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Chapter 9

Summary and outlook

The interaction of (atmospheric) gases with surfaces of man-made metal objects is an important issue in present day society. Consequences of such interactions have become an important part of our daily life. Some of such reactions (*e.g.* corrosion) are in most cases unwanted and require certain steps for their prevention. Others (like nitriding, carburizing and sometimes oxidation) are desirable since they allow to produce novel functional materials. Detailed understanding of gas-metal interactions is also important for the design of catalysts used for the synthesis of chemicals.

This thesis describes studies on a number of gas-metal systems which play an important role in technological applications and are of interest from a fundamental point of view. The first system is Cu–H. Hydrogen does not form chemical compounds with Cu. Yet, the interaction of H with Cu surfaces is important for understanding catalytic processes taking place at Cu surfaces and involving hydrogen. In such processes the catalyst promotes or prevents certain reaction pathways in a complex system while not being consumed in the process. With regards to the Cu–H system, the catalytic action of Cu can be used in the process of epoxidation of ethylene. Another application of the Cu–H system is found in microelectronics. It has been discovered that the presence of H at a Cu surface can promote the surface diffusion of Cu. This can be applied in the process of Cu-reflow in the production of integrated circuits.

All further studies discussed in the thesis address the interaction of Fe with N and O. Part of the interactions studied here take place through a cover layer of Ni

or Ag. The interactions of gases with metal bilayers have not been studied extensively until now. Yet, an understanding of this interaction is of importance for the synthesis of *e.g.* Fe-nitrides and for the protection of Fe layers from oxidation. The main technological importance of this work is the production and protection of conducting thin magnetic layers. Such layers can be used in (multi)layered structures forming electromagnetic devices or media for data storage. Often the thickness of the individual layer is not more than a few nm ($1 \text{ nm} = 10^{-9} \text{ m}$), which is equivalent to some tens of atomic layers. Examples of such devices are heads for reading of magnetically recorded data and tunnel junctions. The last device can be considered as a magnetic version of the well-known transistor. The first application of tunnel junctions is probably in magnetic memories. Such memories may be smaller in size than the memories used now and they are non-volatile, *i.e.* the stored data are not lost when the power is switched off. In most magnetic devices the electric resistance is varied by switching the (in-plane) direction of the magnetization of two ferro-magnetic layers from parallel to anti-parallel (or vice versa). The reason is that conduction electrons in a magnetized layer can be (partly) spin-polarized. If these polarized electrons are transferred to a conducting layer magnetized in the opposite direction, they can have a higher conduction resistance because their spin direction is opposite to the spin direction of (the majority of) the conduction electrons in the second layer. The functionality of such layered structures can be characterized by their magneto-resistance. This is the variation in the electrical resistance due to the switching from parallel to anti-parallel magnetization of the layers. This quantity is very sensitive to the structure of the layers and their interfaces. A new technology, called spin electronics, based on this effect has emerged recently in the world of microelectronics. Obviously, a very important item in spin-electronics is the controlled synthesis of thin conductive ferro-magnetic layers. Magnetite (Fe_3O_4) is a candidate material for application in spin-electronic devices because it is a ferro-magnetic material in which the spins of all conduction electrons are aligned with the magnetization direction.

The layers in certain magnetic devices may consist of small randomly oriented crystallites of the material. The structure of such layers is referred to as polycrystalline. The boundaries between the crystallites can be considered as crystallographic defects. For other applications, a low density of defects is necessary. In this case monocrystalline layers of the material have to be produced.

This can be accomplished by growing epitaxial layers on appropriate (monocrystalline) substrates that have a low-index crystallographic direction perpendicular to the surface. In the case of epitaxy the grown layer has also a low-index crystallographic direction perpendicular to the surface. Crystal planes as well as surfaces of monocrystals are indexed by (often three) coordinates chosen along the main crystallographic directions. A plane is indicated by the direction coordinates of the normal to the plane. In our research we used MgO(001) crystals as a substrate. Under certain conditions the layers grown on such a substrate are epitaxial, meaning that a set of crystal planes of the grown layer is parallel to the surface, and thus to the similar set of planes in the substrate. In some cases the epitaxial layer can be polycrystalline, whereby the crystallites are rotated with respect to each other around an axis perpendicular to the surface. However, in many cases this layer is monocrystalline, with a structure that can be a replica of the crystallographic structure of the substrate. In epitaxy, the best crystalline quality of the material is obtained if during the growth one complete atomic layer (a monolayer) of the material grows after another. This can be achieved by evaporating the material at a slow speed (far less than a monolayer per second) on a substrate that may have a temperature of a few hundred °C. This technique is called molecular beam epitaxial (MBE) growth.

