

## 2. Summary and Outlook

In this work, the following systems

- Cu/Re(0001), Ag/Re(0001), Au/Re(0001),
- Cu/Re(0001)-st, Ag/Re(0001)-st,
- Ag+Cu/Re(0001), Ag+Au/Re(0001), Pd/Re(0001),

were investigated and analysed using the methods TDS,  $\Delta\Phi$ , XPS, AES, LEED and LEED-(I,V). The results are presented and discussed in context with the data of the literature. Mostly based on thermal desorption spectroscopy (TDS), but also supported by the other methods, one could obtain a sum of system parameters, growth modes and kinetics. For this purpose the TDS was modified methodically. The data evaluation was improved or in certain cases corrected (Chap. A 4) and expanded using a special kind of a semisimulation (Chap. C 5.2).

The most important results of the binary systems of this work are presented in the following table:

	<b>Cu/Re(0001)</b> Chap. C 1	<b>Ag/Re(0001)</b> Chap. C 2	<b>Au/Re(0001)</b> Chap. C 3	<b>Pd/Re(0001)</b> Chap. D 1
growth mode	SK <sub>2</sub>	SK <sub>4</sub>	SK <sub>2</sub>	SK <sub>2</sub> (alloy)
ps-cp-transition at $\Theta$ [ML]	0,8	1,0	1,0	-
$E_{des}(\alpha)$ [kJ/mol]	335 ... 338	270 ... 282	350 ... 360	358 ... 371
$T_C$ [K]	1125	1100	(1137)	< 1350
$E_{WW}$ (BWA/real) [kJ/mol]	6,2 / 19	6,1 / 8	- / 10	- / -
$V_z$ [kJ/mol]	270	260	310	-

All adsorbed metals grow in the Stranski-Krastanov-growth mode on the Re(0001)-surface. That means, that after a given number of layers (SK<sub>#</sub>) the growth of three dimensional crystallites (Cu, Au) or open multi layers (Ag) starts (TD-peak  $\alpha$ ). During the growing of the layers many interesting processes occur, with the latter partly induced by the misfit of the lattice parameters of the adsorbate and the substrate, respectively. Especially one can observe phase transitions and/or alloy formation:

One of these phase transitions, an order-disorder-transition, is the two-dimensional evaporation of adsorbed atoms from a solid into a two-dimensional gas phase. This could be used to obtain certain system parameters, especially the critical temperature  $T_C$  of this phase transition and interaction energies of the adatoms with neighbouring atoms ( $E_{WW}$ ) or with the substrate ( $V_z$ ).

A second, in this case an order-order-phase transition, is the ps-cp-transition, where adatoms, first arranged pseudomorphically (ps) on the surface lattice, reorder to grow in a close packed manner (cp), i. e. with their own lattice parameters. As a result, several special film structures appear in the form of wavy arrangements or dislocations. The ps-cp-transition facilitates the interactions between the adatoms and their neighbours in the film. Consequently, ps-cp-transitions occur as soon as the adatom-adatom-interaction are stronger than the adatom-substrate-interactions.

It could be shown in the case of Cu- and Ag-adsorption on a strongly stepped Re(0001)-surface, that the morphology of the substrate has a strong influence of the growth mode of the adatom. From the beginning, the adatoms occupy several adsorption sites and no uniform, flat

film is built. Due to the lowered dimensionality and the influence of the substrate morphology two dimensional alloys from Ag and Cu, i. e. from Ag and Au but also from Pd and Re could be prepared. This result is somewhat surprising, bearing in mind that the volume systems AgCu and PdRe show a wide miscibility gap.

The desorption energy decreases with increasing coverage within the first adlayer of the ternary systems Ag+Cu/Re(0001) and Ag+Au/Re(0001), which is unusual for systems with attractive interactions. But in fact, this behaviour reflects the effect of the mix energy of the two dimensional alloy formation in the range of 10 kJ/mol per pair (CuAg: 17 kJ/mol, AuAg: 8 kJ/mol). A demixing of the first alloy layer occurs, if too many adsorbate atoms with a higher binding or surface energy (Cu or Au) are capable of displacing the Ag-atoms away from the direct contact with the Re-surface.

One can observe strong interactions between the adsorbate and the substrate in the system Pd/Re(0001). Although there are no distinct chemical shifts in XPS-measurements of Re or Pd, but results from  $\Delta\Phi$  measurements justify alloy formation. In particular the interactions become clear in TD-measurements, from which one can conclude, that adspecies (as additional Pd, but also gases like CO) are more weakly bound on this newly formed surface (principally the PdRe-alloy film) than on clean Re or Pd.

By comparison of the systems one could come up with conclusions on the nature of the chemical bonding especially of the coinage metals on well-defined surfaces of refractory metals (groups 5 ... 9). It is obvious that not only the formal pair interactions are decisive, but also the delocalisation of the electrons of the adsorbed metal in the whole metal crystal play a very important role. This causes a binding that is ten times stronger than the pair interaction. It depends on the difference in the electron densities between the adsorbate and the substrate, how a certain "ionic" part plays a role.

Further investigation would be desirable in two directions: First, the knowledge obtained here (especially on the alloy systems) should be extended and solidified by supplementary measurements with the use of other methods. STM-measurements, which can give an insight into the local order of the systems are absent until now as well as surface-sensitive spectroscopic methods like ion scattering or titration (CO- or Xe-TDS, PAX) would be useful in relation with ordering phenomena. With the help of UPS- or IPS-measurement one could get information about the electronic structure. For a verification of the yielded system parameters and to obtain additional physical constants, quantum chemical calculations and/or MC-simulations on the basis of the LEED- and above all the TDS-results are necessary.

Second, it would be useful to investigate additional comparable systems. With regard to the two component alloys the systems Ni/Re(0001) and Pt/Re(0001) are interesting. Cu+Au/Re(0001) would be an interesting ternary system. In this context it would be especially rewarding to investigate the effect of special surface morphologies, like those of the Re(10 $\bar{1}$ 0) can induce one dimensional effects, which could affect the alloy formation.