High temperature growth of Pt on the Rh(111) surface

M. Duisberg a, *, M. Dräger a, K. Wandelt a, E.L.D. Gruber b, M. Schmid b, P. Varga b

a Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, 53115 Bonn, Germany
b Institut für Allgemeine Physik, Technische Universität Wien, Wien, 1040, Austria

Abstract

The epitaxial growth of Pt on the Rh(111) surface at 700 K was studied with AES, UPS, ISS and STM. From AES and ISS measurements a 2D growth mode is concluded at this substrate temperature. The morphology of the surface is studied by photoemission spectra of adsorbed Xe (PAX) and STM. A disperse distribution of the Pt atoms is suggested by PAX and is consistent with an incorporation of these atoms into the first substrate layer. Atomically and chemically resolved STM measurements confirm these conclusions. The interaction of CO with the surface alloy is investigated by UPS. The CO-induced features in UP spectra show significant differences in the peak positions and shape between the clean substrate and the surface precovered with different amounts of Pt. The CO-induced emissions are, thus, used for a quantitative titration of Pt on the Rh surface. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Carbon monoxide; Growth; Low energy ion scattering; Platinum; Rhodium; Visible and ultraviolet photoelectron spectroscopy

1. Introduction

The system Rh/Pt is of wide technological interest as an important industrial catalyst, e.g. for the production of nitric acid and hydrogen cyanide. The main application of this system is, however, the three-way catalyst, which is used for purification of exhaust gases of gasoline-fueled internal combustion engines. On the other hand theoretical interest arises because of the peculiar segregation behavior of Pt/Rh bulk alloys (see e.g. Refs. [1–3]).

The epitaxial growth of Pt on the Rh(111) surface gives the opportunity to design and investigate a model catalyst and, in a further step, to understand the interaction between the two metallic components. To the best knowledge of the authors the Pt/Rh heteroepitaxial system has barely been investigated by now. Thus, our first aim was to investigate the growth mode.

2. Experimental

The experiments were carried out in two different UHV chambers. The UHV chamber in Bonn (base pressure $p_0 < 10^{-10}$ mbar) was equipped with LEED, AES, TDS, angle-integrated UPS, a closed-cycle He refrigerator for sample cooling, and a temperature-controlled e-beam evaporator for Pt deposition. The UP spectra were excited with a He discharge lamp providing He I (21.21 eV) and He II (40.8 eV) radiation.
experimental setup is described elsewhere in more detail [4]. The UHV system in Vienna consisted of a preparation chamber ($p_0 < 10^{-10}$ mbar) and a main chamber ($p_0 < 3 \times 10^{-11}$ mbar) equipped for AES, LEED and ISS and a customized Omicron micro-STM. For all STM measurements a tungsten tip was used.

The Rh(111) surface was prepared by the procedure proposed by Borg et al. [5]. AES was used to check the cleanliness of the surface and the Pt film. Traces of CO were monitored by UPS.

3. Results and discussion

After preparation, Pt was deposited on the Rh surface at 700 K. In a first step the growth mode at this temperature was investigated by AES and ISS between successive deposition steps.

A plot of the normalized AES peak-to-peak height of the Rh 302 eV and Pt 64 eV signals versus the deposition time gives an indication of the growth mode [6]. The plot shows features typical of a 2D-like growth mode allowing a monolayer calibration (the Pt coverage is denoted by $\theta^{\text{AES}}$), i.e. linear decreases of the substrate signal with different slopes for each adlayer. Because of the different chamber geometry in Vienna the deposition rate had to be re-calibrated by AES experiments to ensure equivalent deposition conditions.

