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Photoelectron spectroscopy studies of the Pd/Ru(0001) and (Cu + Pd)/Ru(0001) interfaces

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Abstract

The electronic structures of Pd and (Cu + Pd) overlayers on Ru(0001) have been studied. Photoelectron emission spectroscopy based on synchrotron radiation and radiation from a Mg $K\alpha$ x-ray source has been used to study the valence band of the surfaces and the Ru 3d, Pd 3d and Cu 2p core levels. The interaction of Pd with Ru(0001) is studied in the coverage range of submonolayer to several monolayers. The core level spectra of the Pd 3d_{5/2} level show a new component for Pd coverages above 1 ML. In the submonolayer range the binding energy (BE) of the Pd 3d_{5/2} level is constant at 335.08 eV. A state characterized as an interface state between the Pd adlayer and the Ru substrate is observed at a BE of 1.22 eV. This state, which dominates the valence band for submonolayer Pd coverages, has not been reported earlier and it is seen neither for clean Ru(0001) nor for multilayers of Pd. It is a characteristic that the overlayer d bands are narrower in the low-coverage regime. Deposition of Cu, on a 0.4 ML Pd/Ru(0001) surface up to 1 ML total coverage of Pd and Cu, results in a mixed two-dimensional overlayer.

1. Introduction

A comprehensive review of the physical and chemical properties of bimetallic surfaces was given by Rodriguez [1]. Interest in the electronic and geometrical structures of bimetallic ultrathin films of Pd and Cu is motivated by a desire to achieve a better understanding of alloying conditions and their catalytic properties. In the bulk the Cu–Pd system forms two ordered alloys, CuPd and Cu₃Pd [2]. Depositions of Pd in the submonolayer range on low-index Cu surfaces result in the case of Cu(100) initially in alloying of Pd atoms into the lattice sites of the substrate and, at higher coverages, a c(2 × 2) structure [3]. On Cu(110) a rough surface morphology occurs with alloying in the surface layer and formation of ordered Pd–Cu chains at low Pd coverages which are covered by substrate atoms [4]. The growth mode

of submonolayers of Pd on Cu(111), studied by Bach Aaen *et al* [5], is for temperatures up to 100 °C characterized by Pd-induced phase nucleation at ascending steps and in dendritic islands on large terraces. Deposition of Pd at temperatures above 160 °C results in capping of Cu. In the temperature range 220–300 °C individual Pd atoms are substituted in the first layer and subsurface Pd is observed. Recently, the structure of ultrathin Pd films evaporated on Cu(111) was determined to be a random surface alloy in the first three layers [6]. The opposite deposition sequence, Cu on the three low-index Pd surfaces, results at room temperature in a layer-by-layer growth mode (see [7] and references therein). For the case of Cu on Pd(111), which was studied in [7], it was found that for temperatures higher than 450 K the Cu overlayer alloys with the Pd substrate. Theoretical calculations of the phase diagram for surface alloys are given in the papers [8–10], where both Cu and Pd deposited on a Ru(0001) surface are predicted to stay at the surface. The corresponding calculations for Cu on a Pd substrate show that Cu will alloy in the Pd bulk as proved experimentally in [7]. For Pd on a Cu substrate it is predicted that the Pd atoms will stay at the surface.

Acetylene coupling reactions on Pd and Pd-containing surfaces can yield a variety of linear and cyclic products including heterocycles [11–13]. Acetylene trimerization to benzene was studied on monometallic Pd films and on bimetallic ($\text{Pd}_x + \text{Au}_{1-x}$) monolayer films, with $0 < x < 1$ [14]. The catalytic properties of PdCu alloys have been studied in relation to oxidation of both CO [15] and alkenes [16], hydrogenation of CO [17] and oxidation of CO in combination with reduction of NO [18].

The Ru(0001) surface is a close-packed surface with the same type of packing as the (111) planes of Pd and Cu. Ru has a metallic radius 1.34 Å, in between 1.28 Å for Cu and 1.38 Å for Pd. The relative surface energies of the two admetals are 2.0 J m^{-2} for Pd and 1.9 J m^{-2} for Cu and for the substrate Ru it is 3.4 J m^{-2} [19]. The substrate Ru(0001) is considered as ‘inert’ in the sense that no surface compounds are formed and no interdiffusion between the substrate and the adsorbates, Pd or Cu, is observed. However, as demonstrated in the present paper, there are significant changes in the 3d core level binding energies (BEs) of Ru and the first overlayer.

