Oxide and oxide-supported nanoclusters on quasicrystals

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SVEN BURKARDT
Dipl. Phys. ETH
born on December 16, 1976
citizen of Sirnach, TG

accepted on the recommendation of

Prof. Dr. M. Erbudak, examiner
Prof. Dr. D. Pescia, co-examiner
Prof. Dr. A. Vaterlaus, co-examiner

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## Contents

Abstract iii  
Zusammenfassung v  
1 Introduction 1  
2 Experimental setup 7  
3 Oxidation of the 5f-symmetry surface of icosahedral AlPdMn 11  
  3.1 LEED from the oxidized surface 12  
  3.2 Antiphase domain boundaries 14  
  3.3 Surface reconstruction 16  
  3.4 Crystalline buffer layer 19  
4 Oxidation of the 3f-symmetry surface of icosahedral AlPdMn 21  
  4.1 The 3f-symmetry surface of i-AlPdMn 21  
  4.2 LEED 22  
  4.3 AES 24  
  4.4 Oxygen-induced surface faceting 26  
  4.5 The facet-structure 27  
  4.6 Kinetics 28  
5 Oxidation of the 10f-symmetry surface of decagonal AlCoNi 31  
  5.1 The clean decagonal surface of d-AlCoNi 31  
  5.2 High-temperature oxidation 32  
  5.3 The structure model 35  
  5.4 The interface 37  
6 Al nanoclusters on the oxidized pentagonal surface of i-AlPdMn 41  
  6.1 AES 42  
  6.2 LEED 43  
  6.3 SEI 44  
  6.4 Interface formation 46  
  6.5 Random in-plane growth 48  
7 Conclusions and outlook 51  
Bibliography 55
Appendix
   A  Determination of the domain size using LEED  . . . . . . . . . . . .  63
   B  Acronyms  . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .  66

Publications  67

Curriculum Vitae  69

Dank  71
Abstract

The structural characterization of thin oxide films grown on ordered Al single crystal and Al-based binary alloys has been challenging scientists since decades. It was found that even in its alloying form only Al binds to oxygen forming an atomically thin, well-ordered Al-oxide layer. Despite immense efforts, the detailed structure of these oxide layers has remained unresolved but the results indicate an affinity with known hexagonal Al-oxide phases. In this dissertation, the structure of crystalline oxide layers grown on quasicrystalline substrate upon high-temperature oxidation is discussed. The results facilitate the interpretation in terms of a hexagonal domain structure, which is strongly influenced by the aperiodic atomic ordering of the quasicrystal surface. In a subsequent experiment, one oxide layer, the oxidized pentagonal surface of icosahedral AlPdMn quasicrystal, was used as a substrate for the growth of Al overlayers. The experimental findings show that due to the small lateral extension of the Al-oxide domains, the Al crystallites remain in the nanometer size. The domains possess well-defined polar orientations, while their in-plane azimuthal orientations are randomly aligned. Information about the chemical composition in the near-surface region has been obtained by Auger electron spectroscopy, while structural investigations are based on low-energy electron diffraction and secondary-electron imaging.

The investigation of the oxidation behavior of the pentagonal surface of icosahedral AlPdMn reveals the growth of different oxide layers depending on the sample temperature and its pretreatment. At room temperature, an amorphous oxide layer forms. In contrast, at 700–800 K, five distinct and few-nanometer-large domains grow for small and large coverage, possessing a hexagonal structure with substantial amount of contribution from antiphase domain boundaries. In an intermediate range, a mixture of antiphase domain-boundary contributions and fractional-order spots, characteristic of a $2\sqrt{3}(1 \times 1) R\pm30^\circ$ reconstruction of the oxide layer, is found which additionally stabilized the interface. A third structural phase is observed after ion bombardment of the oxidized surface with subsequent reoxidation. This surface structure is identified as an oxide layer grown on the $(1 \ 1 \ 0)$ surface of a crystalline Al$_{50}$(PdMn)$_{50}$ alloy which forms as a result of the sputtering.

Further information about the complex growth process, which leads to the formation of structurally well-ordered oxide layers on aperiodic substrate, are obtained by the oxidation of the threefold-symmetry surface of icosahedral AlPdMn quasicrystal. The results are consistent with a faceted Al-oxide layer, while each facet is oriented along a high-symmetry direction of the icosahedral bulk structure. It was found that the oxygen take up and the incorporation into the crystalline Al-oxide
matrix is enhanced along the fivefold-symmetry directions of the quasicrystal, favoring an environment, which crystallizes the facets along those directions, while they remain structureless along the twofold- and the threefold-symmetry directions. The faceting of the surface layer can be explained by the most pronounced bulk diffusion of Al in the icosahedral quasicrystal structure along the pentagonal directions.

Comparable results can be obtained by the oxidation of decagonal AlCoNi: initial high-temperature oxygen exposure of the tenfold-symmetry surface of decagonal AlCoNi has revealed the dissociative adsorption of oxygen, leading to a very thin layer of chemisorbed oxygen. Further exposure results in a well-ordered Al-oxide layer possessing a local hexagonal, nanometric domain structure. Each domain is azimuthally oriented along a twofold-symmetry direction of the decagonal surface. However, unlike the oxide layers grown on the pentagonal surface of icosahedral AlPdMn, only one oxide structure is observable. Its diffraction pattern can be explained by a hexagonal antiphase domain ordering, while the size of the domains comply with self-size-selecting arguments. The structural investigation indicates that the separation distances of the domain boundaries, separating domains of equal orientation, are primarily a consequence of the preferential cluster nucleation on decagonal AlCoNi.

The nanometer-size lateral extension of the oxide domains have been used to grow crystalline Al particles in the same size-region by vapor deposition. Metal-oxide surfaces, acting as templates for the growth of thin films, are interesting in regard to catalyst support and applications in microelectronic devices. It was found that the nanocrystals expose their (1 1 1) faces parallel to the pentagonal surface of the quasicrystal, while their in-plane orientations are random. Spot-profile analysis of the diffracted beams indicate that the nanocrystals in fact grow in 3 nm large domains up to a deposition thickness of 51 monolayers. The size of the crystallites are limited by the lateral extension of the oxide domains on the surface and not, as expected in a molecular-beam epitaxy experiment, by the lattice mismatch between the substrate and the adsorbate. No broadening in domain size with deposition thickness can be observed, therefore, no coalescence of the domain structure is expected. Since the deposition quantity can be easily controlled in the experiment, this crystal–crystal interface is an ideal candidate for investigating and tuning size effects in this field of research.
Zusammenfassung


Die Untersuchung des Oxidationsverhaltens der pentagonalen Oberfläche eines ikosaedrischen AlPdMn zeigt das Wachstum von verschiedenen Oxidschichten, welche aus verschiedenen Proben-Temperaturen und -Präparationen resultieren. Bei Raumtemperatur formiert sich eine amorphe Oxidschicht. Hingegen bei 700–800 K formieren sich für kleine und grosse Bedeckungen fünf unterschiedliche, nanometergrosse Domänen, welche eine hexagonale Struktur mit Beiträgen von Antiphasegrenzen zeigen. In einem Zwischenbereich findet man neben der Antiphasestruktur auch Beiträge von fraktionalen Diffractionspunkten, welche charakteristisch für eine $2\sqrt{3}(1 \times 1)R \pm 30^\circ$ Rekonstruktion der Oberfläche sind. Diese Rekonstruktion dient zur zusätzlichen Stabilisierung der Grenzfläche. Eine dritte Strukturphase wird nach Ionenbeschuss von der vorgänglich oxidierten Oberfläche mit anschliessender Nachoxidation beobachtet. Diese Oberflächenstruktur ist identisch mit einer Oxidschicht, welche aufgrund des Sputterprozesses auf der (1 1 0) Oberfläche einer kristallinen Al$_{50}$(PdMn)$_{50}$ Verbindung entsteht.


Chapter 1

Introduction

Well-ordered thin oxide films are important in microelectronics, are attractive as carriers for metal catalysis, and act as an efficient capping on the bulk material against chemical and mechanical imperfections [1–5]. They have been investigated by the complete variety of surface analyzing techniques covering almost all aspects of material science, chemistry, and physics. One advantage of using thin oxide films is a severe experimental problem accompanying the investigation of bulk oxides: the insulation character prevents the application of methods involving charged particles [6]. It has been shown that oxide films with a thickness of just a few Å exhibit physical properties characteristic of the bulk material [7–9], thus, thin oxide films are ideally suited as model systems to investigate and tune physical properties in this field of research. In particular, the properties of thin alumina films grown on NiAl have attracted considerable attention [10]. These layers possess a well-defined structure, a high degree of long-range order, and an excellent reproducibility [1].

Nevertheless, it has not been a straightforward task to grow an ordered Al-oxide layer on (a) Al single crystal [11–19], (b) crystalline binary Al alloys [7, 10, 20–29], or (c) Al-based quasicrystals [30–38] nor to determine the structure of such layers.

