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Surface Characterization by Means of Photoemission of Adsorbed Xenon (PAX)

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Photoemission of adsorbed xenon (PAX) is a very sensitive probe towards the local work function. This is shown with three selected examples, namely a bimetallic Ag/Ru(001) surface, a trimetallic (Ag + Au)/Ru(001) surface and an oxygen exposed Si(111)7 × 7 surface, which prove PAX to be a powerful technique for the qualitative and quantitative characterization of surface heterogeneities on an almost atomic scale.

INTRODUCTION

It is recognized more and more that atomic-scale structural and chemical defects at surfaces play an important role in various physical and chemical surface processes, such as light and particle scattering, nucleation of epitaxial layers and reacted surface compounds, heterogeneous catalysis, etc. Techniques are now available to detect and study various aspects of such surface heterogeneities even on an atomic scale. Here we will demonstrate with a few selected examples that the photoemission of adsorbed xenon atoms (photoemission of adsorbed xenon—PAX) can also provide structural and electronic information about different patches as well as individual sites on heterogeneous surfaces. The intent of the present paper is not so much to discuss the physical and chemical properties and implications of the observed surface heterogeneities and modifications, but to demonstrate the very high surface analytical power of the PAX technique.

THE PAX TECHNIQUE

Figure 1 shows the 5P₃/₂, 5P₁/₂ photoemission spectrum of one monolayer of Xe adsorbed on Ag(111), together with the best fit using three Lorentzian lines. The 5P₃/₂ signal is split into two sub-levels with the magnetic quantum numbers mⱼ = ±3/2 and mⱼ = ±1/2 owing to substrate–xenon and xenon–xenon interactions in the adsorbed layer.₁,² The separation between these two mⱼ sub-levels is substrate dependent,³ for example on Ru(001) the 5P₃/₂ peak is only broadened but not visibly split as on Ag(111) (Fig. 1). Instead, the 5P₁/₂ signal is very sharp and well resolved, so that all following discussions and conclusions exclusively will be based on spectral changes of this peak.⁴ For instance, on Ag(111) the 5P₁/₂ emission peak occurs at an electron binding energy of Eₜ = 7.6 eV (relative to the substrate Fermi level). The basic principle of PAX is the fact that Eₜ(5P₁/₂) (as well as Eₜ of all other electronic levels) of adsorbed Xe atoms varies linearly with the work function of the substrate surface. This has been verified for a large number of homogeneous single crystal surfaces.⁵ As a consequence the difference in electron binding energy ΔEₜ(5P₁/₂) for xenon adsorbed on two different surfaces was found to be:

\[ ΔEₜ(5P₁/₂) = -Δφ \]

with Δφ being the work function difference between both substrates. As also demonstrated in several papers⁶–⁷ this relationship applies also to heterogeneous surfaces. In this case Δφ homogeneous corresponds to the difference in local work function between two unlike sites on the same surface, and which, indeed, results in a superposition of Xe(5p) spectra from Xe atoms residing on both kinds of surface sites and which are again shifted by ΔEₜ = -Δφ homogeneous (see, for example, Fig. 2 and the following text). The adsorbed xenon atoms behave as local probes towards the electrostatic surface potential at their immediate adsorption sites. This potential, of course, depends on the chemical and structural nature of these locations. Since also the adsorption energy of xenon depends on the chemical and geometrical structure of the adsorption site, it is possible to decorate different surface sites successively in the order of decreasing adsorption energy and, hence, to probe the surface potential at each kind of site more or less separately. At Xe monolayer completion the partial Xe(5P₁/₂) intensities provide a measurement of the relative surface concentration of the corresponding kinds of surface sites. For a more complete description of the PAX method we refer to Ref. 5. Of course, the PAX studies should be accompanied by measurements using other surface techniques such as AES, LEED, UPS, XPS, etc.

EXPERIMENTAL

PAX measurements can be performed with any photoelectron spectrometer equipped with a He resonance
fit with Lorentzian lines for the three photoemission final states.

In the present work, the cross-section for Xe(5p) photoionization is about ten times larger with He I (21.22 eV) than with He I (40.81 eV). The spectra shown in the present paper were monitored with a VG ESCA III-type analyser. Obviously, the use of a high-resolution spectrometer would be more advantageous in order to improve the separation of coexisting Xe adsorption states at different surface sites. The sample temperature should be preferably below 80 K because of the very low adsorption energy of Xe on most substrates (~5 kcal mol⁻¹). In the present work this was achieved by connecting the sample holder to the tip of a modified cryo-pump. Particularly good vacuum conditions (≤ 10⁻¹⁰ Torr) are required, since most residual gases displace the weakly physisorbed Xe atoms. Details of the spectral analysis are described in Ref. 5.