As regards the growth mechanisms of Pd on Ru(0001) it has been shown, by low-energy ion scattering results, that the first two Pd layers grow in a layer-by-layer mode [20]. In [21] it was stated that metal overlayers with a electronegativity comparable with that of the substrate, as is the case for Pd and the Ru substrate, will form densely packed islands in the early adsorption stage. Thin Pd films on Ru(0001) were studied using Al $K\alpha$ x-rays in [22]. The BE of the Pd $3d_{5/2}$ level was concluded to be constant at 335.65 eV for all Pd coverages, when measured with the x-ray source.

As a conclusion of the earlier studies, it can be stated that no interdiffusion of Pd and Cu into the ruthenium substrate has been observed. Therefore, two-dimensional interaction, and possible alloying, between Pd and Cu can be studied on Ru(0001).

In the present paper we study changes in the electronic structures at the Pd/Ru(0001) and (Cu + Pd)/Ru(0001) interfaces using photoelectron spectroscopy with synchrotron radiation and Mg $K\alpha$ x-rays. The outline of the paper is as follows. In section 2 the experimental procedures are given. The experimental results in section 3 are subdivided in two sections. Section 3.1 deals with the Pd/Ru(0001) interface characterized by the 3d core level spectra of Pd and Ru, followed by the results of the valence band measurements. Subsequently, in section 3.2, the results for the coadsorbed system, Cu + Pd, are presented. Section 4 deals with discussion of the Pd 3d core level spectra and the interface state (IS) in sections 4.1 and 4.2, respectively. A discussion of the coadsorption results is given in section 4.3. Conclusions are listed in section 5.

2. Experimental details

The experiments were carried out at the SGM1/Scienta beamline at the storage ring ASTRID, Aarhus University, DK. This beamline consists of a spherical grating monochromator and a surface science station equipped with a hemispherical Scienta SES-200 electron energy analyser, with an acceptance angle of 16° . The base pressure is below 3×10^{-10} Torr. There is an angle of 40° between the surface normal and the incidence of the photon beam. Photoelectrons were detected in the direction of the surface normal. The sample was cleaned by cycles of 20 min of Ar^+ sputtering followed by annealing to 1400 K. By use of an electron-beam evaporator Pd was evaporated from a thin rod and Cu from a crucible. To keep the surface free of any residual gas, the sample was kept at 550 K during metal deposition and flashed to 550 K every 15 min during the photoelectron emission measurements. The Pd 3d levels were measured with a photon energy of 400 eV with a total instrumental resolution of 425 meV. The Ru 3d levels were measured with a photon energy of 350 eV with a total instrumental resolution of 325 meV to calibrate the Pd source. The higher resolved core level spectra mentioned in section 3.2 were measured with the same photon energies but with increased total instrumental resolution for the Ru $3d_{5/2}$ spectra to 185 meV (for the Pd $3d_{5/2}$ spectra, not shown here, to 235 meV). Cu 2p spectra were measured with Mg $K\alpha$ x-rays. Energy distribution curves (EDCs) near the Fermi level were measured with a photon energy at 40 eV and a total instrumental resolution of 42 meV. All measurements were carried out at room temperature.

3. Results

3.1. Deposition of Pd on Ru(0001)

3.1.1. Pd $3d_{5/2}$ core level spectroscopy. A series of Pd $3d_{5/2}$ electron EDCs, in the BE interval of relevance, 332–338 eV, are shown in figure 1 for different Pd coverages in the range of 0.5–4.0 ML. The spectra represent the recorded spectra minus the clean Ru spectrum after a normalization in the energy range below the BE of the peak. A pronounced broadening of the spectra is observed for coverages larger than 1 ML. For coverages up to 1 ML, the BE of the Pd $3d_{5/2}$ level is found by fitting to be 335.08 eV.

The intensity decay curve for the substrate displayed in figure 2(a), determined from the total intensity of the Ru $3d_{5/2}$ and Ru $3d_{3/2}$ levels as a function of the Pd coverage, clearly indicates a segmented graph. Each kink of the curve is assigned to the completion of a monolayer and the coverage intervals are equal up to 3 ML. Thus, the substrate intensity decay curve confirms the earlier findings of a layer-by-layer growth [20, 21]. As regards the growth curve of Pd determined from the intensity of the Pd $3d_{5/2}$ peak as a function of the Pd deposition, figure 2(b), there is no clear indication of the 1 ML coverage, whereas the 2 ML coverage can easily be seen. However, there is information on the Pd growth from the above-mentioned increase in the full width at half-maximum (FWHM) of the Pd $3d_{5/2}$ peak with increasing coverage. Both a simple estimation of the FWHM and the FWHM deduced from an approximation of the spectra with a Doniach–Šunjić lineshape convoluted with a Gaussian distribution [23, 24] exhibit a segmented behaviour as demonstrated in figure 3 for the last-mentioned approach. In this approach no constraints for the single peak were used. The sharp increase in FWHM at 1 ML reflects the appearance of a new component at lower BE due to changes in Pd sites and neighbour interactions. Further Pd deposition causes an increase in width, which stabilizes around 2 ML.