(a) The reaction of oxygen with pure Al is strongly exothermic owing to the large negative value of heat of formation for Al$_2$O$_3$. Yet, the oxidation of different crystallographic surfaces of an Al single crystal shows different behavior. Upon oxygen exposure, Al$_2$O$_3$ is formed on Al(1 0 0), while the reaction with oxygen on Al(1 1 1) takes place in a two-step process: (i) via a chemisorbed precursor state followed by (ii) oxide-nuclei formation with subsequent oxide-cluster growth [16–18]. The reaction itself is a complex process and is variable depending on pressure, temperature, exposure time, is strongly dependent on the defect density of the surface, and the adsorption is dissociative rather than molecular [12, 18, 19, 25]. Further, the initial and subsequent stages in the oxide formation have been found to possess very different oxide-film growth kinetics [18]. A stoichiometric Al$_2$O$_3$ layer forms if the exact amount of Al is available for a given oxygen dose. Usually, an amorphous oxide film of self-limiting thickness grows at low temperatures which has Al deficiency. A thin oxide layer prevents Al to diffuse to the surface to further react with oxygen. Similarly, oxygen cannot diffuse through the oxide layer that acts as a diffusion barrier at low temperatures. At the high-temperature limit, the diffusivity does not prevent the supply of Al and O and a continuous growth establishes. An oxide
layer is formed quite often, however, with Al abundance and hence the oxide film still remains amorphous. Crystallization is achieved as a result of prolonged heat treatment at elevated temperatures. The most common crystalline phases of Al$_2$O$_3$ that grow on Al single crystal are the $\alpha$- and the $\gamma$-phase [5, 20, 39–41]. $\alpha$-Al$_2$O$_3$, corundum, is stable and built-on oxygen ions in a slightly distorted hexagonal close-packed lattice, while the Al ions occupy two-thirds of the octahedral interstitial sites. $\gamma$-Al$_2$O$_3$ is metastable and has a cubic, defective spinel structure, i.e., oxygen atoms occupy face-centered cubic (fcc) sites, while the Al cations are found randomly in octahedral and tetrahedral interstices [10, 18, 20]. Al$_2$O$_3$ is very stable and unreactive, extremely hard, has a high melting-temperature, low electrical-conductivity, and an excellent optical transparency [41]. Al-oxide surfaces have usually high surface energies [40], thus, upon oxide preparation, it is not uncommon that structural distortions emerge. For instance, on $\alpha$-Al$_2$O$_3$(0 0 0 1), it was found that the surface layer reconstructs into $\sqrt{3}(1 \times 1)R \pm 30^\circ$, $3\sqrt{3}(1 \times 1)R \pm 30^\circ$, as well as $\sqrt{31}(1 \times 1)R \pm 9^\circ$ [2,42].

(b) For Al-based crystalline binary alloys, it was found that only Al binds to oxygen. This is comprehensible comparing the values for heat of formation per mole O$_2$ of the various oxide that might form on the most commonly used binary Al alloys. For instance, the heat of formation for Al$_2$O$_3$ ($-1680$ kJ/mol) [26] is considerably higher than the corresponding values for NiO ($-225$ kJ/mol) [3], CoO ($-238$ kJ/mol), and Co$_3$O$_4$ ($-891$ kJ/mol) [26]. The more negative the heat of formation, the higher the affinity of the metal in the alloy for oxygen, thus, the more readily a particular oxide forms on the alloy [3]. The structural properties and the oxide growth kinetics have been found to be comparable to those of the oxide layers grown on Al single crystal [7]. In particular, the oxide layer grown on NiAl(1 1 0) has certain similarities with known hexagonal Al-oxide phases [20]. Nevertheless, the atomic structure is complex: the oxide layer is composed of two hexagonal reflection domains exhibiting a network of antiphase and twin-domain boundaries [10]. Due to the extreme shallowness of the film as well as the relatively large unit cell of the oxide domains, the detailed atomic ordering and the registry of the oxide domains with the substrate have not been readily resolved and still present a substantial challenge to surface science.

(c) Quasicrystals are intermetallic alloys and form a third state of solid matter [43]. They lack periodicity, yet possess orientational long-range ordering, however, of crystallographically forbidden symmetries, e.g., fivefold (5f) or tenfold (10f) rotational symmetry. Thus, they are neither disordered like an amorphous solid nor periodic like a crystal. The most prominent representatives are the decagonal ($d$-) AlCoNi and the icosahedral ($i$-) AlPdMn. Early studies on the oxidation behavior of the Al-rich quasicrystals have shown that similar to Al single crystal and ordered Al-transition-metal (TM) alloys, the Al atoms predominantly oxidize in a two-step process [30,33]. It has not been clear whether the TMs are affected by the oxidation process. For instance, in the case of AlPdMn, the thermodynamic data based upon the values of heats of formation for Al$_2$O$_3$ ($-1680$ kJ/mol), Mn$_3$O$_4$ ($-1390$ kJ/mol), and PdO ($-85$ kJ/mol) [32]) do at least allow it in the case of Mn [30], while Pd was suggested to be involved in the oxide formation as well [35]. However, despite of possible effects of the TMs, the experimental results indicate
that the local structure of the oxide layers grown on the quasicrystals is related
to the common phases of Al₂O₃ [30, 31, 35, 44]. The main difference is the self-
size-selected and the self-assembled nature of the oxide layers, phenomena usually
encountered in quasicrystal–crystal junctions (see, e.g., Refs. [45, 46]). Likewise,
the growth kinetics was found to be similar to the oxidation process of Al single
crystal and Al-based binary alloys [32]: at low temperatures, Al-deficient, self-size-
limiting, amorphous oxide layers grow, while at high-temperatures, the oxide layers
transform via a chemisorbed precursor state into a well-ordered Al-oxide film of
continuous growth. These layers become thicker and strongly passivating with in-
creasing temperature. However, Popović et al. [32] have found that the reactivity of
i-AlPdMn quasicrystal is even higher than that of the atomically densest surface of
Al single crystal, the (1 1 1) surface. This is surprising since the outermost layer of
the quasicrystal was not only found to consist primarily of Al but also to have a simi-
lar lateral atomic density than the Al(1 1 1) surface [47]. Further, the diffusivity
of Al in the quasicrystalline matrix is much lower than in its elemental crystalline
form [48, 49]. It is therefore likely that the oxidation of the quasicrystals results in
new surface phenomena, which may be related, in particular, to the quasiperiodic
atomic ordering.

The d-AlCoNi quasicrystal has an average structure, which can be identified
with some high-symmetry features in the CsCl structure of the ordered NiAl alloy
and the i-AlPdMn with the AlPd alloy, respectively [45, 46, 50]. In particular, the
10f-symmetry surface of d-AlCoNi and the pentagonal surface of i-AlPdMn have
great similarities with the (1 1 0) surface of their corresponding crystalline binary
alloys. This gives confidence to compare the structure of the oxide layers grown on
the quasicrystal surfaces with that on NiAl(1 1 0), a crystal surface, which has been
chosen as a model for the selective oxidation of intermetallic binary Al alloys. The
surface unit cell of the oxidized NiAl(1 1 0) was identified with a twinned domain
structure (Fig. 3.1a) in accordance with the twofold (2f) rotational symmetry of
the NiAl substrate [7, 10, 24, 27]. The basic structural elements are two oxygen
domains A and B each possessing a (slightly distorted) hexagonal lattice with the
(1 1 1) surface parallel to the NiAl(1 1 0) substrate and an interatomic distance
of approximately 3 Å. The domains are either oriented along the [1 1 1] direction
(\(A\)) or the [1 1 1] direction (\(B\)) of the NiAl(1 1 0) plane resulting in a twinning
angle of approximately 48°. The crystal structure is comparable to the known bulk
phase of γ-Al₂O₃ but since the surface layer is extremely thin, no exact 2-to-3
stoichiometry has been found [20, 24]. In an attempt to account for the low-energy
electron diffraction (LEED) observations from the oxidized pentagonal surface of
i-AlPdMn quasicrystal, a slightly modified\(^1\) version of this oxide structure was
adopted [35,44]. However, the presence of multiple domains and the rather involved
LEED patterns have complicated the structure determination considerably. Later,
evidence was gained that the twinned domain structure remains a speculation and
its structure was redefined to an antiphase domain ordering (Chapter 3). This
idea is supported by the fact that the domains, which grow on the quasicrystalline
substrate, usually remain in the nanometer size, thus, being considerably smaller

\(^1\) A twinning angle of 46.5° was suggested instead of 48° for the NiAl system.
that the coherence zone of the LEED system. Consequently, a great amount of antiphase domain wall contributions are expected to be disclosed in the LEED experiment. Scanning tunneling microscopy and spot-profile analysis (SPA)-LEED investigations of the oxidized NiAl(1 1 0) surface have revealed twin-domain and antiphase-domain boundaries as the main defects on the oxide surface [10, 51].

