Chapter 7

Summary and Outlook

Quasicrystals are intermetallic alloys with long-range atomic order yet without periodicity. Many of these exhibit conventionally forbidden rotational symmetries. Their discovery has forced scientists to reconsider basic concepts of solid state physics and crystallography which rely on periodic ordering. Aside from these intriguing structural characteristics, unusual physical properties contrary to those of their metallic constituents have attracted significant interest. Many of them are surface-related properties such as a high corrosion resistance or a low coefficient of friction. As their temperature dependence might be of importance for applications, the surface structure and morphology in a wide temperature range are of substantial interest. One great challenge is to resolve the question whether these properties arise from the quasicrystalline structure itself or from the complex alloy composition.

In order to provide a basis to address these fundamental questions, this thesis focuses on two topics: First, the temperature dependent morphology of quasicrystal surfaces and temperature-induced surface phase transitions were characterized. Second, adsorbate layers on quasicrystals were studied. These comprise both epitaxial quasicrystalline films and epitaxial periodic adsorbate islands.

LEEM is the method of choice to directly investigate the morphology on the nm-scale as a function of temperature. The characterization of the morphology of quasicrystals is more complex than for periodic crystals. In periodic crystals, a step-terrace morphology is associated to a limited number of step heights separating planes of equal surface free energy. In contrast, a quasiperiodic ordering perpendicular to the surface yields an infinite number of possible terminations with different surface free energies and incommensurate step heights. The LEEM experiments showed that families of structurally similar planes constitute the observed surface termination on the twofold (10000)- and the twofold $(001\bar{1}0)$-surface of decagonal Al-Ni-Co. Above 650 °C the terraces are several micrometers wide and separated by multiple steps (fig-

ure 4.5). Cooling below this temperature leads to a large increase in step density. A similar roughening was found on the tenfold (00001)-surface. During this transformation a large material exchange between bulk and surface via channels into the bulk can be observed on the twofold samples (figure 4.6). Therefore, the transition is closely related to the bulk structural transformation between the decagonal modifications S1 and type I. The significant decrease of bulk structural vacancies [99] can explain the observed material exchange. Due to an inhibited surface diffusion the equilibrium morphology of the low-temperature type I phase cannot be reached within reasonable time intervals. The observed surface roughening is therefore not an intrinsic feature of the low temperature phase. However, although the step-terrace morphology has not reached its equilibrium, the atomic structure within the planes is in agreement with the expected quasicrystal structure of the type I phase. On the twofold $(001\bar{1}0)$-surface the structural transformation type I to S1 is accompanied by faceting (figure 4.13 and 4.14). Facet planes inclined by $\pm 18°$ from this surface and structurally equivalent to (10000)-planes in combination with flat surface areas characterize the morphology on the $(001\bar{1}0)$-surface of the type I phase. As in periodic crystals the surface free energy of specific net planes is typically lower for higher planar atomic density. This agrees well with the observed facet planes.

At 730 °C the phase transition between the modifcations S1 and basic Ni is manifested in the LEEM data by a characteristic step motion and phase contrast on the twofold (10000)-surface (figure 4.20). While bright-field LEEM images show three classes of terraces of different structure factor during the transition, MEM imaging reveals a varying work function to be associated to the three kinds of terminations. The lowest work function is exhibited by the basic Ni termination, which is therefore concluded to consist of the highest Al density. The S1 phase as well as a surface phase which is thermodynamically stable only in a narrow temperature range of about 10 °C during the transformation are terminated by planes of higher transition metal content. The observed changes in termination can be related to atomic jumps which are known to drive the bulk structural phase transition. This kind of structural transformation is unique to quasicrystals.

Aside from LEEM being of great importance for the characterization of the morphology at high temperatures, these experiments point out the impossibility of passing the structural bulk phase transition between the modifications S1 and type I and achieving an equilibrium morphology. For experimental investigations based on an equilibrium morphology, such as growth studies on quasicrystal surfaces, samples of suitable bulk composition which undergo this phase transition at significantly higher temperatures where the surface diffusion might be considerably larger should be used.

The second part of this thesis focuses on epitaxial films on quasicrystals. The growth of

quasicrystalline epitaxial single element films was motivated by the need for appropriate model systems to study quasicrystallinity independent of a complex alloy composition. Hence, the challenge was to find elements which, adsorbed on a quasicrystalline template, adapt to the substrate's structure. This goal has been accomplished with Sb and Bi. Their deposition onto the fivefold surface of icosahedral Al-Pd-Mn and the tenfold surface of decagonal Al-Ni-Co and appropriate annealing conditions were shown to result in the formation of high quality quasicrystalline monolayers. The Sb and Bi coverage was determined by recording the He specular intensity during the adsorption process on these surfaces as well as on GaAs(110) and modeling the growth process. This comparative study allowed the calibration of the adsorption curves on the quasicrystals finally leading to a coverage determination of one closed monolayer. Moreover, by comparison of thermal desorption temperatures of the monolayers on these three surfaces, strong covalent bonds can be inferred to stabilize films. Their long-range order was investigated by electron and helium diffraction where the monolayers reveal the same bulk derived Bragg peaks as the corresponding substrate (figure 5.7 and 5.9). This demonstrates for the first time the formation of quasicrystalline epitaxial films. As the coverage of the monolayers is less than the atomic density of the terminating substrate planes the monolayer is not a copy of the latter. A structural model of the monolayers was proposed in which the atoms of the monolayers are located on a τ-times enlarged Penrose tiling as compared to the substrate (figure 6.8). As the tiling is self-similar the diffraction spots of the layers are located on identical positions as those of the substrate.

While these quasicrystalline monolayers illustrate epitaxy of quasicrystalline films on quasicrystals the question how epitaxial growth of a periodic structure on a quasicrystal can be understood was still unresolved. Although several examples of such a formation were already known, the question whether a long-range ordered interface is achieved had not been appropriately analyzed. To address this question arsenic was deposited onto the tenfold surface of decagonal Al-Ni-Co and annealed at temperatures above 550 °C. Helium scattering and SPA-LEED revealed the formation of distorted AlAs(111) surface planes which are inclined by 35.14° with respect to the substrate (figure 6.4). The interface planes are represented by Al-Ni-Co($10\bar{2}\bar{2}4$) facets. The tensile strain leading to the distortion of the AlAs(111) planes by 3.2 % from its bulk lattice indicates an energetically favored lattice matching with the substrate. Indeed, it has been found that the main periodic average structure of the quasicrystal is matched by the distorted AlAs lattice (figure 6.14). The importance of finding the appropriate periodic average structure was illustrated by the one-dimensional example of the Fibonacci sequence. It was shown that the unit cell of a periodic average structure potentially relevant for epitaxy is characterized by strong corresponding Bragg reflexes in the quasicrystal's diffraction pattern. Finally, a general

criterion for epitactic growth at interfaces of long-range ordered materials - with or without periodicity - was developed: the coincidence of the diffraction patterns of the interface planes in selected high intensity diffraction spots.

In conclusion, the morphology of three low index surfaces of decagonal Al-Ni-Co was characterized by LEEM. By changes in surface morphology phase transitions were identified and their relation to bulk structural transitions was discussed. Epitaxy on quasicrystals was investigated by the successful growth of single element quasicrystalline monolayers and the detailed structural analysis of a periodic to quasiperiodic interface. From these results a new generalized criterion for epitaxy on quasiperiodic materials was established.