The structure of (multi)layers can be influenced to a large extent by the conditions applied both during production and utilization. For this reason a detailed understanding on an atomic scale of the chemical and physical processes taking place during fabrication of the layers as well as their interaction with the ambience is of great importance. The obtained knowledge is crucial for controlled production of high-performance devices with a long service time.

The main emphasis of the research described in this thesis is on the structure of the surfaces and the bulk phases formed during gas-metal interactions. The interaction of gases with metals is a complex process and some basic knowledge of the main steps in this process would be beneficial for further understanding of the studies described. For this reason a brief introduction to the subject of gas-metal interactions is given in Chapter 1. In this chapter, the main steps of the interaction are described and illustrated with a few examples of the gas-metal systems studied in this work. The total gas-metal interaction is divided into two main stages: (i) processes taking place at the metal surface, and (ii) processes involving bulk diffusion of the reacting atoms and phase formation. As a reflection

of this division, the thesis consists of two parts.

Applying a physics approach, the gas-metal interactions are studied in this thesis using a large variety of experimental techniques. These techniques are described in Chapter 2. In this summary we indicate, without further explanation, what can be learned by applying the various techniques. The composition of the samples was analyzed by x-ray photoelectron spectroscopy (XPS) and conversion electron Mössbauer spectroscopy (CEMS). XPS gives information on the species present in the top 5 nm in the sample, their amount and oxidation state. From CEMS spectra, information can be derived on the compound formed. With CEMS the local magnet field at the ^{57}Fe atoms can be determined. Natural Fe contains only 1.9% of this isotope. Therefore, in a part of the research we used the isotope ^{57}Fe . The elemental composition of the layers was determined as a function of depth with Rutherford backscattering spectroscopy (RBS). The crystallographic structure was studied with x-ray diffraction (XRD) as well as with RBS by making use of the channeling effect. With XRD and RBS/channeling the types of crystallographic lattices present and their mutual orientation can be determined. From this, data can be obtained on the phases of the compounds and on the orientation of the crystallites with respect to the orientation of the substrate. The surface structure was investigated on an atomic scale by low-energy ion scattering (LEIS), low-energy electron diffraction (LEED), and reflection high-energy electron diffraction (RHEED). The probing depth of these experimental techniques is limited to a few atomic layers of the sample what makes these techniques suitable to study surface reconstructions. LEED and RHEED were also used to monitor the growth of monocrystalline metallic layers. As stated before, such monocrystalline layers were grown by evaporating the metal onto monocrystalline MgO(001) substrates in ultra-high vacuum (UHV). Alternatively, metal oxides were grown by evaporating the metal in the presence of a flow of oxygen or an oxygen-containing gas. The morphology (*i.e.* organization of the material consisting of *e.g.* small crystallites) was analyzed with scanning electron microscopy (SEM) and atomic force microscopy (AFM). These techniques provide information on the arrangement of crystallographic domains, surface topography, macrodefects, such as pinholes and cracks.

The first part of the thesis deals with reconstructions of surfaces. The reconstructions take place to minimize the total energy of the newly formed system and involve displacement of metal atoms. The reconstructions may be of different