Oxide surfaces that serve as templates for the assembling of ordered metal particles have attracted much interest due to their prospects in industrial applications [1]. In particular, surface structures with uniform, well-defined size and shape and a high spatial density have raised considerable attention as it may find application in future ultra-high density recordings [52] and nanocatalysis [53]. A great variety of adsorbate has been deposited onto oxide thin films, a selection is shown in Table 1.1. The grown layers differ in their epitaxial growth conditions but they all have in common that the adsorbate grows in nanometer-size clusters on the oxide surface. Further, the formation of the interface is predominantly dominated by the oxide surface morphology [63, 64]: in the early stage, the adatoms move along preferred

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Support</th>
<th>Epitaxy</th>
<th>Growth mode</th>
</tr>
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<tbody>
<tr>
<td>Ag [54]</td>
<td>Al₂O₃(01(\bar{1})2)</td>
<td>fcc((1\bar{1}0))[(1\bar{1}0]) (R \approx 57.75^\circ )</td>
<td></td>
</tr>
<tr>
<td>Au [55]</td>
<td>(\theta)-Al₂O₃/ NiAl(100)</td>
<td>fcc(001)[(1\bar{1}0])</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\gamma)-Al₂O₃/ NiAl(110)</td>
<td>fcc(001)[(1\bar{1}0)]</td>
<td></td>
</tr>
<tr>
<td>Al [56]</td>
<td>Al-oxide/ 5f-(\text{AlPdMn})</td>
<td>random fcc(111)</td>
<td>clusters (D ≈ 3 nm)</td>
</tr>
<tr>
<td>CdTe [57]</td>
<td>Al-oxide/ 5f-(\text{AlPdMn})</td>
<td>random fcc(111)</td>
<td>clusters (D ≈ 3.5 nm)</td>
</tr>
<tr>
<td>PdTe</td>
<td>random fcc(001)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co [58, 59]</td>
<td>(\theta)-Al₂O₃/ NiAl(100)</td>
<td>fcc(001)[(1\bar{1}0)]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al₂O₃(100)[010]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu [60]</td>
<td>(\alpha)-Al₂O₃(0001)</td>
<td>fcc(111)[(1\times1)]Al₂O₃(0001)</td>
<td>Stranski-Krastanov</td>
</tr>
<tr>
<td>Pd [61]</td>
<td>(\alpha)-Al₂O₃(11(\bar{2})0)</td>
<td>fcc(111)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fcc[112]</td>
<td></td>
<td>Al₂O₃[0001]</td>
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<tr>
<td></td>
<td>fcc[110]</td>
<td></td>
<td>Al₂O₃[1100]</td>
</tr>
<tr>
<td>W [62]</td>
<td>Al₂O₃(11(\bar{2})0)</td>
<td>bcc(110)</td>
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<tr>
<td></td>
<td>bcc[111]</td>
<td></td>
<td>Al₂O₃[0001]</td>
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<tr>
<td></td>
<td>bcc[112]</td>
<td></td>
<td>Al₂O₃[1100]</td>
</tr>
</tbody>
</table>

Table 1.1: Selection of adsorbates deposited onto various Al-oxide surfaces. In contrast to crystalline substrate, the adsorbates on the oxidized quasicrystals exhibit predominantly a random in-plane orientation. The deposition of Al onto the oxidized pentagonal surface of \(i\)-\(\text{AlPdMn}\) is discussed in detail in Section 6.
binding sites on the substrate surface leading to an unusual nucleation behavior for the metal clusters. For instance, the metal deposition onto $\theta$-Al$_2$O$_3$/CoAl(1 0 0) was found to be strongly influenced by the characteristic streak structure of the oxide layer, which contains protrusions propagating along the [1 0 0] or the [0 1 0] directions [65]. Consequently, elongated lines of clusters are formed along the main crystallographic directions of the CoAl alloy. In general, knowledge about the structural properties of the oxide layer including chemical composition and surface morphology are instrumental for the understanding and controlling the conditions under which a peculiar and stable interface forms.

The growth of thin metal films on oxide surfaces is divided into the following steps [1, 18, 66]: (i) adsorption–desorption, (ii) diffusion–migration, and (iii) nucleation–growth. (i) An incoming metal atom, usually by vapor deposition, has to become thermodynamically accommodated to the surface. The atoms, which arrive at the surface, may reside on the oxide for a certain time. Due to re-evaporation, i.e., desorption, a net sticking coefficient smaller than one is obtained. (ii) Once adsorbed, the atoms move across the surface depending on their diffusion coefficient, i.e., depending on the diffusion activation energy. The surface mobility is the most important kinetic process in film growth and it influences to a great extent whether the film growth is smooth in a layer-by-layer fashion or rough in a three-dimensional cluster growth. (iii) Subsequently, the adatoms form a stable nuclei by aggregation and then grow into islands of the condensed phase. Two limiting cases can be distinguished: heterogeneous and homogenous nucleation. The former is dominated by the defect structure of the surface, the latter is dependent on the diffusion coefficient of the adsorbate on the surface and the vapor flux. As the nucleation continues, the average distance which adatoms need to travel to get accommodated decreases and eventually becomes constant. At this stage, the saturation density of the nucleation sites is reached and the stage of island growth begins. Upon further metal deposition, the coalescence of islands can be observed which in time results in a continuous film growth.

If the particles are provided that at least one dimension is small enough that quantum-mechanical effects prevail, their physical and electronic properties can exhibit novel properties such as charge and energy quantization. However, structures in the nanometric scale give rise to a basic prerequisite [67]: at this scale, the ratio of surface-to-volume atoms is strongly enhanced leading to a domination of the surface over the bulk properties of the nanoparticles. Thus, understanding and controlling surface and interface play a crucial role, in particular, by developing new model structures in the nanometer regime. Systems with a spatial resolution where significant quantization effects appear can be obtained with self-organized techniques: in atomic-beam epitaxy, the lattice mismatch between the substrate and the adsorbate dictates the growth mode of the surface film [68]. In this perspective, owning to the fundamental structural difference in crystal–quasicrystal interfaces, the epitaxial growth of crystalline matter on quasicrystalline substrate results in self-size-selected clusters with a lateral dimension of typically 2–4 nm [45, 46]. Recently, a novel approach for the fabrication of nanometric metal particles has been found in the case of metal deposition onto oxidized quasicrystals [35, 44]. The natural limit of the lateral domain size in the order of a few nm promotes the Al-oxide
domains to attractive templates for nanometer-scale epitaxy without restoring to self-size-selected processes.

In this dissertation, the formation of well-ordered Al-oxide layers is discussed as a result of high-temperature oxygen exposure on \(i\)- and \(d\)-quasicrystals. In a subsequent experiment, the oxide layer grown on the pentagonal surface of \(i\)-AlPdMn quasicrystal was used as a template for the growth of Al overlayers. It was found that the nature of the oxide and the Al crystallites evolve according to the properties of the quasicrystalline atomic ordering. The results can be interpreted in terms of a domain structure, which remains in the nanometer size and, in the case of the oxide layers, locally commensurate with the symmetry of the quasicrystals. The structure of the thesis is as follows: first, details of the experimental methods used in this study are provided in Chapter 2. In Chapter 3, the results for the oxidized pentagonal surface of \(i\)-AlPdMn quasicrystal are presented, in Chapter 4 for the threefold (3f)-symmetry surface of \(i\)-AlPdMn, and in Chapter 5 for the 10f-symmetry surface of \(d\)-AlCoNi. The deposition of Al thin films onto the oxidized pentagonal surface of \(i\)-AlPdMn is discussed in Chapter 6. Finally, Chapter 7 summarizes and concludes the results and ends with a short outlook.
Chapter 2

Experimental setup

A single-grain \(i\)-AlPdMn (\(d\)-AlCoNi) quasicrystal with a nominal bulk composition of \(\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}\) (\(\text{Al}_{72.9}\text{Co}_{16.7}\text{Ni}_{10.4}\)) was polished using diamond pastes with grain sizes down to 0.1 \(\mu\)m, mounted on a goniometer, and introduced into an ultrahigh-vacuum (UHV) chamber with a base pressure in the \(10^{-10}\)-mbar region. In order to obtain a clean surface for the experiment, the sample was prepared in UHV by cycles of \(\text{Ar}^+\)-ion sputtering (2 keV, 0.5 \(\mu\)A/mm\(^2\)) at 670 K (770 K) and annealing at 740 K (890 K) for 60 min to restore the quasicrystalline surface order. The sample was heated from the backside using a resistance heater and the temperature was measured with a chromel–alumel (K-type) thermocouple pressed onto the sample surface. This sample preparation is expected to lead to a bulk-terminated quasicrystalline surface exhibiting a terrace-step configuration, based upon real- and reciprocal-space observations [69–71]. The procedure was monitored by the quality of the LEED pattern and the AES signal. For the experiment, the sample could be cooled down to room temperature (RT) using a Cu cooling feed, which was brought in contact with liquid \(\text{N}_2\).

During the oxidation process, oxygen of 99.998+% purity is introduced into the UHV chamber and the quasicrystal surface was then exposed to typically several hundred Langmuirs\(^1\) \((\text{L})\) \(\text{O}_2\) at 700–800 K (940–970 K) to grow well-ordered oxide layers. The oxygen take up and the reaction of oxygen with the surface was confirmed by AES. The AES technique utilizes the emission of an outer shell electron and is based on the Auger effect [72–74]. A core hole is filled by an electron from the same or higher energy level of the atom whereby the transition energy can be carried away by a so-called Auger electron. The transition energy is characteristic of the energy levels of the ejecting atom, thus, AES is suited to investigate the chemical composition in the near-surface region. Representative AES spectra of the clean and oxygen-adsorbed pentagonal surface of \(i\)-AlPdMn quasicrystal are shown in Fig. 2.1. From the spectra, it is evident that predominantly Al atoms bind to oxygen, although, in principle, the thermodynamic data based upon the values of heats of formation (Chapter 1) suggest that the oxide formation possibly involves all of the quasicrystalline alloy constituents. The evolution of the AES spectra of Al, Pd, Mn, Co, Ni, and O was observed as a function of time during the oxidation process in order to draw conclusions about the oxide growth kinetics.