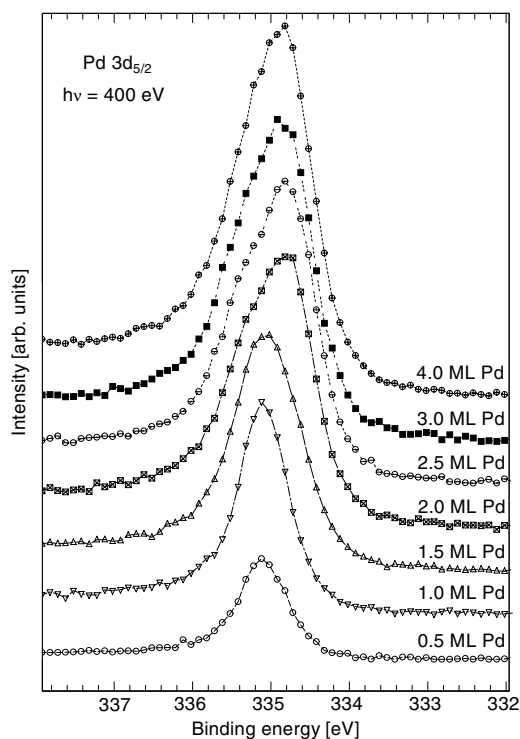


Figure 1. A set of EDCs of Pd 3d_{5/2} as a function of the amount of Pd deposited. The amount of Pd is derived from the growth curves in figure 2. The curves shown are measured spectra normalized at the low-BE side of the peak, and with a spectrum measured from the clean Ru substrate subtracted.

3.1.2. Valence band study of Pd/Ru(0001). Valence band spectra of different Pd coverages are shown in figure 4. All valence band spectra are measured over an energy interval large enough for checking for CO adsorption during measurement (only the low-BE range is shown in the figures). The spectra shown in figure 4(a) are normalized at the Fermi level and moved along the ordinate. As a reference point the Fermi level is chosen for the clean Ru(0001) spectrum. A state with a BE of 1.22 eV is seen to develop as the Pd coverage increases to ~ 1 ML. This state can be distinguished in the spectra up to a coverage of 2 ML Pd. At a 2 ML thick Pd layer this state is still present in the spectra but the high intensity near the Fermi level, which is characteristic for Pd multilayers, dominates the spectrum. We assign the state at 1.22 eV, which is not present for the pure Ru or Pd, as reflecting the interaction at the Pd–Ru(0001) interface, and therefore refer to it as the IS.

A comparison of the Ru features at BEs of 5.7 and 7.6 eV for clean Ru and Ru with increasing Pd coverage shows constant peak energies up to 2 ML and attenuation of the intensity due to the Pd overlayer. Changes in the valence band spectra become much clearer in the difference spectra displayed in figure 4(b), where the clean Ru spectrum has been subtracted from the ‘overlayer spectra’ after normalization to the same peak height at 5.7 eV. Note, however, that due to the curvature/shape of the clean Ru spectrum, the BE of the IS changes to 1.20 eV in figure 4(b) compared to the 1.22 eV in figure 4(a). The IS is seen to increase in intensity up to 1.3 ML Pd, whereafter the signal changes towards the Fermi level to form a Pd bulk-like signal. At 1.3 ML Pd the width of the IS is 0.7 eV and at 3.8 ML Pd the width of the Pd bulk-like signal near the Fermi level is 1.2 eV.

