

8 Summary

This thesis presents results of investigations of the growth of rhodium on the graphite(0001) (**HOPG**, **H**ighly **O**rientated **P**yrolytic **G**raphite) and the rhenium(0001) surface.

The Rh/Graphite system was studied by means of STM, UPS and XPS, after metal deposition on the basal plane of graphite in UHV at room temperature. The STM images show clearly that Rh grows as three dimensional particles on the graphite substrate even at coverages far below a monolayer (Volmer–Weber growth mode). Under the experimental conditions employed in this study no chemical interaction between adsorbate and substrate, e.g., the formation of carbides or intercalates, could be found. Rhodium atoms exhibit very high mobility, resulting in a high rate of defect nucleation and step decoration. Beginning at a coverage of approximately 1.65 monolayers, fractal growth of Rh islands is observed. The islands are partially built up by spherical Rh segments. The spherical shape of these segments is consistent with the observation that Rh had no tendency of wetting the graphite surface and with its high cohesive energy.

Information on the electronic structure of the Rh clusters was obtained by analysis of the shape and the binding energy E_b of the photoelectron lines as a function of the coverage of the metal. We were able to demonstrate that the binding energy of the core level 3d electrons increases by 0.3 ± 0.1 eV. This increase is accompanied by a FWHM increase of about 1.5 eV for the smallest amount of the deposited metal (up to 0.2 ML). We interpret the core level shift as a consequence of rehybridisation effects (initial state effect) on one hand and the change in core hole screening as a function of cluster dimension on the other (final state effect). In UPS we detected three different Rh signals at 0.75, 3.2 and 4.4 eV below the Fermi level. By comparison with UV–photoelectron spectra of the Rh(111), Rh(100) and Rh(110) single crystal surfaces it was concluded that the islands and the round segments are predominantly close packed. The valence electron signals can be identified with the Rh d–band (0.75 eV), an s-d hybrid band (4.4 eV). The emission at 3.2 eV was interpreted as rhodium atoms with essentially the electronic structure of isolated atoms and not of bulk Rh. In the coverage region of 0.2–0.4 monolayers the FWHM of the d–band is stagnating before increasing with increasing cluster size. In the same coverage region, the d–band intensity begins to grow, accompanied with the development of the Fermi-edge. From these data it was calculated that the insulator/metal–transition occurs at cluster sizes of 70–100 Rh atoms.

The investigation of the Rh/Re(0001) system with STM, AES, LEED, XPS and TDS shows that rhodium grows for the first two monolayers in a layer-by-layer fashion (pseudo Frank-van-der-Merwe growth mode), followed by a transition to a three dimensional (or Stranski-Krastanov) growth mode. In LEED experiments, no ordered layer could be proved neither at $T = 300$ K nor at $T = 900$ K. At low coverages, the homogenous nucleation process dominates, in line with the low mobility of the metal atoms resulting from a strong metal-surface interaction. As an indicator for the strength of the adsorbate/substrate interaction the desorption behaviour of CO was investigated as a function of rhodium cluster size. The TPD spectra for the highest Rh coverage were consistent with those of the CO/Rh(111)-system but with a reduced desorption temperature of 113 K or 32.5 kJ/mol (Redhead analysis). The strong interaction with the substrate and the charge transfer from rhodium to the surface weakens the $2\pi^*$ -backbonding and therefore also the CO-Rh bond. The picture of closed-packed rhodium islands is supported by the fact that the recombination signal decreased with increasing rhodium concentration on the surface. This is reminiscent of the CO-desorption behaviour on the Rh(111) and Rh(100) surfaces. As a consequence of the packing density the misfit should become greater, which could be the reason for the beginning Stranski-Krastanov growth mode after completion of the first two layers. At $T > 900$ K, volume alloying starts by thermally induced rhodium diffusion into the rhenium bulk. This was proven by several temper experiments in a temperature region far below the desorption temperature of rhodium (1849 K for the monolayer and 1822 K for the multilayer).