\(^1\)1 \(\text{L} = 1.3 \times 10^{-6}\) mbar-s.
2. Experimental setup

Fig. 2.1: AES spectra of the clean and oxidized pentagonal surface of $i$-AlPdMn quasicrystal. (a) An overview spectrum is shown, while (b–d) are the enlarged regions of the AES transitions of the AlPdMn alloy. Similar to the formation of the oxide layers on Al-based ordered binary alloys, only Al binds to oxygen. Analogous information can be obtained by the oxidation of $d$-AlCoNi quasicrystal.

In a subsequent experiment, oxide-supported Al nanoclusters were grown by molecular-beam epitaxy (MBE) using a power-regulated atomic-beam source while the sample was held at RT. The as-deposited films were post-annealed at several temperatures up to 500 K for 30 min in order to enhance surface diffusion of the adsorbate atoms. The deposition rate of $0.90 \pm 0.05$ Å/min was calibrated in a separate experiment by evaporating Al onto a polycrystalline Cu and monitoring the $L_3MM$ Auger signal of Cu during deposition. For the inelastic mean free path of these electrons in Al, at the relevant energy of 920 eV, 18.4 Å was taken in accordance with the model of Tanuma et al. [75]. During the deposition, the pressure never exceeded $2 \times 10^{-9}$ mbar.

The surface atomic order was investigated using secondary-electron imaging (SEI) and LEED. SEI probes the local atomic arrangement in real-space revealing the symmetry as a central projection [76]. In contrast, LEED examines long-range properties in reciprocal-space and shows information on the size and symmetry of the surface grains [77]. In LEED, low-energy electrons (30–300 eV) are elastically backscattered from the surface. Electrons in this energy range possess a wavelength comparable with typical interatomic distances of a few Å and a minimal penetration depth of a few atomic layers. Thus, LEED is a surface sensitive technique. The diffracted beams form a pattern, which is the source for the experimental
interpretation. In SEI, primary electrons with an energy of about 2 keV excite secondary electrons at localized atomic positions. These electrons are scattered at the Coulomb potentials of the neighboring atoms. Consequently, the secondary electrons are focused in the forward-scattering direction and predominantly channelled along densely packed atomic rows. Another characteristics of SEI are the so-called Kikuchi bands, which originate from Bragg diffraction at parallel planes of high atomic density [76,78]. Both techniques were carried out with the same back-view, three-grid display system with a total opening angle of about 45° (50°) from normal incidence.

The patterns were recorded using a 16-bit charge-coupled device camera and subsequently normalized by the overall response function of the display system in order to eliminate spurious signals. This technique is known as flat-field correction and is used to improve the contrast in digital images [79]. Uneven illumination, impurities on the lens or, in the case of LEED, on the grid-system, and variations in the pixel-to-pixel sensitivity can result in a poor image quality. The convectional method for this process is

\[ I_C = \frac{I_R - I_D}{I_F - I_D} \cdot M, \]

where \( I_C \) is the intensity of the corrected image, \( I_R \) of the raw image, \( I_D \) of the dark-frame image, and \( I_F \) of the flat-field image, respectively. \( M \) is the mean pixel value of \( I_F \). Thus, this method requires recording an additional (flat-field) image from an area where no structural information is delivered and a dark-field image, which is usually automatically taken by the digital camera. After applying the flat-fielding correction, the signal in each pixel is normalized by its individual response factor with respect to the average signal gain, creating a uniform signal output. Any further signal will be due to the structure being detected and not due to systematic errors.
Chapter 3

Oxidation of the 5f-symmetry surface of icosahedral AlPdMn

The investigation of the oxidation process of the pentagonal surface of \( i \)-AlPdMn quasicrystal started a series of work, which lasts until now, dealing with a new kind of crystal–quasicrystal interface: the oxidized surfaces of quasicrystals. Whereas earlier work [30–34] primarily dealt with the oxide growth kinetics, our work emphasizes the understanding of the structural properties based on LEED.

The oxide layer grown on the pentagonal surface was initially described to consist of twin domains rotated by multiples of \( 2\pi/5 \) with respect to each other in accordance with the rotational symmetry of the quasicrystal each of which having one 2f-symmetry direction of the substrate as a mirror plane (Fig. 3.1a) [35,44]. Later [80], evidence was gained that the twin structure, which was adopted from the oxide model for NiAl [27], is based on speculations, since, unlike NiAl(1 1 0), the pentagonal surface of \( i \)-AlPdMn is not 2f- but 5f-symmetric and the twin-domain model delivers considerably more diffraction spots with the composite pattern than detected in LEED (not shown). Furthermore, it was realized that the twin-domain separation of approximately 46.5° can also be constructed by a simple comparison of the quasicrystal and the hexagonal symmetry, as illustrated in Fig. 3.1b.

![Fig. 3.1: (a) Initially proposed twin-domain model for one single domain of the oxide layer grown on the pentagonal surface of \( i \)-AlPdMn [35,44]. The unit cell is represented by the lattice parameters \( a_1 \), \( a_2 \), and \( \alpha \). In this model, the twin domains are separated by 46.5°, which is close to (b) multiples of 72–60° obtained by a comparison of the quasicrystal and the hexagonal symmetry.](image-url)
The reinvestigation of the structural properties revealed the growth of different oxide structures depending on the sample temperature and its pretreatment: at RT, an amorphous oxide layer forms. In contrast, five distinct and few-nanometer-large domains possessing a hexagonal structure and an antiphase domain ordering grow at 700–800 K for small and large coverage. In an intermediate range, a mixture of antiphase domain-boundary contributions and fractional-order spots, characteristic to a $2\sqrt{3}(1 \times 1)R \pm 30^\circ$ reconstruction of the surface oxide layer, is found which additionally stabilized the interface. The previously reported twin-domain model, which was derived after ion bombardment of the preoxidized surface with subsequent reoxidation (cf. Fig. 1c of Ref. [35]), is identified as an oxide layer grown on the $(1 1 0)$ surface of a crystalline Al$_{50}$(PdMn)$_{50}$ alloy as a result of the sputtering.

### 3.1 LEED from the oxidized surface

Fig. 3.2a shows a LEED pattern from the clean pentagonal surface of $i$-AlPdMn quasicrystal. The 5f rotational symmetry with fairly well-defined spot-profiles is clearly visible. The pentagonal surface contains five 2f-symmetry axes, one of which is indicated in the pattern. These axes are determined in a straightforward way by comparing the LEED pattern with the SEI pattern recorded with the same sample geometry, since the latter gives real-space information [76]. In Table 3.1, some experimentally determined components of the scattering vectors parallel to the pentagonal surface $k_\parallel$ and the real-space values corresponding to $|k_\parallel|$ are listed. Within an experimental uncertainty of $\pm 0.05 \text{ Å}$, the real-space values agree well with those reported in the literature (see, e.g., Refs. [45, 46, 69]), thus, confirm the bulk termination of the $i$-quasicrystal.

Figs. 3.2b–d report patterns after different oxygen exposures. Several features can be recognized by visual inspection of the patterns: (i) oxygen adsorption at the surface produces thirty fairly strong spots that appear at a polar angle of $35.7 \pm 1^\circ$. (ii) The spots show polar, and to a larger extent, azimuthal smearing. (iii) Beside the thirty main diffraction spots, there are numerous minor spots with smaller intensity either distributed radially in concentric groups of $5n$, where $n$ is an integer, evenly over the screen (Fig. 3.2c) or (iv) located on rings accompanying the main diffractions spots, best observable in Fig. 3.2d. (v) The diffraction spots originating from the oxide structure gradually appear and become sharper as the surface is exposed to more oxygen while only the intense spots from the quasicrystalline substrate are discernible at every stage of oxidation (without any major change in


d| $(n_1n_2n_3n_4n_5)$ | $|k_\parallel|$ (Å$^{-1}$) | $a$ (Å) |
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>1</td>
<td>$(1 1 0 0 1)$</td>
<td>1.015</td>
</tr>
<tr>
<td>2</td>
<td>$(2 1 0 0 1)$</td>
<td>1.639</td>
</tr>
<tr>
<td>3</td>
<td>$(2 1 0 0 2)$</td>
<td>1.944</td>
</tr>
<tr>
<td>4</td>
<td>$(3 2 0 0 2)$</td>
<td>2.665</td>
</tr>
</tbody>
</table>

Table 3.1: LEED spots observed in Fig. 3.2a. The spots are identified with the indices $(n_1n_2n_3n_4n_5)$ using the basis vectors $e_i$, as depicted in the figure. The third column lists the values of $|k_\parallel|$, and in the fourth, the corresponding real-space distances $a$, respectively.
Fig. 3.2: LEED patterns at a primary-electron energy of 64 eV obtained from (a) the clean and (b–d) the exposed pentagonal surface of \( 7 \)-AlPdMn to 36, 126, and 144 L of oxygen at 740 K, respectively. One 2f-symmetry axis at the surface is indicated by a thin line and two arrows at the rim of the pattern. The encircled features and the enumerated spots are discussed in the text.

spot profile). It is noted that due to the intensity saturation of the electron detector intense spots seem to have a large angular spread. These observations apply to more-or-less all the oxidized surfaces shown in Figs. 3.2b–d. In the following, conclusions about the global and local structural properties of the oxide film and its interface with the quasicrystal are drawn.