RESULTS

In this section we describe PAX results from model studies with bimetallic and trimeatalic surfaces as well as with modified Si(111) samples. The examples selected are to substantiate the statements from the previous section as well as to emphasize the surface diagnostic power of the PAX method. We have chosen to show many figures because, in general, figures have a high information density.

Bimetallic Ag/Ru(001) surfaces

Combined AES, TDS, LEED and work function measurements⁵ ⁶ ¹⁰ have shown unambiguously that well-annealed sub-monolayer deposits of silver form islands on the Ru(001) surface which are monoatomic thick and which exhibit a compressed (111)-like structure.¹¹

Figure 1. Xe(5p₃/₂, 5p₁/₂) photoemission spectrum of a complete monolayer of xenon adsorbed on Ag(111) together with the best fit with Lorentzian lines for the three photoemission final states 5p₃/₂ (m_j = ±3/2), 5p₁/₂ (m_j = ±1/2) and 5p₃/₂ (m_j = ±1/2).

lamp for UPS. The cross-section for Xe(5p) photoionization is about ten times larger with He I (21.22 eV) than with He I (40.81 eV).⁸ The spectra shown in the present paper were monitored with a VG ESCA III-type analyser. Obviously, the use of a high-resolution spectrometer would be more advantageous in order to improve the separation of coexisting Xe adsorption states at different surface sites. The sample temperature should be preferably below 80 K because of the very low adsorption energy of Xe on most substrates (~5 kcal mol⁻¹). In the present work this was achieved by connecting the sample holder to the tip of a modified cryo-pump. Particularly good vacuum conditions (≤ 10⁻¹⁰ Torr) are required, since most residual gases displace the weakly physisorbed Xe atoms. Details of the spectral analysis are described in Ref. 5.

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Bimetallic Ag/Ru(001) surfaces

Combined AES, TDS, LEED and work function measurements⁵ ⁶ ¹⁰ have shown unambiguously that well-annealed sub-monolayer deposits of silver form islands on the Ru(001) surface which are monoatomic thick and which exhibit a compressed (111)-like structure.¹¹ 5p₃/₂, 5p₁/₂ spectra of different amounts of xenon adsorbed at 60 K on such a Ru(001) surface covered with θₐg = 0.2 ML Ag (in the form of well-annealed Ag islands, as sketched in the inset of Fig. 2(a)) are reproduced in Fig. 2(a).⁶ (The metal coverages reported in this paper were best determined by TDS of the respective metal at the end of an experiment.) At low exposures (≤ 3 L Xe) we find the typical two-peak Xe(5p₃/₂, 5p₁/₂) spectrum with Eₐ(5p₃/₂) = 6.7 eV (peak A). This value is the same as on pure Ag(111). For exposures > 8 L Xe, however, a second 5p₁/₂ peak (B) appears and grows at Eₐ(5p₁/₂) = 7.6 eV. This energy position is the same as on pure Ag(111). Hence, the two 5p₁/₂ signals at 6.7 eV and 7.6 eV are indicative of Xe atoms being adsorbed on free Ru patches and Ag islands on this bimetallic surface, respectively. The separation between both peaks is identical to the work function difference between pure Ag(111) and Ru(001). Furthermore, spectrum c in Fig. 2(a) (2.1 L Xe) exhibits a clear asymmetry of peak A to higher binding energies, which, in fact, could be shown to arise from the third possible Xe state (C) on this bimetallic surface, namely from Xe atoms at the Ag-island boundary sites [Xe(Ag/Ru)], which are also step-sites, because the Ag islands are on the Ru(001) surface.⁶ Figure 2(b) shows incremental PAX spectra from the 0.2 ML Ag/Ru(001) surface, i.e. difference spectra between successive spectra from Fig. 2(c). These increments accentuate the successive population of the three possible surface sites, Xe(Ru), Xe(Ag/Ru) and Xe(Ag), in the order of decreasing adsorption energy and emphasize the different 5p₁/₂ peak positions for the latter two. Starting from the Eₐ(5p₁/₂) values suggested by Fig. 2(b) for all three Xe states, Fig. 2(c) shows a least-mean-squares-fit to the Xe monolayer spectrum on this 0.2 ML Ag/Ru(001) surface (spectrum g in Fig. 2(a); 15.3 L Xe), using three sets of 5p₁/₂ peaks as defined in Fig. 1. Note that most peak positions, separations and relative intensities are known from calibration measurements with pure Ag(111) and Ru(001) surfaces as well as from Fig. 2(b), so that the relative intensity of each Xe adsorption state as a whole is mainly the only variable parameter. In the present case the Xe(Ag) intensity suggests 20% of the Xe atoms (at Xe monolayer saturation) to sit on Ag sites. This is in excellent quantitative agreement with the original Ag coverage of 0.2 ML. Likewise the partial 5p₁/₂ intensities of the Xe(Ru) and the Xe-(Ag/Ru)-state are a measure of the relative abundance of these two kinds of surface sites. In particular, PAX provides a 'titration' of the 'mixed' Ag/Ru step-sites, which may be especially important for catalytic processes on such bimetallic surfaces.