Additionally the growth mode was investigated by ISS using 1.1 keV He$^+$ ions. Between each ion beam scan the sample was exposed to Pt at 700 K. The acquisition time was kept short to reduce sputtering damage. Two peaks at $E_{\text{kin}} = 975$ eV (Rh) and $E_{\text{kin}} = 1017$ eV (Pt) are clearly separated, so that the intensity of each peak could be converted into a first layer fraction using Pt and Rh single crystals as standards. The deposition times were converted into coverages using the monolayer calibration made by AES and plotted versus the coverage (Fig. 1). Up to $\theta^{\text{AES}} = 0.9$ ML the Pt first layer fraction increases linearly. At coverages higher than 1.0 ML only a small amount, and at a coverage of 1.25 ML no Rh is detectable any more. Since ISS is sensitive strictly to the first monatomic layer this result shows that the first layer is essentially filled completely with Pt atoms before adatoms start to nucleate in higher layers starting at a coverage beyond 0.9 ML. Both AES and ISS yield a 2D growth mode for the heteroepitaxial Pt/Rh(111) system at a substrate temperature of 700 K.

To investigate the morphology of the Pt film, PAX spectra and STM images were taken. According to the PAX theory [7] the positions of the Xe 5p$_{3/2}$ and 5p$_{1/2}$ peaks referring to the vacuum level are independent of the substrate. Therefore the adsorbed Xe detects the local work function of the substrate. The work functions of the pure metals Rh(111) and Pt(111) differ by 700 meV. The deposition of different amounts of platinum leads to a continuous shift of the Xe-induced signals to lower binding energy (Fig. 2). No second peak system appears that would indicate islands of pure Pt. Instead, the presence of only one peak system in the whole submonolayer region indicates a disperse distribution of platinum at the surface, since the Xe atom is so large that it probes an area of a few substrate atoms and is not able to differentiate between two adjacent unlike atoms. This was also observed for alloy surfaces [8]. It is also seen in Fig. 2 that

![Graph showing surface fraction of Pt and Rh measured by ISS (1.1 keV He$^+$, scattering angle 90°) as a function of Pt coverage $\theta^{\text{AES}}$. The fractions were calculated using single crystals as standards.](image-url)
there is no difference between the spectra from 0.9 ML Pt and higher coverages, indicating that only Pt is present at the surface and confirming the coverage calibration made by AES. Because of the lack of a second peak system even at high coverages (0.7 ML) it is concluded that the Pt atoms are dispersely embedded into the first layer of the substrate.

This conclusion is confirmed by an atomically and chemically resolved STM image of 0.9 ML Pt on the Rh(111) surface shown in Fig. 3a (the image was contrast enhanced for reproduction). STM studies of PtRh bulk alloys [9,10] showed that Rh atoms have a greater apparent height than Pt atoms. This allows different chemical species to be distinguished. Obviously Pt does not form islands, but individual atoms are embedded into the substrate layer forming a surface alloy. The corrugation of the Rh atoms shown in the line

![STM image](image)

**Fig. 3.** (a) Atomically and chemically resolved STM image of 0.9 ML Pt on the Rh(111) surface shown in Fig. 3a (the image was contrast enhanced for reproduction). The white line in (a) passes over the centers of both Pt atoms (dark) and Rh atoms (bright) on the upper terrace, showing that both share the same lattice. Rh atoms have a greater apparent height about 30 pm larger than the Pt atoms and are therefore imaged more brightly. Therefore, and in agreement with the linescan, Pt and Rh form an alloy in the first monolayer. (b) STM image of 0.1 ML Pt (100 nm × 40 nm, U_b = −1 V, I_t = 0.46 nA). The linescan shows that the seam is imaged about 30 pm higher than the Rh terrace.
scan is about 0.03 nm above the Pt atoms. The height of the step edge is approximately 0.2 nm, and thus it is a monatomic step. Calculations by Hofer et al. [11] for a PtRh(100) bulk alloy surface showed that the different apparent heights between Pt and Rh is caused by local density of state (LDOS) changes due to alloying. In contrast, calculations show a much less corrugated LDOS above PtRh(111) surfaces [11], indicating that the chemical contrast there is caused by tip-sample interaction as already proposed, e.g. for PtNi(111) [12,13]. As seen in the STM image the terrace is divided into two different parts (left and right of connecting line A-B): right of line A-B near the descending step there are only few Rh atoms and Pt forms a compact seam. The centers of the Rh atoms (bright) occupy regular lattice sites of the surrounding Pt seam. Thus, both types of atoms share the same lattice. Left of line A-B towards the ascending step (arrow) the Pt fraction is much smaller. The sharp border between these two parts reflects the fact that most Pt atoms diffuse to the step edge, are trapped there, and intermixing is still limited at 700 K. An STM image of 0.1 ML Pt deposited at the same temperature (Fig. 3b) shows a Rh terrace with a bright seam at the step edge. The small-scale height variations (roughness) of the seam allow it to be identified as a Pt/Rh surface alloy, which is imaged brighter (higher) than the pure Rh areas at these tunnelling conditions.