The common characteristics of the patterns are thirty diffraction spots that already appear at the early stage of oxidation. This arrangement of spots has been encountered for epitaxial films that crystallize in sixfold-symmetric textures on the pentagonal surface of \( 7 \)-AlPdMn quasicrystal [71,81]. It represents a hexagonal domain structure that is repeated five times in equal azimuthal increments of \( 2\pi/5 \). In the present case, chemical analysis of the film confirms that only Al binds to oxygen, while Pd and Mn remain unaffected by the exposure [35]. The polar ra-
Oxidation of the 5f-symmetry surface of icosahedral AlPdMn

dius of $35.7 \pm 1^\circ$ corresponds to an interatomic distance of $d = 3.01 \pm 0.05 \text{ Å}$ in a hexagonal mesh and reflects the distance of oxygen atoms in the Al-oxide film, which is expanded by 4–5% relative to the $\text{Al}_2\text{O}_3$ bulk lattice constant [7]. The spots show an angular (polar) distribution, which is compatible with a domain size of $30 \pm 5 \text{ Å}$ (see Appendix). From the pattern, it is evident that a well-defined orientational relationship between the surface film and the substrate exists, i.e., the diffraction spots due to the oxide layer are aligned with the 2f-symmetry axes of the pentagonal surface. In all the patterns shown in Fig. 3.2, the diffraction spots originating from the quasicrystal are distinctly observable indicating that the oxide film is relatively thin. In the earlier work [32,35], the thickness was estimated to be 5 Å similar to the oxide films grown on the ordered Al–TM alloys [7,10,20,51,82,83].

For the film at low oxygen exposure (Fig. 3.2b), the diffraction pattern due to the quasicrystalline surface is not modified signaling that the quasicrystalline structure is preserved at the interface (see also Section 5.2). Consequently, there is no intermediate layer between the quasicrystalline substrate and the crystalline oxide layer. However, this statement cannot be substantiated for the oxide films shown in Figs. 3.2c and 3.2d, as discussed in Section 3.3. There is also to mention that within our capabilities, one cannot draw any firm conclusion about the growth mode of the oxide layer. However, the fact that the faint spots are not discernible for thicker oxide layers implies that the diminishing intensity is due to the oxide layer thickness (layer-by-layer growth, exponential decay) rather than a change in area, which is not covered by the oxide (island growth, linear decay), therefore, suggesting the growth of a closed oxide layer [84].

The pattern shown in Fig. 3.2b mainly consists of a 5f repetition of a hexagonal oxygen lattice. Such a diffraction characteristics is also found in Fig. 3.2d, which shows a pattern from a surface with a thicker oxide layer. Additionally, a diffraction feature accompanies the main hexagonal spots which is similar to the satellite spots encountered in antiphase domain-boundary structured surface films [85–87]. The pattern shown in Fig. 3.2c, on the other hand, displays additional minor spots evenly distributed over the screen signaling a surface reconstruction of the hexagonal domains. It is noted that some diffraction patterns show an uneven distribution of intensity in the main and/or the satellite spots, signaling a preferential occupation of the five otherwise equally probable domain orientations.

### 3.2 Antiphase domain boundaries

The patterns shown in Figs. 3.2b and 3.2d have in common that the main diffraction feature can be assigned to a 5f repetition of a hexagonal mesh with some satellite spots arising from antiphase domain boundaries. The thirty main spots correspond to five hexagonal meshes, each placed in equal azimuthal increments of $2\pi/5$ with respect to the others, with an interatomic distance of approximately 3 Å.

In order to account for the satellite spots, a real-space model is presented in Fig. 3.3a. The idealized alignment of the domains on the surface gives rise to additional hexagonal diffraction spots oriented along the [1 1] direction with respect to the main diffraction spots. For the formation of the nanometer-size domains, there
3.2 Antiphase domain boundaries

Fig. 3.3: (a) A real-space arrangement of four oxide domains, and (b) its reciprocal-space image. (c) The same inverted image superposed 5 times in equal azimuthal increments of $2\pi/5$ in order to mimic the experimental pattern shown in (d). The main spots drawn bold correspond to the hexagonal structure within the domains. The spots due to the quasicrystalline substrate are indicated as crosses.

are 5 degrees of freedom for the rotational alignment on the pentagonal surface of the $i$-quasicrystal. Consequently, 5 groups of domains are required on the surface with equal probability, each rotated by multiples of $2\pi/5$ with respect to the others. Hence, the observed diffraction pattern is reproduced by adding the contributions of the single domain characteristics, as shown in Fig. 3.3b, to a composite, intensity inverted diffraction pattern, as illustrated in Fig. 3.3c.

The as-generated pattern reproduces satisfactorily the spots of the experimental diffraction pattern shown in Fig. 3.3d. The antiphase components along the [1 1] direction of the hexagonal structure is close to $\frac{1}{9}$ of the reciprocal lattice vector. Thus, the real-space domain-boundary distances are approximately 28 Å, which can be well reproduced by the idealized arrangement of the domains.

This arrangement of the domains is the simplest interpretation of the LEED patterns. Most likely, there are further antiphase domain-boundary contributions delivered indicated by the bright centers of the patterns. A more complex ordering is observed by the oxidation of the 10f-symmetry surface of $d$-AlCoNi quasicrystal.
3. Oxidation of the 5f-symmetry surface of icosahedral AlPdMn

(Section 5.3). In the present case, the inferior quality of the patterns, which is most likely a consequence of the presence of a highly corrugated surface arising from an unfavorable oxide preparation condition, hampers any firm conclusion about the exact ordering of the hexagonal domains on the surface. Nevertheless, the patterns confirm the growth of an antiphase domain ordering.

3.3 Surface reconstruction

The initial stage of the surface oxidation presented in Fig. 3.2b shows faint diffraction features indicating the presence and the interaction of the domain walls, while most of the quasicrystal details remain discernible. On the surface shown in Fig. 3.2d, on the other hand, almost all of the minor quasicrystal spots are concealed and the features due to the antiphase domain boundaries dominate the pattern. A further oxide structure is shown in Fig. 3.2c. Its diffraction characteristics indicates a reconstruction of the surface layer but it is conceivable that the pattern shows simultaneously contributions from antiphase domain boundaries as well as contributions from a crystalline buffer layer, as discussed in Sections 3.2 and 3.4.

The spots arising from the reconstruction can be identified by the formation of thirty concentric spots of equal azimuthal increments and intensity. In contrast, the additional spots due to the antiphase domain boundaries show often an uneven distribution of intensity consisting of double pairs of spots of the same brightness being rotated in equal azimuthal increments with respect to each other, while the spots in between are fainter. This is comprehensible considering the averaging nature of the LEED experiment: while the intensity distribution of the antiphase domain diffraction characteristics sensitively depends on the orientation of the neighboring domains, that for the surface reconstruction does not. In order to reproduce the contribution due to the reconstruction, several different surface atom arrangements have been tried. Fig. 3.4a presents the most-likely atomic structure in reciprocal-space. The integer-order spots, drawn bold, originate from the hexagonal mesh of the surface oxide layer with the basis vectors $a^*$ and $b^*$. The basis vectors $a_{s}^*$ and $b_{s}^*$ of the surface unit mesh correspond to a $2\sqrt{3} (1 \times 1) R \pm 30^\circ$ reconstruction. In matrix notation, it can be expressed as $\frac{1}{5}\begin{pmatrix} 1 & -1 \\ 2 & 1 \end{pmatrix}$ in reciprocal-space. Since there are five distinct domains on the surface, each contributing equally to the observed pattern, five individual reconstructions are superimposed in order to mimic the diffraction pattern. The composite pattern is shown in Fig. 3.4b. For comparison, a LEED pattern from the oxidized pentagonal surface similar to that shown for 126 L of oxygen exposure is presented in Fig. 3.4c. A favorable comparison of the generated and recorded patterns is achieved by aligning a 2f-symmetry axis of the pentagonal surface with the direction $(a_{s}^* + b_{s}^*)$ of the surface reconstruction. The agreeable comparison allows the conclusion that this structure to be the most probable one. However, it is noted that it was not possible to reproduce all the diffraction spots observed in Fig. 3.4c. The diffraction characteristics from the reconstruction and the antiphase domain boundaries are illustrated with the black

1 The d-AlCoNi quasicrystal can be prepared and oxidized at much higher temperatures compared to the i-AlPdMn quasicrystal due to different melting temperatures, see, e.g. Ref. [71].
3.3 Surface reconstruction

Fig. 3.4: (a) A reciprocal-space representation of one single oxide domain. The main spots with the unit vectors $a^*$ and $b^*$ are drawn bold compared to the minor spots due to the reconstruction, indexed with $a_s^*$ and $b_s^*$. (b) Schematic pattern obtained by adding the signal from (a) 5 times in equal azimuthal increments of $2\pi/5$ to a composite pattern in order to mimic the observed diffraction pattern shown in (c). The superimposed pattern in (c) is discussed in the text. Some quasicrystal spots are highlighted with crosses.

dots as well as the small empty circles. There are some diffraction spots, one set is indicated by the black arrow, which are not covered by the surface structures so far. A further antiphase domain-boundary component, illustrated by the large empty circles, is suggested but the spots may also arise from the crystalline buffer layer, as discussed in the next section. Any firm conclusion is also obstructed regarding that the film thickness is in the same order of magnitude as the mean free path of the electrons used in LEED. Thus, multiple scattering effects involving the substrate are expected to contribute to the pattern and possibly are responsible for the features not accounted for by single scattering at the oxide layer.