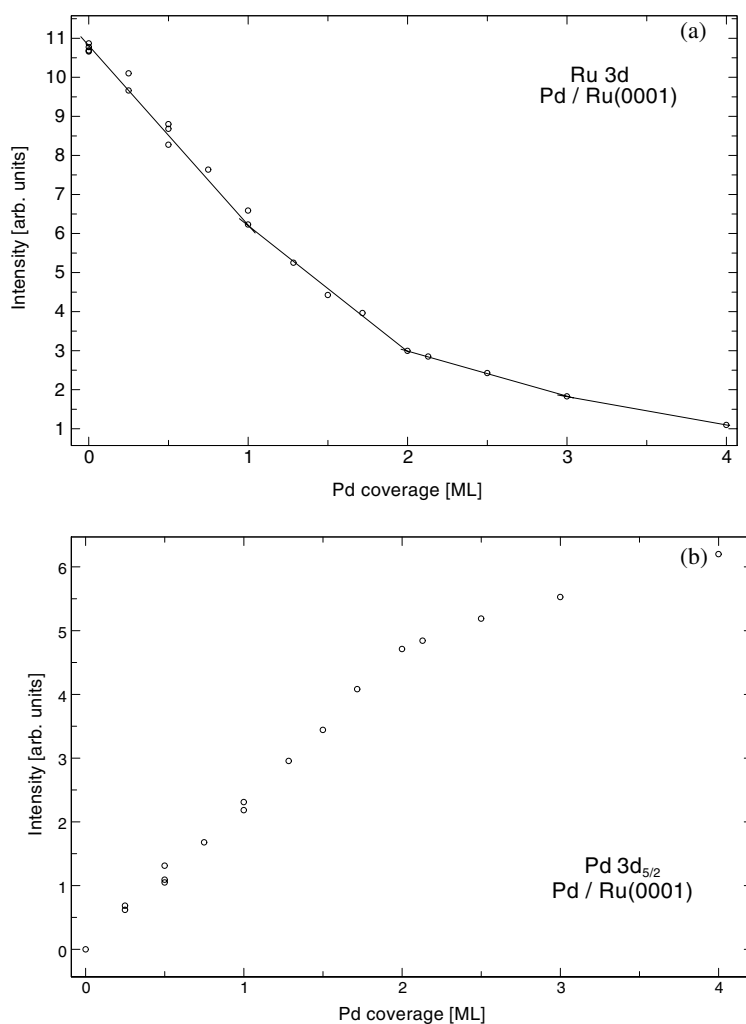


Figure 2. The growth characteristic of Pd on Ru(0001); Ru 3d and Pd 3p_{5/2} signals are used. Palladium was deposited with the sample kept at 550 K. (a) Total intensity of the levels Ru 3d_{3/2} and Ru 3d_{5/2} as a function of Pd coverage. (b) Intensity of the Pd 3d_{5/2} level as a function of Pd coverage. It is not possible to identify the 1 ML point.

Valence band EDCs measured with different photon energies at a coverage of 0.67 ML Pd are shown in figure 5. The BE of the IS is constant upon changing the excitation energy. The intensity, however, changes and is largest at an excitation energy of 42 eV.

The effect of adsorption of oxygen on the sample was checked. Neither an energy shift nor a decrease in intensity of the IS were observed after adsorption of 4 L oxygen.

3.2. Codeposition of Cu and Pd on Ru(0001)

The influence of Cu deposition on the 0.4 ML Pd/Ru(0001) system and possible mixing were studied. The effects on the core levels, Pd 3d_{5/2}, Ru 3d_{5/2} and Cu 2p_{3/2}, were measured, together with the influence of Cu on the IS, for a total coverage up to 1 ML.

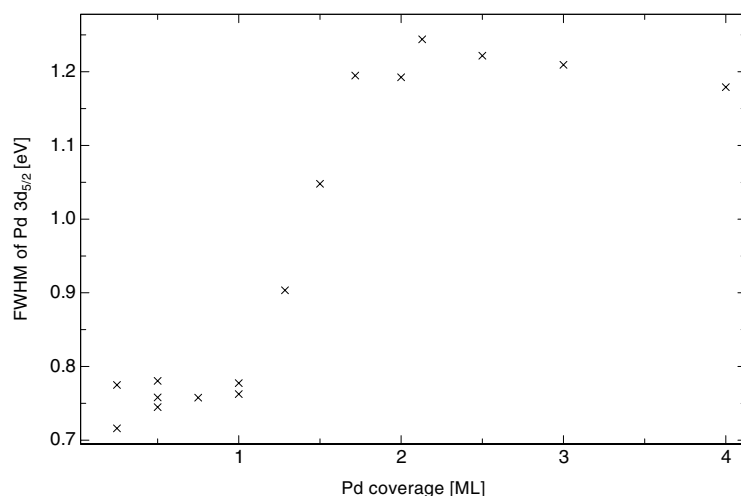


Figure 3. The FWHM of the Pd 3d_{5/2} level as a function of coverage shows a sharp increase at 1 ML coverage even though the growth curve in figure 2(b) does not indicate a kink after deposition of 1 ML Pd.

