sites created by intermixing between the Ag islands (concluded above from fig. 7b) and the Au underlayer.

Finally annealing at 760 to 10 min causes the formation of a more or less homogeneous AgAu alloy throughout both layers as judged by the single $5p_{1/2}$ signal in fig. 7d. The continuously increasing $5p_{1/2}$ peak width with increasing Xe coverage may be taken as an indication for the successive population of more and more Ag-rich sites (see below).

The above described observations from the (integral) PAX-spectra in figs. 6a–6d and 7a–7d can be refined somewhat by taking difference spectra between pairs of consecutive traces. Examples of such difference spectra as obtained from figs. 7a–7d are shown in figs. 8a–8d and are called “incremental spectra”, because each one of them corresponds to an addition to the Xe coverage (increment). These incremental spectra accentuate the successive population of different surface sites in the order of decreasing Xe adsorption energy, and help to isolate the spectral characteristics of the various kinds of surface sites. For instance, fig. 8a shows more clearly the initial saturation of the “mixed” step-like sites on this surface before the Au sites and then the Ag sites are populated. Obviously, the adsorption energy E_{ad} of the Xe follows the sequence $E_{ad}(\text{step}) > E_{ad}(\text{Au}) > E_{ad}(\text{Ag})$. In fig. 8b (obtained from 7b) the obvious splitting of the $5p_{3/2}$ signal of Xe on Ag (upper two increments) supports much clearer the extended island structure of the Ag than fig. 7b.

Fig. 8. Difference spectra between successive traces from the corresponding panel in fig. 7. Each difference spectrum corresponds to an addition to the Xe coverage and is therefore termed "incremental spectrum". These incremental spectra accentuate the successive population of inequivalent surface sites.

Also fig. 8c improves the splitting of the $5p_{3/2}$ signal, and finally fig. 8d explains the continuous $5p_{1/2}$ peak broadening in fig. 7d as a continuous peak shift to higher binding energy, probably due to a continuous change in AgAu composition of the successively occupied surface sites. The increase of $E_B^F(5p_{1/2})$ with increasing Xe coverage suggests a successive population of

more and more Ag-rich sites in agreement with the relative adsorption energies (see above).

Since the incremental spectra have the tendency to isolate the spectral properties of Xe atoms adsorbed at individual types of surface sites, they can be used advantageously to establish the fit-parameters for the related partial $5p_{3/2,1/2}$ spectra, as described in the following section.

3.2.2. PAX-spectra – quantitative aspects

The quantitative analysis of the PAX-spectra from figs. 6 and 7 is based on a decomposition procedure as follows: First the *incremental* spectra corresponding to figs. 6a–6d (not displayed here) and from figs. 8a–8d were fitted in the order of increasing Xe coverage with a set of three Lorentzian functions per Xe state as depicted in fig. 4 and discussed earlier. The thus determined *electron binding energies* per Xe state were then used as input to repeat the fit procedure with the *integral* spectra shown in figs. 6a–6d and figs. 7a–7d in order to find the *partial intensities* for all Xe states contributing to the respective Xe monolayer spectrum. As explained before the $Xe(5p_{1/2})$ electron binding energy per Xe state is a measure of the local work function at the corresponding kind of surface site, while the partial intensity per Xe state provides the relative concentration of this particular type of surface site.

Examples of the finally obtained best fits of Xe monolayer PAX spectra are displayed in fig. 9 for the two most important situations in the present study, namely the 0.3 ML Au/1 ML Ag system annealed at 275 K (fig. 9a) and the 0.5 ML Ag/1 ML Au system annealed at 275 K likewise (fig. 9b). Qualitatively the spectral distinction between the two systems could hardly be more clearcut: in the first case the single $5p_{1/2}$ peak suggests intermixing between Ag and Au, while in the second case the two $5p_{1/2}$ peaks indicate the persistence of pure Au and pure Ag. Quantitatively, the best fit to spectrum 9a results in three Xe states, which, based on their $5p_{1/2}$ electron binding energies, suggest 30% of the Xe atoms (of a complete Xe monolayer) to sit on pure Ag sites, while (61% + 9%) sit on “mixed” sites effected by Ag and Au. Certainly no Xe state characteristic of pure Au is found #2. The best fit to spectrum 9b requires four Xe states, with 35% of the atoms emitting from pure Au sites, 54% of the Xe atoms sitting on pure Ag sites, and (5% + 6%) of the intensity coming from “mixed” sites. We do not claim to know the exact assignment of the various “mixed” states (they were simply needed in order to account for the broad emission at these intermediate energies reflecting a distribution in structure and composition of these sites), but we do claim to be able to distinguish quantitatively between the three classes of sites on the respective surface, namely pure Au-, pure Ag- and “mixed” sites.

#2 According to our long experience these percentages are accurate within $\pm 5\%$.