Fig. 3.5a reports a hexagonal structure for the oxygen-terminated oxide layer in real-space with the unit vectors $a$ and $b$. Oxygen atoms form a domain as large as 30 Å in diameter with the interatomic distance of approximately 3 Å, as deduced from the LEED patterns. The superstructure is a hexagonal mesh, which is obtained by Fourier transforming the schematic pattern shown in Fig. 3.4a. It is evident that the surface reconstruction can be represented in real-space by the basis vectors $a_s$ and $b_s$ and the matrix $2\left(\begin{array}{c}1 \\ -1/2\end{array}\right)$, which is abbreviated as $(1 1 1) 2\sqrt{3} (1 \times 1) R \pm 30^\circ$. Each reconstructed surface unit cell has an area of $6\sqrt{3} d^2$, where $d$ represents the average interatomic distance and is thus twelve times larger than the unreconstructed cell of $\sqrt{3}/2d^2$ expected from the bulk-terminated $(1 1 1)$ surface and, therefore,
sufficiently large to produce its own diffraction pattern. This is the simplest model for the reconstruction where oxygen atoms are placed on a perfect hexagonal mesh and the resulting reconstructed cell is also hexagonal. More precise experimental findings with different methods will certainly refine this idealized model.

In an attempt to understand the formation of the large unit cell of the surface reconstruction, a comparison in real-space of the reconstructed oxygen layer with the atom distribution at the pentagonal surface of \( i \)-AlPdMn is shown in Fig. 3.5b. This procedure gives very good results in reciprocal-space \[88\] and is also shown to be promising for real-space data analysis \[81\]. The quasicrystal is represented by an Al-rich layer with some Mn atoms present \[89\]. In order to search for possible mechanisms that cause the reconstruction, an approximately 30 Å large domain is superimposed onto the quasicrystal surface. For clarity, the oxygen atoms other than those at the corners of the reconstructed cells are omitted. Additionally, some displacement of these corner atoms have been allowed. In Fig. 3.5b, it is evident that there is a considerable registry between the aperiodic and the crystalline structures over the entire domain. It is recalled that the LEED spots show a certain relaxation in the azimuthal direction. This relaxation provides an additional stabilization of the crystalline domains on the quasicrystal surface. A similar adsorbate constellation with azimuthal relaxation has been encountered for chemisorbed oxygen layers grown on the 10f-symmetry surface of \( d \)-AlCoNi \[36\].

The reconstructed surface unit cell is spanned by two basis vectors \( a_s \) and \( b_s \). Only the alignment of the atomic rows along \( (a_s + b_s) \), or perpendicular to \( b_s \), parallel to a 2f-symmetry direction of the substrate, as shown in Fig. 3.5b, results in a satisfactory registry with the substrate. This registry results by virtue of the overlap.

![Fig. 3.5: (a) One of the five surface oxide domains in real-space, which is about 30 Å large. The termination of oxygen atoms form a hexagonal mesh with the basis vectors \( a_s \) and \( b_s \), while the superstructure with the basis vectors \( a_s \) and \( b_s \) is twelve times larger. (b) The interface between the pentagonal surface of \( i \)-AlPdMn and oxygen atoms of an oxide layer. The quasicrystal surface is represented by computed coordinates \[89\] with Al (small) and Mn (large) atoms, while for the oxygen mesh only the superstructure atoms are drawn.](image-url)
of the reconstructed surface with the atomic positions of the quasicrystal surface, which it is taken as the driving force for this super-cell quasi-epitaxy. The exact registry of the Al-oxide islands on i-AlPdMn is observed in reciprocal-space, i.e., in the LEED patterns and, additionally, found in the real-space model considerations. Thus, for the alignments of the domains in a way shown both in reciprocal- and real-space, illustrated in Figs. 3.4 and 3.5, respectively, the mismatch between the crystalline and quasicrystalline lattice goes through an energy minimum. Consequently, the result is an interface, which has a high degree of structural registry and, together with the azimuthal degree of freedom by a few degrees, could explain the stabilization of the crystalline oxide islands at the quasicrystal surface without an intermediate layer.

3.4 Crystalline buffer layer

Al deficiency at the surface of the AlPdMn alloy was reported to shift the quasicrystalline equilibrium towards the CsCl structure [90]. The quasicrystalline ordering is restored as soon as Al is replenished by diffusion from the bulk to the surface as a result of heat treatment. In the present case, Al atoms bind to oxygen and will be absent in the alloy. This may similarly shift the alloy stoichiometry towards the binary alloy and destroy the quasicrystalline ordering. But, since the oxidation is performed at elevated temperatures, Al diffusion is effective in the bulk quasicrystal and an Al-oxide film forms without adversely modifying the quasicrystalline stoichiometry and structure of the surface. Hence, there is a balance between the diffusion of Al to the surface [81] and the rate of oxidation for a particular temperature and oxygen dose [17].

The formation of a buffer layer on the quasicrystal surface in the CsCl structure can still be induced by the conditions during oxidation, e.g., a lower sample temperature that hinders sufficient Al replenishment from the bulk. Alternatively, a buffer layer can be formed by Ar$^+$ ion bombardment that reduces the Al concentration in the alloy and shifts the structural stability towards the cubic crystal [45, 46]. While in the first case the buffer layer is expected to be extremely thin due to the shallowness of the oxide layer, the impact of the ion bombardment on the surface is rather drastic [91]. In an earlier attempt to characterize the oxide structure on the pentagonal surface [35], brief sputtering of the oxidized surface and subsequent high-temperature reoxidation was used to identify one single domain out of the five equally probable multiple domains on the surface. As communicated elsewhere [80], this oxide structure is almost identical with the oxide layers grown on binary Al–TM alloys [7, 10, 20–29, 51, 82, 83, 92]. Previous studies with thin Gd$_2$O$_3$ layers have shown that the range of impact of Ar$^+$ ions is in the order of magnitude larger than the Al-oxide layer thickness [91]. Therefore, it is not surprising that an oxide layer forms on the sputtered surface, which is characteristic to crystalline binary Al–TM oxides. The structure of these oxide layers can be summarized as a slightly distorted $6 \times 2\sqrt{3}$ reconstruction [35]. The twinning is caused by the fact that the 2f-symmetry axes of the quasicrystal coincide with a mirror plane of the buffer layer in the CsCl structure [90]. The reproduction of the LEED pat-
tern obtained from the Ar$^+$ ion bombarded surface using the twin model is very convincing (the reader is referred to Figs. 1c and 1d of Ref. [35]). Such patterns contain a characteristic feature in the form of pairs of double spots near the rim of the collector screen and outside the set of diffraction spots due to the hexagonal mesh. One pair is encircled in Fig. 3.2c and signals the presence of a buffer layer for this surface.

In summary, exposure of the pentagonal surface of the $i$-AlPdMn quasicrystal to oxygen at high-temperatures results in the growth of a thin, crystalline Al-oxide layer. With the aperiodic atomic order of the quasicrystalline template, the system finds the best compromise by breaking up into domains ordered in hexagonal structure whereas each domain remains locally commensurate and in registry with the substrate. This registry leads to five distinct orientations with respect to the substrate, while the small domain size is determined by the large interfacial strain energy. Beside this basic structural consideration, the registry of the Al-oxide islands with the aperiodic substrate structure is realized locally by the superstructure of the surface layer, i.e., the Al-oxide islands reconstructs in order to lower the interfacial strain energy. This case can be considered as a typical epitaxy-stabilized reconstruction. The reconstruction is not observed for low and high coverage. Instead, the electron diffraction patterns signal the interaction of the grain boundaries of the domains.
Chapter 4

Oxidation of the 3f-symmetry surface of icosahedral AlPdMn

Although, there has been an immense effort in the structural characterization of the pentagonal surface (see, e.g., Ref. [71]), little work is known to the present author about the 3f-symmetry surface. The aim of this chapter is to discuss the oxidation behavior of the 3f-symmetry surface of i-AlPdMn as a result of high-temperature exposure. By comparison with the available data on the pentagonal surface, as discussed in the previous chapter, further insight into the complex growth process, which leads to the formation of structurally well-ordered oxide layers on aperiodic substrate, is gained. The results obtained from LEED and AES are consistent with a faceted Al-oxide layer, while each facet is oriented along a high-symmetry direction of the i-bulk structure. Since the surface was initially planar, it can be deduced that the oxidation process favors the formation of the facets.