The 2D growth mode and the disperse distribution of Pt atoms in the surface suggested by PAX are thus confirmed by STM. The Pt coverage found by AES is in good agreement with the one found by STM. Thus Pt atoms are embedded only in the topmost layer and only a small fraction of Pt forms an alloy in deeper substrate layers at high coverages greater than 0.9 ML.

The interaction of CO with the surfaces of the two pure metals Rh and Pt has been thoroughly investigated (e.g. [14–16]). Photoemission spectra of CO (CO-covered minus bare or Pt-covered surface) at different amounts of Pt on the surface are shown in Fig. 4. The CO-induced emissions at saturation coverage show striking differences (H AES = 3.3 ML) the spectra are fitted with three Lorentz peaks peak position and shape. Up to 1 ML Pt on the high energy side of both CO emissions a shoulder begins to evolve, and at a coverage of 0.7 ML Pt
a distinct peak develops. For Pt coverages of 1 ML and higher the spectra remain identical, confirming the coverage calibration made by AES. The clear distinction between the two peak systems is surprising in some respects. CO adsorbs on the pure metals not only in on-top but also at bridge (Pt) [16] and three-fold hollow sites (Rh) [15]. As seen by STM and PAX experiments, Pt is embedded dispersely into the first substrate layer, and therefore a measurable contribution to the spectra of CO adsorbed at mixed Pt-Rh bridge or three-fold hollow sites should be expected. But the peak systems are separated throughout the Pt submonolayer region and no additional emission appears. We have not yet found a complete explanation for these results. An IRAS study [17] with a Pt$_{0.25}$Rh$_{0.75}$(111) single crystal showed that CO adsorbs predominantly in atop sites. This is similar to our results. The spectra at CO saturation of the thick (3.3 ML) Pt film is identical with measurements on Pt(111) [18] shown additionally in Fig. 4a (dotted line). The shoulder on the low energy side of the 4\,s peak from CO adsorbed on the thick Pt film is considered to be a feature due to a compressed CO overlayer structure [18].

Because of the clear separation of the CO-induced emissions, a quantitative evaluation was possible. The spectra of the pure metals were fitted with three Lorentz functions as shown in Fig. 4. By superposition of these functions the spectra of the mixed Pt-Rh surfaces were fitted and the Pt fraction of the surface was obtained. The plot of the Pt fraction thus determined versus the deposition time is shown in Fig. 4. Additionally the Pt coverage obtained from the AES measurements is shown in the plot. Up to 1 ML Pt there is a linear dependence as expected for a 2D growth mode. At higher coverage no Rh fraction is found. In comparison with ISS, photoelectron spectroscopy of adsorbed CO makes it possible to titrate the Pt coverage in the submonolayer region.

4. Conclusions

Pt grows twodimensionally on the Rh(111) surface at a substrate temperature of 700 K by embedding individual Pt atoms dispersely in the topmost layer. A step flow mechanism with an intermixing process taking place at the former Rh step edges is consistent with the presented observations. This surface alloy is limited to the topmost layer as the Pt coverages detected by AES, ISS and STM are almost identical. In STM images with atomic resolution, the Rh atoms appear higher than the Pt atoms in the surface alloy as in the case of PtRh bulk alloys. CO adsorption on the surface alloy yields a separation of the CO-induced emissions in UPS experiments. This gives the opportunity to titrate the first layer Pt fraction by photoemission of adsorbed CO.

Acknowledgements

This work was supported by the ‘Deutsche Forschungsgemeinschaft’ at the SFB 334 and the Austrian ‘Fonds zur Förderung der wissenschaftlichen Forschung’.

References