3.2.1. Core level spectroscopy. Highly resolved core level spectra of the Pd 3d_{5/2} and Ru 3d_{5/2} levels were measured during the (Cu + Pd)/Ru(0001) experiment. The intensity of the core level Pd 3d_{5/2} (spectra not shown) decreases by approximately 6% as the first 0.25 ML Cu is deposited on the 0.4 ML Pd/Ru(0001) system and decreases approximately by 12%, compared to the Pd 3d_{5/2} signal from 0.4 ML Pd/Ru(0001), when the Cu coverage increases to 0.5 ML Cu. The BE of the Pd 3d_{5/2} level changes by -0.05 eV after deposition of 0.5 ML Cu, with an estimated error of ± 0.02 eV.

The measured EDCs of the Ru 3d_{5/2} level are shown in figure 6. The clean Ru 3d_{5/2} spectrum consists of two components. The curve fitting shown in figure 6 is performed as described in [25]. The measurements by Lizzit *et al* [26] were carried out with higher energy resolution than the measurements presented here and the clean Ru spectrum was fitted with three components. The surface core level shifts of the first- and second-layer Ru atoms were determined as -366 and $+125$ meV, respectively, compared to the BE of the Ru bulk signal (table I, strategy (i) in [26]).

Compared to the spectrum of the clean Ru surface, the following changes in the Ru 3d_{5/2} signal can be observed: after deposition of 0.4 ML Pd the intensity decreases by 20% mainly at a BE corresponding to the surface component (see figure 6). Subsequent deposition of 0.25 ML Cu causes the intensity to decrease by 25% and another 0.25 ML Cu leads to an overall decrease of 36%. At this coverage the Ru 3d_{5/2} spectrum has its main contribution from bulk-like ruthenium, indicating that the two admetals cover the Ru surface.

It is known that the BE of Cu 2p_{3/2} is constant within the first monolayer of Cu on Ru(0001) [25]. At coverages higher than 1 ML Cu on Ru(0001) the BE of the Cu 2p_{3/2} level shifts towards higher BEs [25]. The BE of the Cu atoms deposited on 0.4 ML Pd/Ru(0001) is 0.03 eV lower than the BE of 1 ML Cu on Ru(0001).

3.2.2. Valence band study of (Cu + Pd)/Ru(0001). The intensity of the IS depends on deposition of another metal on the Pd/Ru(0001) system. On deposition of copper on 0.4 ML Pd the intensity of the IS decreases, as seen from the curves in figure 7(a).

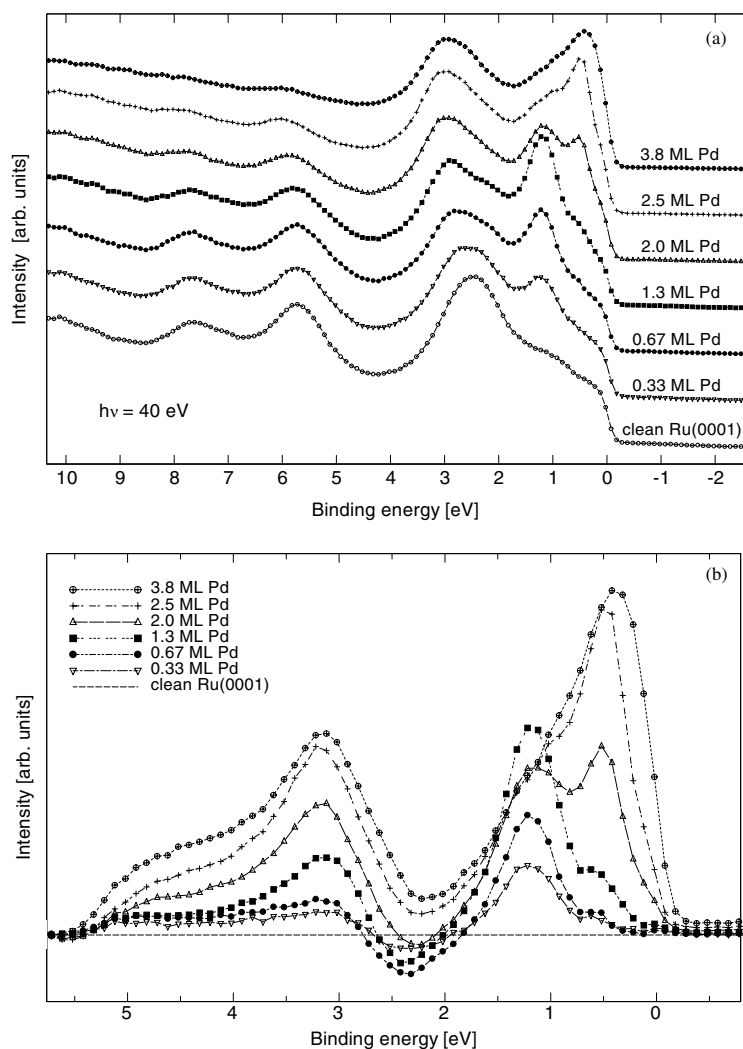


Figure 4. Valence band spectra measured for the Pd coverages 0.33–3.8 ML. (a) The spectra shown are normalized at the Fermi level and moved along the ordinate. An IS is observed at 1.22 eV for coverages 0.33–2.0 ML Pd. (b) Difference spectra, obtained from the spectra in (a) by subtracting the clean Ru spectrum from the ‘overlayer spectra’.