4.1 The 3f-symmetry surface of i-AlPdMn

The structure of AlPdMn quasicrystals can be identified with the (m35) point-group symmetry of the icosahedron [43]. Thus, it possesses three high-symmetry directions, as illustrated in Fig. 4.1a, which are perpendicular to the corresponding high-symmetry planes of the i-quasicrystal. The SEI pattern shown in Fig. 4.1b, obtained from the 3f-symmetry surface at a primary-electron energy of 2 keV and near-normal incidence, reveals the atomic arrangement in real-space as a central projection [76]. In the pattern, equilateral triangles whose corners are either at a polar angle of approximately 21°, corresponding to 2f-symmetry axes of the icosahedron, or at 37.5°, corresponding to 5f-symmetry axes [78], are recognized. These axes are identified and labeled accordingly. Further, the inner triangle shares its sides with pentagons. Thus, the observation is consistent with the local i-symmetry of the quasicrystalline surface revealing the local atomic arrangement of the 3f-symmetry surface with its high-symmetry axis in the center. The black arrows help identify one of the three 2f-symmetry axes lying in the 3f-symmetry plane, as described in Section 4.2. Note that there is a misalignment by approximately 2° between the surface normal of the sample and the display axis. A consensus has been reached that each high-symmetry surface of i-quasicrystals has different stability [93,94].
The most stable surface is found along the 5f-symmetry axis, while the other high-symmetry surfaces represent terminations of higher surface (free) energy [47, 95], therefore, are prone to reconstruct. Hence, depending on the sample preparation, faceting has been observed for the 2f- and 3f-symmetry surface [93–96].

Fig. 4.1: (a) Local symmetry of the i-AlPdMn quasicrystal represented by the icosahedron. The high-symmetry directions are indicated by arrows and labeled accordingly. (b) SEI pattern of the 3f-symmetry surface of i-AlPdMn.

### 4.2 LEED

Fig. 4.2a shows a LEED pattern of the clean 3f-symmetry surface of i-AlPdMn quasicrystal at a primary-electron energy of 40 eV. The 3f orientational symmetry is clearly visible. This high-symmetry surface contains three 2f-symmetry directions, as indicated in the pattern by the thin black lines. The azimuthal determination of these axes is straightforward by a comparison of the LEED pattern with the SEI pattern shown in Fig. 4.1b, which was obtained with the same sample geometry. One of them is indicated by the black arrows. The width of the LEED spots corresponds to a real-space dimension greater that 150 Å and its determination is limited by the transfer width of the LEED system. As discussed in the previous section, the 3f-symmetry surface of i-AlPdMn can exhibit a certain degree of faceting depending on the sample preparation. Some faint traces of a faceted structure are observed by increasing the primary-electron energy. However, by doing so, the majority of the LEED spots converge towards the (0 0) beam, thus, it is certain that the LEED pattern in Fig. 4.2a is consistent with the presence of a predominantly unreconstructed planar 3f-symmetry surface of i-AlPdMn.

In Figs. 4.2b–d LEED patterns are shown after exposure to several tens of L at 740 K. The following observations can now be made based on the LEED investigations: (i) after an exposure of 20 L, a new diffraction feature characteristic of three distinct segments of rings, which consist of individual spots, are visible. By tilting the sample in the polar direction (around the sample-holder axis), the rings are identified to consist of thirty spots. Additionally, three new (0 0) beams are observable. (ii) The segments are rotated azimuthally by $2\pi/3$ with respect to each other and are concentric about a symmetry axis, that is tilted away from the 3f-symmetry axis by a polar angle of approximately $37^\circ$. (iii) The thirty individual spots on the segments are elongated in the azimuthal direction with respect to the tilted symmetry axes. The alignment of the spots with the diffraction characteristics of the clean 3f-symmetry surface, as illustrated in Fig. 4.2c by the black circle, indicates a well-defined epitaxial relationship of the Al-oxide domains with the quasicrystal surface. (iv) The diffraction spots originating from the clean 3f-symmetry
surface of the quasicrystal become broadened at the early stage of oxidation and then progressively sharper and fainter as the surface is exposed to more oxygen. (v) After an exposure of 140 L, the LEED spots characteristic of the quasicrystal are not observable anymore.

From observations (i–iii) it can be inferred that a faceted surface structure has formed on the 3f-symmetry surface, while each facet is perpendicular to a 5f-symmetry direction of the i-bulk structure, as indicated by the white lines superimposed on Fig. 4.2d. The diffraction characteristics of one facet, the collection of thirty concentric spots, has also been observed in the patterns obtained from the oxide layers grown on the pentagonal surface of i-AlPdMn (cf. Fig. 3.2). They represent a hexagonal mesh repeated five times in equal azimuthal increments of

Fig. 4.2: LEED patterns obtained at a primary-electron energy of 40 eV from (a) the clean 3f-symmetry surface of i-AlPdMn and (b–d) from different stages of the oxide formation. A faceted well-ordered Al-oxide structure forms on the 3f-symmetry surface, each facet perpendicular to a 5f-symmetry direction of the i-bulk structure, as discussed in the text. The patterns are recorded after the exposure at 740 K to (b) 20, (c) 80, and (d) 140 L of oxygen.
2π/5 in accordance with the local and global rotational symmetry of the pentagonal surface. The polar-angle profiles of the diffraction spots suggest a lateral domain size of at least 100 Å. Apparently, there is no constraint on the domain size, a phenomenon, which results from the large interfacial strain usually encountered in quasicrystal–crystal junctions [35–37]. It is noted that for the oxide layer grown on the pentagonal surface of i-AlPdMn, the small lateral domain size leads to antiphase domain boundary contributions. Additionally, under certain conditions, the interfacial strain is lowered by the formation of a surface reconstruction (as discussed in Chapter 3), thus, producing several minor diffraction spots distributed over the LEED screen. None of the above mentioned contributions can be observed in the present case.

From observations (iv and v), it follows that after an initial increase in the domain size of the oxide structure an oxide layer covers the entire surface and becomes gradually thicker during the oxidation process. Eventually, the layer becomes sufficiently thick to obliterate the spots from the quasicrystal. In accordance with previous studies on oxidized quasicrystals [35–37], the quasicrystalline order at the interface is preserved. However, within our capabilities, no firm conclusion about the exact nature of the oxide layer can be drawn. Both, the formation of an amorphous oxide layer, which covers the entire surface and acts as a seed for the crystalline Al-oxide domains along the 5f-symmetry directions $^1$ as well as the formation of a pyramid-shaped crystalline Al-oxide layer that covers continuously the surface, are consistent with the LEED observations.

The above interpretation in terms of a pyramid-shaped surface structure, as illustrated in Fig. 4.2d, is the simplest approach to the observations. However, a close inspection of the LEED patterns from the oxidized surface reveals three additional bright spots, which gradually appear at a polar angle of approximately 42°, best observable in Fig. 4.2d. The spots do not move by varying the energy of the primary-electron beam. Since in LEED, diffraction angles are detected by twice the angle of the real-space structure, these spots are assigned to specularly reflected beams from the 2f-symmetry surfaces, as discussed in Section 4.5. Additionally, there is still some intensity left in the (0 0) beam specularly reflected by the 3f-symmetry surface. Consequently, it is observed that as a result of oxygen exposure the morphology of the 3f-symmetry surface changes from initially flat to a faceted shape, while each facet is perpendicular to a 2f-, a 3f-, or a 5f-symmetry direction. The oxide layers on these facets remain structureless except in the latter case.

### 4.3 AES

The growth kinetics of the oxide formed on the 3f-symmetry surface of i-AlPdMn quasicrystal was studied with AES. In agreement with earlier reports involving Al-based quasicrystals [30–32,35], only Al binds to oxygen, thus, the AES investigation was focused on the O KLL (504 eV), the Al LVV (68 eV), as well as the interatomic Al–O Auger transition around 54 eV. In addition, the Pd MNN (330 eV) Auger

$^1$This idea is based on the well-established growth kinetics on Al single crystal as well as ordered Al–TM alloys.
transition was monitored. In Fig. 4.3, the peak-to-peak heights of the derivative AES signals are plotted as a function of oxygen exposure. The (open and filled) circles represent the AES data and the (solid and dashed) lines are (linear, parabolic, or exponential) fits to the data.

Upon oxygen exposure, one can distinguish three different stages in the oxide formation, as shown in Fig. 4.3a: (i) up to an exposure of approximately 20 L, adsorption of elemental oxygen is observed. The O \( KLL \) Auger signal in this range increases linearly. (ii) Oxide formation is detected after 20 L exposure, which is indicated by the onset of the linear Auger signal for the \( \text{Al}(L_{2,3})\text{O}(L_{2,3})\text{O}(L_{2,3})' \) transition [56]. However, the exact point is difficult to determine, as discussed in Ref. [30]. (iii) For further exposures, a rapid parabolic increase in the O \( KLL \) as well as the interatomic Al–O Auger transition signals can be observed.

For comparison, the data for the 5f-symmetry surface is shown. Surprisingly, the 5f-symmetry surface exhibits a strikingly different initial oxidation behavior. Compared to the 3f-symmetry surface, the pentagonal surface exhibits a stronger linear increase in the O \( KLL \) Auger signal below 20 L exposure. Thus, the oxygen sticking coefficient on the 3f-symmetry surface, as indicated by the slope of the oxygen curve, is lower. Larson and Launderback [97] have shown that surface defects on Al(1 0 0) dramatically increase the rate of oxygen adsorption during formation of both the chemisorbed and the oxide phase. Similar effects have been reported by several groups in the past [17,19,98]. The above observation is therefore surprising since one rather expects an increase in oxygen uptake on the 3f-symmetry surface due to the rougher surface morphology.