For a given Ag coverage, θₐg, the number of Ag/Ru boundary sites, of course, depends on the distribution of the silver on the surface. Figure 3 shows a plot of the partial Xe(Ag/Ru) intensity as a function of Ag coverage for two different preparations of the Ag overlayers. The dashed curve was obtained for sub-monolayer Ag films deposited onto Ru(001) at room temperature and well annealed at 500 K. By contrast, the full curve was obtained for sub-monolayer Ag films deposited at 90 K and heated to 500 K. According to nucleation theory
Figure 2. (a) Xe(5p3/2,1/2) spectra for increasing coverage of xenon on a Ru(001) covered with 0.2 monolayers of Ag. The spectrum g corresponds to Xe monolayer saturation, and the 5p$_{3/2}$ signals A, B and C to Xe atoms being adsorbed on free Ru sites, on top of Ag islands and at Ag-island boundary sites, respectively. (b) 'Incremental' spectra as obtained by taking the difference between neighbouring spectra from Fig. 2(a). These incremental spectra accentuate the successive population of the three possible sites on this bimetallic 0.2 ML Ag/Ru(001) surface, namely Xe(Ru), Xe(Ag/Ru) and Xe(Ag), in the order of decreasing Xe adsorption energy. (c) Decomposition of the Xe monolayer curve from the 0.2 ML Ag/Ru(001) surface (spectrum g) in Fig. 2(a) into three sets of Xe spectra as defined in Fig. 1.
this latter low-temperature deposition should yield many small Ag nuclei while the room-temperature deposition is expected to result in fewer, but larger Ag nuclei, because at room temperature Ag is already somewhat mobile. This difference is clearly revealed by Fig. 3. The full curve (low-temperature deposition) goes through a pronounced maximum around $\theta_{Ag} \approx 0.3$ ML, indicating a much higher number of Ag/Ru boundary sites (many small islands), in contrast to the dashed curve (room-temperature deposition). Beyond $\theta_{Ag} \approx 0.3$ ML the decrease of the full line suggests the beginning of coalescence of Ag islands, which is accompanied by the elimination of Ag/Ru sites. Thus, PAX measurements provide (indirect) information about the distribution at bimetallic surfaces. Considering both the Xe(Ag)- and the Xe(Ag/Ru)-intensity it is even possible to estimate the average size of the Ag islands (assuming they are circular in shape). 

Figure 3. Plot of the partial Xe(5p$_{1/2}$) intensity originating from Xe atoms at Ag/Ru boundary sites on Ag/Ru(001) surfaces as a function of Ag coverage. The full and dashed curves are measured for two different preparations of the Ag overlayers. Full line: deposition at 90 K followed by short annealing at 500 K. Dashed line: deposition at 270 K followed by short annealing at 500 K.

Figure 4. (a) PAX spectra from a Ru(001) surface which was precovered with well-annealed Ag islands ($\theta_{Ag} = 0.21$ ML Ag) and then exposed at 60 K to an additional amount of 0.21 ML Au. At this low temperature the Au atoms remain statistically distributed across the surface as sketched in the small inset. (b) Incremental PAX spectra as obtained by taking the difference between neighbouring spectra from Fig. 4(a). (See also Fig. 2(b).)
Trimetallic Ag/Ru(001) surfaces