types depending on the nature of the gas-metal interaction and, thus, on the particular gas-metal combination. In Chapter 3, the interaction of H with the (110) surface of Cu is studied. Adsorption of H₂ at the Cu surfaces is negligible at room temperature (RT) and above, and its dissociation into atomic H has to be activated. For these reasons, in our experiments the Cu(110) surface was exposed to a beam of atomic H at 245 K (273 K = 0°C). The interaction of H with Cu(110) results in a change in the surface structure, as seen with LEED. From the analysis of the LEIS angular scans it was found that the change is caused by restructuring of the Cu(110) surface in such a way that every other [110] atomic row in the topmost layer is missing. As a consequence of such restructuring, the surface becomes terminated with facets of Cu(111). The Cu(111) face is more densely packed and, therefore, more stable. Detailed studies of the atomic positions at the reconstructed surface revealed that H atoms occupy trigonal hollow sites formed by two first-layer Cu atoms and one second-layer Cu atom. It was determined that H-saturation is reached at 0.5 monolayer (ML) coverage. At this coverage, the H atoms are arranged in a zig-zag way along the Cu[110] atomic rows. From the exact coordinates of atoms at the surface, the length and type of the Cu–H bonding can be derived. Our analysis also gave evidence for quantum delocalization of H at the Cu(110) surface. Quantum delocalization would give rise to a high mobility of H atoms this surface. The adsorption and desorption of atomic H was determined as a function of temperature. The information obtained in our studies is of interest for further understanding and application of the H–Cu system, mainly in catalysis.

In Chapter 4, the structure of the (001) surface of magnetite (Fe₃O₄) is discussed. As stated before this structure is very important for the possible application of magnetite layers in electromagnetic devices. This structure has been the subject of many publications. Still it has not been possible yet to determine this structure unambiguously. A part of the confusion on the structure may be due to differences in the way the samples were produced. We prepared the layers by O₂-assisted MBE of Fe on an MgO(001) substrate. From the very beginning of the growth, LEED revealed a ($\sqrt{2} \times \sqrt{2}$)R45 reconstruction of the surface which also remained when the growth process was terminated. The symmetry of the LEIS scans measured on such samples revealed that Fe₃O₄(001) layers consist of mutually perpendicular crystallographic domains. These domains must be separated by stacking faults. The appearance of the domain structure is due to differences

in the symmetry and the size of the unit cell between the substrate and the layer grown. By fitting the LEIS scans calculated for assumed trial structures to the experimental data it was found that the surface is terminated with Fe atoms and that only half of the possible Fe positions were occupied. The $(\sqrt{2} \times \sqrt{2})R45$ surface reconstruction observed with LEED is in agreement with this model. The loss of coordination at the surface was found to result in a large inward relaxation of the topmost atomic layer. The surface structure, as determined in our studies, gave the best fit to the experimental data in comparison to a number of other structural models proposed in the literature. The presence of domain boundaries and the surface reconstruction has an influence on the electromagnetic properties of Fe_3O_4 -based films and multilayer structures.

In the second part of the thesis, the structure of bulk phases formed during gas-metal reactions is studied. All the described studies concern interactions of gases with Ag/Fe and Ni/Fe bilayer systems. To understand the phase transformation processes occurring during the gas-solid interactions, we first studied the structure and morphology of metallic Ag/Fe and Ni/Fe bilayers deposited on MgO(001). The results of these studies are presented in Chapter 5. Both types of the bilayers were found to be epitaxial and to have sharp interfaces. The Fe layer was found to be monocrystalline with an atomically smooth surface as seen with AFM. The same observations were made for the Ag cover layer. In contrast to the Ag/Fe case, the Ni/Fe system has a more complex structure. It was observed that first three atomic layers of Ni form a monocrystalline layer with a crystallographic structure isomorphous with the underlying α -Fe. For larger thicknesses, a phase transformation takes place in the Ni layer. The new phase is still epitaxial and consists of crystallites with four different orientations. The size of the crystallites in a 20 nm thick Ni layer was observed with SEM to be in the range 60–120 nm. A model is proposed explaining the phase transformation in terms of a martensitic transition, *i.e.* a transition in which the metal atoms move simultaneously over only small distances compared to the interatomic distances.