The influence of Cu deposition on the 0.4 ML Pd/Ru(0001) system at low BEs is seen in figure 7. For figures 7(a) and (b) the same procedure of normalization as described for figure 4(b) is used. Photoelectrons from the Cu 3d level are observed in the BE range between 2.0 and 4.0 eV. The width of the Cu 3d signal is estimated to be 0.7 eV after deposition of the first 0.25 ML Cu. As seen in the figure, further deposition of Cu up to 0.5 ML has a pronounced effect. The intensity of the IS decreases remarkably and the width of the Cu 3d contribution increases to 1.0 eV. The results of the valence band measurements for the coadsorption show that the intensity of the 4s + 4p bands, characteristic of the Pd/Ru(0001) surface and Pd–Pd interactions, is strongly reduced with addition of Cu.

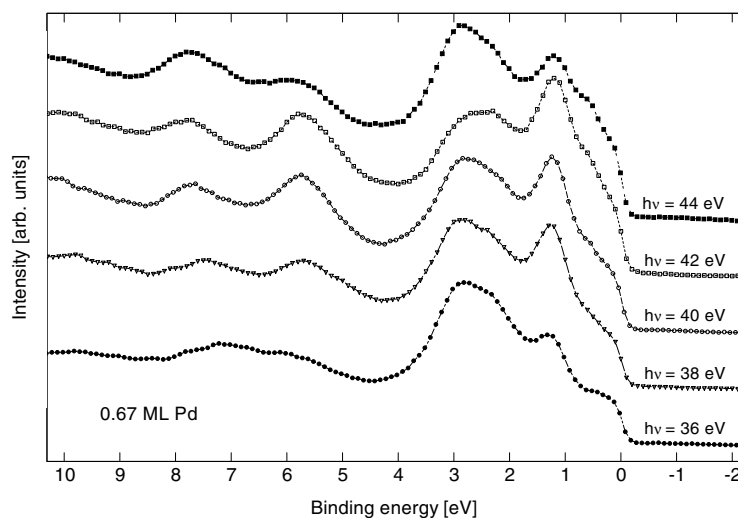


Figure 5. The valence band measured from 0.67 ML Pd/Ru(0001) with photon energies varying from 36 to 44 eV, moved along the ordinate. The BE of the IS is unaffected by the different excitation energies. The intensity is observed to be highest at 42 eV.

4. Discussion

4.1. Pd $3d_{5/2}$ core level spectroscopy

In the submonolayer range the BE of the Pd $3d_{5/2}$ level is found by fitting to be 335.08 eV referenced to the Fermi level. This value differs by approximately 0.5 eV from the value determined in [22]. This difference may be due to the experimental uncertainty. In [22] the BE of the Pd $3d_{5/2}$ level was referenced against the Ru $3d_{5/2}$ level and estimated to have an experimental error of ± 0.03 eV. The BE value determined here corresponds (within 0.1 eV) to the bulk value of the Pd $3d_{5/2}$ level determined in the papers [27, 28] and [29].

The increased FWHM of the Pd $3d_{5/2}$ signal after deposition of 1 ML Pd (figure 3) corresponds to a new component at lower BE due to changes in Pd sites and neighbour interactions. The new low-BE component may correspond to the surface component detected at lower BEs than the Pd $3d_{5/2}$ bulk signal for the three low-index surfaces of Pd in [28].

4.2. Interface states

ISs have also been observed for other systems where Pd is deposited on a metal substrate. For the Pd/Cu(100) surface Pope *et al* [30] measured a Pd feature at 1.6 eV until coverages above 0.5 ML Pd were reached; thereafter the intensity near the Fermi level increased. The authors concluded that the Pd feature at 1.6 eV appears to be characteristic of isolated Pd atoms in a Cu surface. A similar Pd 4d feature at 1.6 eV, up to a monolayer Pd, is described in [31], for Pd deposited on Au(111). Also for Au deposited on Pd(111) for coverages up to 1 ML Au a structure at a BE of 1.5 eV is observed, which is much stronger and sharper than for clean Pd [32]. Au deposited (and codeposited with Cu) on Ru(0001) was investigated by Kuhn *et al* [33, 34] who observed a state in the 1.3 eV region uncharacteristic of pure Ru and Au. They conclude that this IS probably arises from a hybridization of the Au 5d and Ru 4d bands.