Figure 4(a) shows PAX spectra for increasing amounts of Xe adsorbed on a trimetallic surface which was prepared as follows. The Ru(001) substrate was first covered with 0.2 ML of Ag and then well annealed in order to form Ag islands again. This island structure was cooled to 60 K and then covered with an additional 0.21 ML of Au from the vapour phase. At this low temperature the impinging Au atoms are immobile and therefore are expected to be distributed statistically across the whole surface, as sketched in the inset of Fig. 4(a). As a consequence many 'mixed' Au/Ru- and Au/Ag-sites are formed at the expense of Ru- and Ag-sites. The $E_{BF}^{(5p_{1/2})}$ values of all these mixed sites (including the Ag/Ru sites from the original Ag boundary sites) fall between the limiting values of Xe(Ag) and Xe(Ru), because $E_{BF}^{(5p_{1/2})}$ on Au is very similar to $E_{BF}^{(5p_{1/2})}$ on Ru(001). This is exactly the message of Fig. 4(a), and there is hardly any free Ru surface left and certainly no more resolved Xe(Ag) state as in Fig. 2(a). The variable shape and peak maximum position of the total Xe ($5p_{1/2}$) signal in Fig. 4(a) suggests the successive population of different kinds of sites owing to differing adsorption energies. This is again emphasized by the corresponding incremental spectra in Fig. 4(b). At lowest Xe coverage (0.5 L Xe) the few Ru sites are populated first. Between 0.5 L and 5 L xenon adsorbs at least at two kinds of 'mixed' site, while at exposures >5 L two more kinds of site are populated, with the one at lower binding energy of 6.8 eV corresponding to Xe on Au. Also, the number of pure Ag sites must be very small according to the negligible Xe(Ag) intensity. Already these qualitative considerations show that PAX spectra may furnish information about the chemical distribution at surfaces containing even three metals, and we shall mention that a more quantitative decomposition at surfaces containing even three metals, and we shall mention that a more quantitative decomposition of the spectra from Fig. 4(a) and (b) is also very possible if $E_{BF}^{(5p_{1/2})}$ reference values are available for the three possible sites on each corresponding bimetallic system, for example Au/Ag, Ag/Ru and Au/Ru. In another paper we have used this approach to study in more detail the two-dimensional intermixing between the Ag islands and the co-deposited Au atoms upon annealing at successively higher temperatures.

Oxygen adsorption on Si(111)(7 × 7)

Figure 5 shows incremental PAX spectra for the interval of 2 L-1 L Xe incremental PAX spectrum. The lowest curve has a shape close to the corresponding incremental spectrum in Fig. 5 proves the very high sensitivity of the PAX technique towards traces of surface impurities. The further changes of the $5p_{1/2}$ increments in Fig. 5 as a function of oxygen precoverage will be discussed in greater detail elsewhere. Here we note that they qualitatively suggest the occurrence of (at least) two new, oxygen-induced (Xe adsorption) sites on this surface. HREELS studies have led to the conclusion that such low adsorption temperatures oxygen first dissociates, but then at somewhat higher coverages co-exists in an atomic as well as molecularly adsorbed state on Si(111). The two new states in the PAX spectra, marked by vertical dashed lines in Fig. 5, occur at lower electron binding energies suggesting higher local surface potentials at these sites. This appears compatible with the high electronegativity of the oxygen particles.

Finally, Fig. 6 displays the influence of temperature treatment of a Si(111) surface precovered with 0.5 L O$_2$ at 60 K on the 2 L-1 L Xe incremental PAX spectrum. The lowest curve has a shape close to the corresponding curve in Fig. 5. (In fact, the small differences suggest an (unintentionally) slightly lower oxygen coverage in the
former case, which again demonstrates the rather high surface sensitivity of PAX.) Warming up to room temperature for 10 min results in a shift of $5p_{1/2}$ intensity back to higher binding energies, most probably due to dissociation of the molecular oxygen species and/or some diffusion of oxygen into the bulk. Heating to 500°C for 10 min leads to a continuation of this trend. But note that the shape and position of the $5p_{1/2}$ increment of the spectrum obtained after annealing at 500°C are still very different from the pure Si spectrum (lowest trace in Fig. 5), because AES still shows oxygen present on the surface and LEED now shows a (1 x 1) pattern.

CONCLUSION

We have shown with the three selected examples, namely the bimetallic Ag/Ru(001) system, the trimetallic Ag, Au/Ru(001) surface and the low-temperature interaction of oxygen with the Si(111)(7 x 7) surface, that PAX (after appropriate calibration) provides information not only about the quantitative chemical composition at surfaces but also about the distribution of the surface constituents, namely whether they are in the form of extended islands (patches) or in the form of a more atomic dispersion. Temperature-induced changes of this distribution, of course, can be used to study surface diffusion processes. Furthermore, the Xe($5p_{1/2}$) electron binding energy $E_B^{Xe}(5p_{1/2})$ is a measure of the local work function (surface potential) and, therefore, probably of the local charge density. As shown in earlier papers, dissimilar surface sites which are less than 10 Å apart can be distinguished. Although the presented examples in this paper are studies with well-prepared model surfaces, an important advantage of the PAX technique lies in the fact that it can also be applied to more realistic kinds of samples, for example powders. The only limiting condition is the same as for any photomission experiment: the sample must be conducting in order to avoid charging problems.

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4. Of course, the $5p_{3/2}$ signal undergoes the same variations, but is more difficult to analyse.