In Chapter 6, the thermal stability and oxidation of Ag/Fe and Ni/Fe bilayers is studied. The thickness of the Ag and Ni cover layers was 20 nm. Since Ag forms a continuous monocrystalline layer on Fe(001), good protection of the Fe against oxidation is expected in such a bilayer system. In the Ni/Fe(001) case, the Ni layer consists of small crystalline grains. The grain boundaries are easy diffusion paths for both Fe and gas atoms. Thus, oxidation of the underlying Fe can be

expected along the grain boundaries in the Ni cover layer. From our experiments it appeared that annealing of a Ag/Fe bilayer in UHV for a few hours in the 200°C–320°C temperature range resulted in a discontinuity of the Ag cover layer. Round holes are formed in the Ag layer. Oxidation of a Ag/Fe bilayer in pure O₂ in the same temperature range resulted in rapid oxidation of Fe, whereby a very rough Fe-oxide layer is formed on top of a still epitaxial Ag layer. The oxidation speed is comparable with that of unprotected Fe. We propose a model to explain the results. In this model the discontinuity of the Ag layer is caused by patches of FeO formed at the Ag/Fe interface. In spite of the UHV conditions applied, the small amount of O, necessary to form the patches, could have accumulated in the Ag layer during growth. The Ag retracts from these patches due to a smaller adhesion of the Ag/FeO couple compared to the Ag/Fe and Ag/Ag couples. The applied temperature is sufficiently high for the necessary diffusion of Ag atoms along grain boundaries. This same process takes place to an even larger extent during exposure to O. During this exposure a small amount of O can dissolve in the Ag layer and diffuse to the interface. The high rate of Fe-oxidation observed was explained by a possible faster diffusion of Fe along the Ag/FeO interfaces at holes, compared to the diffusion through the already formed FeO layer as it occurs during oxidation of bare Fe. Thus, in contrast to the expectations, a continuous monocrystalline Ag cover layer does not protect the underlying Fe from oxidation at the conditions applied.

For the Ni/Fe bilayers the thermal stability and the oxidation resistance were found to be higher. The limited interdiffusion of Fe and Ni found after a vacuum anneal step of 30 hours at 300°C is probably along the grain boundaries present in the Ni cover layer. It appears that during the oxidation step (40 hours in 10⁻⁶ mbar of pure O₂ at 200°C) only a small fraction (about 4 nm) of Fe was oxidized. According to the experimental data, the oxidation takes place near the surface of the sample. This means that the oxidation is mainly due to diffusion of Fe, and not of O atoms. Contrary to the case of a Ag-covered Fe layer no holes are formed in the Ni layer as was checked with SEM. The Ni may be covered with a layer of NiO.

In Chapter 7, phase transformation upon gaseous nitriding of Fe layers covered with a 20 nm thick Ni layer is studied. The nitriding was done in an NH₃ + H₂ gas mixture at temperatures of 200°C and 300°C. The Ni layer was used to avoid possible oxidation of the underlying Fe and to promote dissociation of the gas

molecules. Nitride layers produced in this way are continuous *i.e.* have no pores or other macrodefects as is often the case when uncovered Fe layers are nitrided. The absence of such defects is a necessary condition for a detailed investigation of the phase transformation processes on an atomic scale. At the conditions applied, practically all Fe-nitride phases could be obtained. The α' -Fe₈N, α'' -Fe₁₆N₂ and γ' -Fe₄N phases are electrically conductive and ferro-magnetic what is of potential interest for applications in magneto-recording and in magnetic devices. Our studies showed that during gaseous nitriding of α -Fe in the 200°C – 300°C temperature range, the phase transformations occur sequentially. This means that phases with a higher nitrogen content are formed from phases with a lower content of nitrogen. For gaseous nitriding of uncovered Fe this sequence is not always observed. The specific way of phase formation has consequences for the orientation of the crystallites in the newly formed layers. We demonstrated that at the relatively low temperatures applied here, where diffusion of Fe atoms can be neglected, phase transformations in the Fe–N system can be well described in terms of martensitic transitions, as far as the Fe-sublattice is concerned. From the measured XRD scans, information on orientation relationships between different phases was derived and models of phase transformations on atomic scale are proposed. The models predict the structures formed during the phase transition. It was found that an epitaxial and monocrystalline mixture of the α' and α'' phases with the same composition (Fe₁₆N₂) was formed. The γ' phase was found to be polycrystalline with a small, well-defined deviation from epitaxiality. The same was found for the ε phase. From the mechanisms of phase transformations it was derived that each step of the $\alpha' \rightarrow \gamma' \rightarrow \varepsilon$ transformation cycle is accompanied by grain refinement. This information is of value for the fabrication of Fe-nitride based layers with a nano-crystalline structure. Such layers are expected to have special magnetic properties.

