Chapter 1

Introduction

The discovery of conventionally forbidden crystallographic point symmetries in solids in 1984 was the starting point of intense research focusing on many different aspects of these new materials which were given the name ‘quasicrystals’ [1]. Their intriguing symmetries in connection with long-range order exposed significant limitations of the well accepted rules of crystallography, such that eventually in 1992 the definition of a crystal was changed to a solid possessing an ‘essentially discrete’ diffraction pattern [2] in order to also encompass quasicrystals.

Quasicrystals of eight- and twelvefold point groups have been observed in metastable alloys only, while five- and tenfold rotationally symmetric quasicrystals have been successfully grown in sufficient size for structural analysis [3-6]. Two prominent examples of these are icosahedral Al-Pd-Mn and decagonal Al-Ni-Co, both of which were investigated in this thesis. Subject to various studies regarding their structural and physical properties, they have yielded many surprising results. These aluminum-rich alloys reveal properties not at all typical for their components, such as an extremely high electrical resistivity decreasing with temperature and rising with the degree of order, brittleness and hardness at low temperatures in contrast to a high ductility at high temperatures, a high corrosion resistance, and a low coefficient of friction [7]. The most important question, i.e., whether these properties are related to a complex alloy composition or exclusively to the quasicrystalline structure, has not been resolved, yet.

The investigation of quasicrystal surfaces was hindered for a long time by the lack of samples of sufficient size. However, even with their availability the first hurdle to overcome was the preparation of high structural quality quasicrystalline surfaces. After several years of intense research, recipes for the preparation of clean surfaces of quasicrystalline structure in agreement with possible bulk terminations were established. However, depending on the details of the annealing conditions a variety of different morphologies have been observed. The reason for these annealing temperature-dependent results has not yet been fully understood. In order to address this question, temperature dependent investigations of the structure and morphology of quasicrystal surfaces were necessary, but had not been carried out prior to this thesis. In addition to purely morphological changes, structural bulk phase transitions, as expected from the phase diagram of Al-Ni-Co [8], might play an important role during annealing. Any structural or morphological changes which are not equilibrated during the preparation process will influence the results. As the quasicrystals' surfaces had not been investigated at temperatures above room temperature, possible effects have not been discussed up to now. This lack of experiments might be related to the fact that surface sensitive methods are usually hard to handle at elevated temperatures (due to thermally activated atomic vibrations and consequently a large Debye-Waller factor, diffraction experiments are almost impossible, while scanning probe techniques have to overcome thermal drift problems). Moreover, time-resolved observations under change of temperature are desirable. The method of choice to address these questions is low-energy electron microscopy, as this technique provides direct information about morphological and structural changes on the nanometer-scale with varying sample temperature. The experiments discussed in chapter 4 of this thesis have been carried out in the lab of Prof. Horn-von Hoegen where one of the few LEEM instruments worldwide is available.

While quasicrystalline surfaces themselves constitute a fascinating topic of current research, due to their intriguing symmetries and physical properties, the interaction of adsorbates with the clean surface is even more interesting from several points of view. Firstly, phenomena such as a low surface energy, a non-sticking behavior and a low coefficient of friction are surface-related and important for industrial applications. From a technological perspective, a basic insight into how the surface properties can be modified by coatings is desirable. It is therefore straightforward not only to study the structure itself, but also the interactions of adsorbates with the surfaces. Especially quasicrystalline films of a single element could be of importance, as they could provide an answer to the important question whether the outstanding properties of quasicrystals are solely due to the complex alloy composition or to quasicrystallinity itself. In addition to this property-derived interest, basic questions concerning the structure formation and classification at the interface arise, such as: Is it in principle possible to obtain a quasicrystalline film of a single element on a quasicrystal substrate? If so, how is this kind of film stabilized? Would there be a long-range order at the interface between a periodic and quasiperiodic lattice? The characterization of the interfacial structure between a quasicrystalline and a periodic material requires a new approach which goes beyond the description of interfaces between periodic crystals. Up to now it has been assumed that a long-range commensurability of the lattices is impossible [9]. The final question is: What is to be understood by epitaxy on quasicrystals?

The first question has already been addressed in a large variety of experimental investigations.

Many of them start with the study of submonolayer coverages of specific adsorbates in order to determine the adsorption sites. Indeed, some results have shown that the adsorbates occupy preferential adsorption sites in high symmetry atomic arrangements of the substrate. However, with increasing coverage the long-range quasicrystalline order is destroyed [10-13]. On the other hand, adsorption of Au, Pt and Al has demonstrated that long-range order can indeed exist in films on quasicrystal surfaces, but not in a quasicrystalline structure. Their diffraction patterns exhibit the rotational symmetry of the substrate due to multiply twinned periodic domains [9, 14-16]. The only reports of any epitaxial quasicrystalline films with long-range order on a quasicrystal are ion bombardment and annealing-induced compositional changes in the topmost surface layers, leading to decagonal films on the fivefold Al-Pd-Mn surface. Examples for these are a film of $Al_{22}Pd_{56}Mn_{22}$ [17] and a layer consisting of the stable decagonal $Al_{69.8}Pd_{12.1}Mn_{18.1}$ bulk phase [18].

In an effort to find suitable adsorbates for the formation of quasicrystalline films, the growth of bismuth and antimony on the fivefold surface of icosahedral-Al-Pd-Mn and the tenfold surface of decagonal-Al-Ni-Co is investigated in chapter 5. One monolayer thick films have been observed to obey the long-range quasicrystalline order of the substrates, and therefore constitute the first single element quasicrystalline films.

The second group of interesting adsorbate structures comprises those of the periodic arrangements on the quasicrystalline substrate as they could provide an answer to the other basic questions introduced above. So far, several systems of periodic structures on quasicrystalline surfaces have been found. Some of them were prepared by sputtering the quasicrystal surface, where the preferential removal of Al atoms induces the transformation to a periodic approximant structure [19-22]. Other periodic overlayers were obtained by deposition of single elements such as Au, Pt, and Al [9, 14-16]. All these systems consist of multiple domains which are aligned along the five- or tenfold rotational axis of the respective substrate. These observations have led Shimoda et al. to stretch the meaning of epitaxy to describe 'the phenomenon in which films grown on a quasiperiodic substrate maintain the directional order of the substrate' [15]. However, the long-range order of the atomic structure at the interface has not yet been completely resolved. It has only been discussed locally with the remark that deviations of the atomic positions of the adsorbate layer from the substrate could be small, such that a stable film could be formed [14]. In this thesis an example for a periodic system on the tenfold surface of d-Al-Ni-Co has been found by preparation of an AlAs structure; it will be presented in chapter 6. A detailed structural analysis of the interface shows that long-range order between a periodic crystal and a quasicrystal can indeed exist. On the basis of a general model the term epitaxy can be shown to agree with the original meaning of matching lattices at the interface. A general criterion for epitaxy on any kind of long-range ordered material will be given.