Fig. 9. Examples for the best fits of Xe monolayer PAX spectra (using triplets of Lorentzian functions as defined in fig. 4 for (a) a 0.3 ML Au/1 ML Ag film on Ru(001) annealed for 10 min at 275 K, and (b) a 0.5 ML Ag/1 ML Au film on Ru(001) annealed for 10 min at 275 K likewise. Note the clear difference in the $5p_{1/2}$ peak shape, namely a single peak in panel (a) and a double peak in panel (b). The different sets of three Lorentzian lines correspond to Xe atoms adsorbed at different surface sites, and the percentages represent their relative surface concentrations (see text).

A compilation of the fit results from all Xe monolayer PAX-spectra shown in figs. 2a, 2b, 6a–6d and 7a–7d is given in fig. 10. At the top the electron binding energy scale is divided into three regimes, namely two vertical lines at ~ 6.8 eV and ~ 7.6 eV indicating the positions of the $\text{Xe}(5p_{1/2})$ signal on a pure Au (fig. 2a) and a pure Ag monolayer (fig. 2b) on Ru(001), respectively, and a broad regime between 7.0 and 7.4 eV, which encompasses the $\text{Xe}(5p_{1/2})$ binding energies from all kinds of “mixed” sites including a substitutional AgAu alloy surface (see line AgAu in the center). The black bars mark the $5p_{1/2}$ position as they came out from the decomposition of the experimental Xe monolayer spectra. As mentioned above no further attempt is made in order to assign the various “mixed” states from one surface. The percentages in fig. 10 denote the relative intensity of each decomposed state. The small atomistic models are to visualize the conclusions about the chemical distribution and structure of the different treated (Au + Au)-films.

A careful inspection of the numbers in fig. 10 reveals several very interesting details which go much beyond the qualitative observations described earlier. As pointed out before, a temperature of 275 K suffices to activate intermixing between the 0.3 ML Au overlayer with the 1 ML Ag underlayer. The numbers in the upper half of fig. 10, however, further suggest that *always*

Fig. 10. Compilation of $5p_{1/2}$ electron binding energies (black bars) and relative intensities (percentages) of coexisting Xe adsorption states on differently annealed (Ag+Au) films on a Ru(001) substrate, as obtained from a decomposition of all the Xe monolayer PAX-spectra shown in figs. 6a–6d and 7a–7d. These data support the small structure models shown on the right-hand side.

~ 30% of the surface are Ag-like, even after annealing at the very high temperature of 760 K (see shoulder in spectrum 6d).

These 30% agree with the amount of 0.3 ML Au originally deposited. This strongly suggests, that the adsorbed Au atoms have *completely* penetrated into the Ag underlayer, thereby displacing an equivalent number of Ag atoms into the second layer where they then form *monatomically* thick islands of pure Ag. Furthermore, the corresponding relative intensities of the “mixed” states are compatible with a lateral growing of these pure Ag islands with increasing annealing temperature (see the atomic models), because the number of island boundary sites decreases from 9% to ~ 0%. The high value of the Xe($5p_{1/2}$)

electron binding energy (7.4 eV) of the final “mixed” state (68% after 760 K) is suggestive of a Ag-rich alloy in the first layer.

Also in the second experiment with the Au underlayer two interesting details may be concluded from the numbers compiled in the lower half of fig. 10. Firstly, upon annealing from 60 to 275 K the relative intensity of the Xe state on pure Ag sites *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 K to 350 K does *not* change the intensity of the Xe state on pure Au sites (34%), while on the other hand the Xe(Ag) signal 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 on top 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 at 760 K leads to a homogenization of the AgAu alloy parallel to the surface.

4. Summary and conclusions

As a result of these model experiments we find, that an Ag/Au-interface (on Ru) is thermally more stable than an Au/Ag interface. In the first case (initial Au underlayer) Ag does not penetrate into the Au layer below 275 K. Conversely, in the second case (initial Ag underlayer) the Au atoms exchange site with underlying Ag atoms already at 275 K, leading to the formation of a monolayer of an $\text{Ag}_{0.7}\text{Au}_{0.3}$ alloy covered with pure, monatomically thick Ag islands. This remarkable difference appears easily conceivable in terms of the energy terms involved:

- (1) The adsorption energy of Au on Ru(001) is significantly higher than that of Ag [9].
- (2) The surface free energy of Ag is lower than that of Au [17].
- (3) The lateral interaction energy between adsorbed Ag atoms (on Ru(001)) is attractive [9].
- (4) The heat of formation of AgAu alloys is slightly exothermic [18].

The first two terms favor Au atoms to get in contact with the Ru substrate and Ag atoms to be exposed in the second (outer) layer. This process, however, will compete with the exothermicity of the AgAu alloy formation which tends to maximize the number of Ag–Au bonds. Finally, the attractive Ag–Ag interaction explains the formation and the growth of the 2D Ag islands in the second layer of the first system (initial Ag underlayer).

A further conclusion from the present study certainly is, that the 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. Of course, the (Ag + Au)-system was only chosen as a case study. The investigations described here can be carried over the other metal/metal combinations.

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