Results on the oxidation of an Fe-nitride layer formed under a 20 nm thick Ni cover-layer are discussed in Chapter 8. Although Fe-oxynitrides are already applied in a number of commercial technological processes as corrosion-resistant coatings, there are many unresolved questions concerning their composition and structure. No attempts have been made to investigate the magnetic properties of this material. In the literature, there is a controversy on the existence of Fe-oxynitrides as a compound with characteristics different from Fe-oxides. The oxidation was done in 100 mbar O₂ at 275°C. The Fe-oxide phase formed upon

oxidation of the Ni/Fe–N bilayers was identified to have a spinel-like structure and to be constituted mostly by Fe^{3+} ions. Since CEMS spectra obtained for the oxidized Fe-nitride could not be ascribed to any of the Fe-oxide or Fe-hydroxide phases known, it is plausible to conclude that a new compound containing both N and O was formed. The Fe atoms in the compound were found to sense a large (about 51 T) local magnetic field. The value of this field is comparable to that of maghemite $\gamma\text{-Fe}_2\text{O}_3$ which is widely used as a recording material in magnetic tapes. In this respect, Fe-oxynitride may also find application in magnetic recording. After oxidation the sample shows blisters which are probably bubbles of N_2 gas formed due to recombination of excess N atoms produced in the reaction.

In this thesis gas-metal interactions were studied for a fairly broad scope of systems. For each of the systems studied meaningful results were obtained. These results must be seen as another step forward in the understanding of what is happening at the atomic scale during the interactions, and in the ability to produce layered structures with desired properties. As is mostly the case, more research would be useful. This extra work could not be done as a part of this project because of time restrictions, and because the proper techniques are not developed yet, or were not available to us. Below we give some possible directions for further research.

We determined the reconstruction of the Cu(110) surface as a result of its interaction with H, as well as the location, the mobility and the absorption and desorption characteristics of H at this surface. For catalysis it would be useful to have this type of information also for other low-index surfaces, as well as for defected surfaces. Stepped (vicinal) surfaces could serve as a model system for defected surfaces. It is generally believed that defects on the (Cu) surfaces play an important role in catalysis.

We grew epitaxial magnetite (Fe_3O_4) layers and we determined the structure of the (001) surface. For a theoretical understanding of this structure it would be required to perform model calculations in an attempt to reproduce this structure. For application in multilayered systems it would be useful to determine how the surface structure is translated into an interface structure when another functional layer is grown on top of magnetite.

A model was presented to explain the interaction of O_2 with Ag covered Fe layers. The model describes the fast oxidation of the Fe, whereby a very rough Fe-

oxide layer is formed on top of the Ag. Also, bilayers of Pt/Fe and Pd/FeTi form a very rough surface oxide upon oxidation. It would be worthwhile to investigate if the proposed mechanism also applies to these and other bilayer systems. Possibly, the model can be extended so that it would predict the protection against oxidation in O₂ offered by other metal cover layers on Fe.

It was demonstrated that a monocrystalline mixture of the α' -Fe₈N and α'' -Fe₁₆N₂ Fe-nitride phases can be formed by low-temperature nitriding of thin layer of monocrystalline Fe covered with Ni. The α'' -Fe₁₆N₂ phase has the highest saturation magnetization of all magnetic materials and is therefore interesting from a theoretical standpoint and for applications. At the same time the difficulties encountered in producing this meta-stable material in its pure form has prevented a precise measurement of its magnetization. Possibly, thin layers of the material can be synthesized in its pure form using the method tried here.

As a result of measurements done on Fe-nitride layers obtained by nitriding monocrystalline layers of Fe covered with Ni, models were developed to describe the transitions to the different nitride phases on an atomic scale. It was postulated that the phase transitions to the phases would be different if the nitriding was performed under the same conditions on uncovered Fe layers. Verification of this postulate would be important to understand the issue of nitriding of Fe in more detail. The internal structure predicted by the models for phase transitions has a large influence on the magnetic and the mechanical properties of the nitride layers formed.

The oxidation in pure oxygen of Ni-covered Fe-nitride layers was investigated. It was found that the Fe-oxide layer containing nitrogen is possibly a new compound. More research is required to establish if indeed a new compound is formed and to investigate its magnetic properties in view of possible applications.