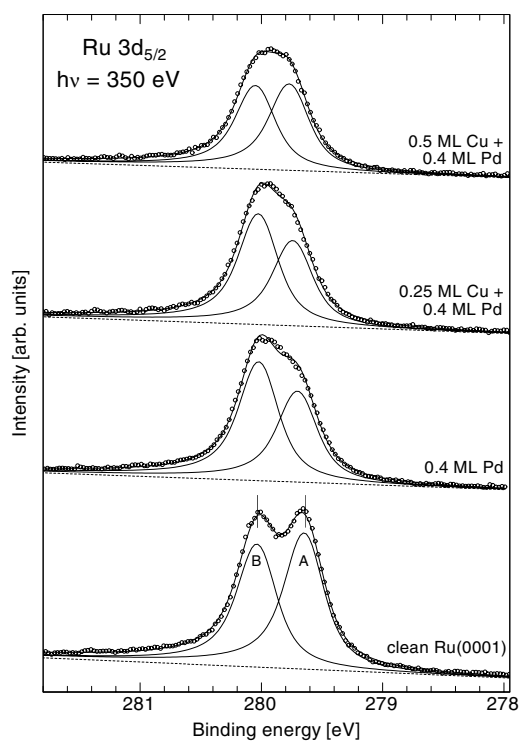


Figure 6. Highly resolved Ru $3d_{5/2}$ spectra fitted with two components as described in [25] and moved along the ordinate. For the clean Ru(0001) spectrum, the vertical line with the label A indicates the BE of the surface layer component (279.64 eV) and that with the label B the position of the component from the second + bulk layer (280.03 eV).

4.2.1. The Pd–Ru-substrate interface state. The IS presented in this work has a BE of 1.20 eV (in figure 4(b)) and is strong for coverages below 1 ML. A very weak intensity feature is observed at a BE of 0.62 eV for a coverage of 0.67 ML Pd. This feature shifts around 0.24 eV towards lower BE (~ 0.38 eV), close to the Fermi level, as the Pd overlayer approaches bulk Pd. This peak probably has a low intensity for small Pd coverages due to population of the IS. The decay of the intensity of the IS is followed by a substantial intensity increase in the Pd multilayer peak(s). Accordingly, the IS is assigned as a hybridization of the Pd 4d and Ru 4d bands. Besides the BE shift and intensity increase of the low-BE Pd feature with increasing Pd coverage, a significant broadening of the structure from a coverage of 2.0–3.8 ML is observed. This effect is ascribed to the development of a band-like structure with increasing Pd–Pd interactions as the coverage increases. The increased width corresponds to an increased coordination number and formation of a bulk-like Pd layer on top of the Ru substrate.

Cu deposition causes the intensity of the IS to decrease as seen in figure 7. The pronounced effect on the Cu 3d signal, after deposition of the last 0.25 ML Cu, suggests that a copper band has been formed. The deposited Cu atoms perturb the Pd–Ru(0001) bonding and cause the decreased intensity of the IS.

Below 1 ML, the Pd valence band (see figure 4(a)) is dominated by the IS. First, for coverages above 1.3 ML new (states) features at BEs of 0.38 and 3.2 eV are clearly observed. Another pronounced effect connected with increasing Pd coverage above 1 ML is the broadening of the states constituting the peak at a BE of ~ 0.38 eV. In particular, the states

