11 Summary

In this work, we studied the growth and structure of titanium dioxide films on two morphologically different transition metal surfaces, namely the trench-like rhenium(10-10) and the hexagonal ruthenium(0001). The following methods were used: X-ray photoelectron and Auger-electron spectroscopy (XPS and AES), low energy electron diffraction (LEED), low energy Helium-ion scattering (LEIS), scanning tunneling microscopy (STM) and X-ray diffraction (XRD).

Titanium dioxide films on rhenium(10-10) were synthesized by co-adsorption of titanium vapor in an oxygen atmosphere up to a thickness of 500 Å and investigated by means of LEED, LEIS, XPS and XRD. In order to calibrate the titanium flux, the growth mode of titanium on the Re(10-10) surface was determined by means of LEIS, XPS and LEED. At room temperature titanium grows layer by layer on Re(10-10) with its own lattice parameter.

The parameters for co-adsorption with constant titanium flux, i.e. temperature, oxygen partial pressure and the constitution of the substrate interface turned out to be very important for the structure of the films.

For oxygen pressures above $5x10^{-7}$ mbar and a temperature of 830 K the films consist already in the monolayer (ML) range of TiO_2 as shown by XPS Ti 2p signal whereas the Ti:O stoichiometry reached the ratio 1:2 only for thicker films because of the oxygenated rhenium interface. As function of coverage starting from the (1x3)-2O/Re(10-10) a p(2x2), a dim (1x1) and finally a stable pg(2x2) LEED pattern with respect to Re(10-10) was observed. The origin of the latter could be Brookite(001) as well as (2x1) reconstructed rutile(011). Based on the occurrence and analysis of faceting phenomena, i.e. LEED spots not running towards the nominal (0,0) reflex with increasing primary electron energy, Brookite(001) could ruled out and as result two domains of rutile(011)-(2x1) each with two (2x1) similarly reconstructed rutile(011) facets. This result, rutile(011)-(2x1)$||$ Re(10-10), was also obtained by XRD at the Berlin synchrotron facility BESSY.

In addition to the faceting phenomena the slow decrease of the rhenium LEIS signal as well as the increase of the rhenium XPS signal during heating at 920 K indicates island growth. Comparison of the change of XPS Ti 2p intensity during film growth with a uniform simultaneous multilayer growth model developed in this work yields an average island height of (50 ± 10) layers. The disappearance of the (1x3)-2O/Re(10-10) oxygen phase in LEED experiments and the development of the O:Ti XPS signal ratio indicate that the rhenium surface is fully covered after 1-1.5 ML of titanium oxide deposition. Therefore we assign the growth mode with these parameters as Stranski-Krastanov-like of rutile(011)-(2x1) on Re(10-10).

If we grow titanium oxide on one monolayer Ti on Re(10-10) keeping the other parameters constant we get fully oxidized titanium dioxide in addition to the rutile(011)-(2x1) LEED phase another so called pseudo(1x1) LEED pattern with respect to Re(10-10). Analysis of the recurring faceting phenomena reveals rutile(100) island growth with two {110} facets. Both of these LEED patterns are observed in all deposition experiments at temperatures of 720 K and below, on some occasions after oxidation at higher temperatures.

Only films prepared at 830 K in $1x10^{-7}$ mbar oxygen did not exhibit the pg(2x2) LEED pattern of rutile(011)-(2x1). These films have different LEED patterns and consist of partially oxidized titanium oxide (XPS). Prolonged heating in $5x10^{-7}$ mbar oxygen was necessary for fully oxidized films. Analysis of the resultant streaky LEED patterns with a multiplicity of reflexes suggest growth of rutile(100) in at least three mosaic domains, one parallel to Re(10-10), the others slightly tilted.

Possible reasons for the unusual growth behavior are the ability of rutile(100) to grow as a reduced (1x3) reconstructed surface and the apparent necessity of a fairly thick buffer layer to grow rutile(011)-(2x1).

The growth of titanium dioxide on the hexagonal ruthenium(0001) surface was investigated by means of STM, XPS and AES. Due to the alloying affinity of Ti and Ru, a titanium oxide film pre-grown at low temperature was finally/fully oxidized at elevated temperature and pressure. The first titanium oxide layer fully covers the Ru(0001) surface as Moiré. While XPS intensities of O 1s and Ti 2p signals suggest this Moiré consists of titanium dioxide, we interpret atomically resolved STM images as two hexagonal oxygen layers with titanium atoms in the octahedral positions also yielding TiO_2. After a second poorly ordered layer, island growth begins. Atomically resolved STM images revealed the growth of rutile(110) on Ru(0001). Comparing statistics of the island heights with the uniform simultaneous multilayer growth model gives an average island height of (33 ± 5) layers.

First experiments concerning the growth of gold on these titanium dioxide films are presented. One important result of the ongoing work is the imaging of gold clusters with 2-5 atoms in the troughs of rutile(110) beside the typically observed clusters with 3 nm diameter by STM.