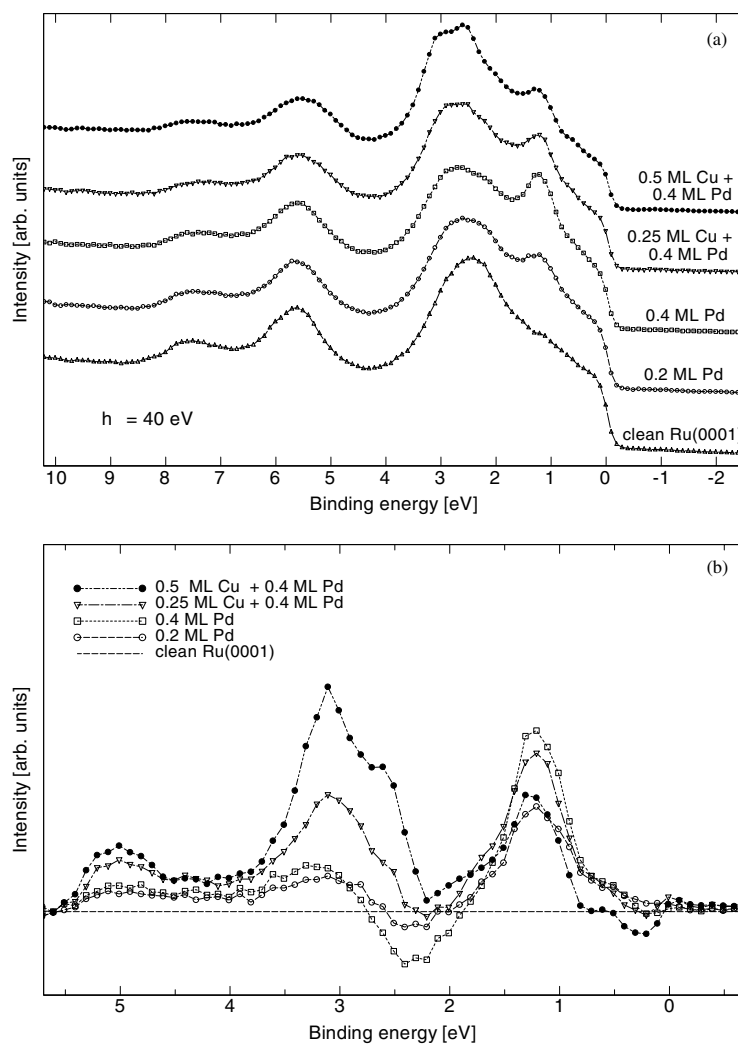


Figure 7. Valence band spectra measured during the codeposition of Cu and Pd on Ru(0001). The intensity of the Pd/Ru(0001) IS depends on the deposition of copper. The IS is detected at 1.22 eV below the Fermi level and the Cu 3d signal in the BE range from 2.0 to 4.0 eV. (a) The spectra shown are normalized at the Fermi level and moved along the ordinate. (b) Difference spectra, obtained from the spectra in (a) by subtracting the clean Ru spectrum from the ‘overlay spectra’.

near the Fermi level are created for coverages above 2.5 ML. Also the broad band positioned in the ~ 3.2 eV region develops for coverages above 2 ML.

Thus, the build-up of the Pd valence band on Ru(0001) with increasing number of layers is distinctive, with a dominating IS at 1.22 eV in two dimensions. Three-dimensional Pd is characterized by a band close to the Fermi level and a broad feature at a BE of ~ 3.2 eV.

4.3. Codeposition of Cu + Pd on Ru(0001)

In our experiment, with 0.5 ML Cu + 0.4 ML Pd deposited at 550 K on Ru(0001), the Ru 3d_{5/2} spectra (figure 6) clearly show that the bimetallic monolayer wets the Ru substrate, since at

one-monolayer coverage there is only a contribution from Ru bulk-like atoms. We conclude that a substantial part of the deposited Cu bonds to the Ru substrate. This is also confirmed by the small decrease (12%) of the intensity of the Pd 3d_{5/2} signal upon deposition of 0.5 ML Cu.

Deposition of the last 0.25 ML Cu has a remarkable effect on the IS (figure 7) where the Cu coverage of 0.5 ML perturbs the Pd interface bonding to the Ru substrate. The occurrence of Pd–Cu mixing is confirmed by the reduced 4s, 4p intensity in the valence band, figure 7, when Cu is added. This effect demonstrates a reduced Pd–Pd coupling due to Cu–Pd interaction and a mixing of the adsorbed metals.

The Cu atoms influence the IS, but we cannot decide whether this perturbation originates from a complete mixture of Cu and Pd on top of the Ru substrate or the perturbation is caused by boundary effects from larger two-dimensional Cu clusters.

5. Conclusions

We have shown with photoelectron spectroscopy that:

- The BE of the Pd 3d_{5/2} level at the Pd/Ru(0001) surface is constant in the submonolayer range at 335.08 eV. For coverages above 1 ML Pd, the Pd 3d_{5/2} level was found to consist of an additional component at lower BE, which is attributed to the growth of Pd on the first monolayer.
- For Pd overlayers adsorbed on Ru(0001) an IS is formed with a BE of 1.22 eV. The intensity of the IS dominates the valence band spectrum for coverages below 1 ML.
- For Pd coverages above 1 ML new bands develop close to the Fermi level and at 3.2 eV the widths of these bands increase with increasing coverage up to 2 ML.
- For coadsorption of Cu and Pd on Ru(0001), mixing occurs for a total coverage of 1 ML.

Acknowledgment

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