Fig. 4.3: AES peak-to-peak heights of the derivative AES signal from (a) the interatomic Al–O Auger transition around 54 eV and the O \( KLL \) at 504 eV, as well as (b) the Pd \( MNN \) at 330 eV and the Al \( LVV \) at 68 eV. The data, fitted by the dashed lines, are obtained from the 5f-symmetry surface of Ref. [30] and are shown for comparison. The vertical dashed lines, labeled by (b–d), correspond to the LEED patterns shown in Fig. 4.2 and are guides for the eye.
As the oxidation proceeds, a general trend in Fig. 4.3a can be observed: while the AES signals obtained from the pentagonal surface are comparable to those reported in the literature, see, e.g., Refs. [17, 18], the data obtained from the 3f-symmetry surface yield an abrupt change in the trendline where a change from a linear to a rapid parabolic growth mode is observed. The linear and parabolic growth behavior is in good agreement with the two limiting forms of the growth model developed by Deal and Grove [99]. However, the kink in the curve cannot be explained thereby. The sudden increase in signal is interpreted with the enhancement of the surface area due to the faceting, as discussed in Section 4.6. It is noted that the oxide layer formed on the pentagonal surface is assumed to wet the surface domain-like, which is reasonably explained by the exponential attenuation of the substrate signal presented in Fig. 4.3b. In the case of the 3f-symmetry surface, the LEED and AES data indicate a wetting of the surface followed by the formation and growth of faceted island-like clusters. In the literature, this growth mode is referred to as Stranski-Krastanov and consequently the substrate signal, the Pd MNN signal, is expected to exhibit a slower attenuation in intensity due to the island formation [84]. This behavior is indeed observable in Fig. 4.3b. However, even though a layer-by-layer and a layer-by-island growth characteristics, as mentioned-above, would result in qualitatively different AES spectra, a clear distinction only on the basis of AES is difficult to make if the surface topology is more complex, as in the present case.

Furthermore, the rate at which the Pd MNN signal decreases is comparable for both surfaces, therefore, it can be concluded that the difference in the oxidation process solely involves Al atoms of the quasicrystalline alloy. A difference in fact arises form the Al LVV signal, as seen in Fig. 4.3b. While the pentagonal surface exhibits only a slow decrease of the Al LVV intensity, the signal is much stronger suppressed in the oxide layer grown on the 3f-symmetry surface. The stronger attenuation of the Al signal for larger exposures can be explained by the increased oxygen uptake on the 3f-symmetry surface compared to the pentagonal surface. On the contrary, the AES results of the initial stage of the oxidation process remain unexplained.

### 4.4 Oxygen-induced surface faceting

Due to the differences in stability of each high-symmetry surface, lateral atomic rearrangements have been observed on the 3f- and the 2f-symmetry surfaces, leading to surface faceting and to a rougher terrace fine structure compared to the pentagonal surface, the most stable high-symmetry termination of i-AlPdMn quasicrystal. In particular, faceting can be observed if the surface preparation deviates slightly from the optimum preparation condition required for the formation of an ideal quasicrystalline bulk truncation. Nevertheless, clean and well-prepared surfaces are usually not prone to faceting. For crystals, a low-index surface is associated with a low surface free energy $\gamma$. Since high-index surfaces have higher surface free energies, faceting is usually not energetically favored. However, the presence of adsorbates can lead to a large change and enhancement of the anisotropy in $\gamma$, especially in an environment, which interacts strongly with the substrate surface atoms (e.g., oxy-
4.5 The facet-structure

There are many systems displaying adsorbate-induced faceting, such as, e.g., the oxidation of the NiAl(1 1 1) surface, which results in a pyramid-shaped (1 1 0) surface structure [103], the pyramid-shaped oxygen-covered Ir(2 1 0) surface with {3 1 1} and (1 1 0) facets [100], but faceting is also observed in metal overlayers on ordered substrates, as Al deposition onto the pentagonal surface of $i$-AlPdMn quasicrystal [104]. It is to mention that faceting involves some mass rearrangement on the surface, therefore, this phenomenon usually occurs only at elevated temperatures for which surface diffusion is effective allowing to overcome all thermodynamic barriers for facet formation. Additionally, a slightly prefaceted clean surface, as the 3f-symmetry surface of $i$-AlPdMn, promotes the mass transport for faceting, therefore, is an ideal precursor for the formation of larger-scale Al-oxide facets along high-symmetry directions of the substrate.

Fig. 4.4: (a) Interpretation of the LEED patterns shown in Fig. 4.2 in terms of a rhombicosidodecahedral surface structure. The structure consists of 2f-, 3f-, as well as 5f-symmetry facets, some of which are highlighted in the figure. The dotted rings represent the diffraction characteristics from the oxidized 5f-symmetry surfaces. Each ring arises from three Al-oxide domains, each domain rotated by $2\pi/5$ with respect to each other, with a hexagonal atomic structure. One domain orientation is illustrated in the figure by the hexagon. The larger dots represent the specularly reflected (0 0) beams of the different facets. (b) Spatial illustration of the model shown in (a) highlighting the major symmetry planes around a 3f-symmetry axis.

4.5 The facet-structure

In order to reconcile the diffraction characteristics obtained from the oxidized 3f-symmetry surface of $i$-AlPdMn quasicrystal, it is helpful to resort to a schematic illustration of the faceted oxide layer represented by a rhombicosidodecahedron, as shown in Fig. 4.4a. The rhombicosidodecahedron is the simplest structure with $i$-symmetry that exposes all the three high-symmetry surfaces [105]. It is oriented
such that one 3f-symmetry axis is perpendicular to the substrate surface, coinciding with the plane of the figure. The proposed surface structure possesses facets in the vicinity of the surface normal inclined by an angle $20.9^\circ$ as well as $37.4^\circ$, which agree well with the angles formed between the surface normal of the quasicrystal and the off-axis (0 0) beams of the oxidized surface observed by LEED. Thus, the oxidized surface can therefore be unambiguously identified to consist of facets along the high-symmetry directions of the $i$-bulk structure. A perspective view is shown in Fig. 4.4b. The resulting LEED patterns are then a superposition of the diffraction characteristics arising from each facet, as illustrated in Fig. 4.4a. While the diffraction patterns from the facets along the 5f-symmetry directions show the same epitaxy and oxygen sublattice as the oxide layers grown on the pentagonal surface [35], the facets formed along the other high-symmetry directions are structureless.

Analogous information can be obtained by the oxidation of the 2f-symmetry surface of $i$-AlPdMn quasicrystal, as shown in Fig. 4.5. The surface of the sample is oriented along an axis, which is fairly tilted away from the 2f-symmetry direction of the bulk. Not surprisingly, one can observe already some degree of an unidentified surface reconstruction and faceting on the clean quasicrystal surface. Nevertheless, the 2f-symmetry is clearly detectable. Upon high-temperature oxidation, the pattern shows the same tendency as the 3f-symmetry surface: while structurally well-defined Al-oxide layers grow in a quasi-epitaxial manner on the facets along the 5f-symmetry directions (as illustrated by the black circle), no structural contribution to the pattern can be resolved from the facets along the other high-symmetry directions. The LEED pattern shown in Fig. 4.5b is consistent with a rhombicosidodecahedronal surface structure. However, the presence of several new (0 0) beams around the 2f- and 3f-symmetry axes indicates on an additional faceting of the structureless 2f- and 3f-symmetry facets. Unfortunately, the inferior quality of the pattern hampers any firm conclusion about the effective surface structure.

![Fig. 4.5: LEED patterns obtained at $E_p = 50$ eV from the 2f-symmetry surface of $i$-AlPdMn (a) clean and (b) after oxygen exposure to 140 L at 740 K. Similar to the 3f-symmetry surface, a faceted Al-oxide structure forms.](image)

### 4.6 Kinetics

The growth kinetics of the oxide layers formed on the Al-rich quasicrystals have been found to show great similarities with the oxidation behavior of Al single crystals [30, 32]. This gives us confidence to compare the oxidation behavior of the 3f-symmetry surface of $i$-AlPdMn with that of the Al surfaces. Depending on the
4.6 Kinetics

crystal orientation, the first step in the oxide formation on Al involves the molecular adsorption of oxygen [18,106]. Then, a continuous Al-rich amorphous oxide growth develops, which is controlled by the outward-diffusion of Al cations towards the interface. Lüscher et al. [49] have demonstrated that the diffusivity of Al in i-AlPdMn quasicrystal is enhanced along the 5f-symmetry direction compared to the 3f-symmetry direction. This difference in Al segregation is likely to favor the formation of a faceted oxide layer. The driving force of energy minimization then favors the growth of facets along the high-symmetry directions of the quasicrystal. Further oxygen exposure crystallizes the oxide layer along the 5f-symmetry directions.

It has been found [18,106] that the crystallization is not attained through outward ion transport in the substrate but is due to the inward-diffusion of oxygen ions to the interface. This mechanism of crystallization is critically influenced by the rate of oxygen supply. In Fig. 4.3a, the oxygen uptake and the oxidation rate are shown as a function of the exposure. Both AES signals, for the interatomic Al–O as well as for the O KLL transition from the 3f-symmetry surface, are characterized by an initial linear growth rate followed by a rapid parabolic increase in signal for further exposures. The initial linear increase can be interpreted as an incubation time for the formation of the surface facets. The subsequent rapid increase in signal is in accordance with the oxygen-induced faceting of the Al(1 1 1) surface, as reported by Testoni et al. [98]. In this case, the presence of steps on the faceted surface structure was found to increase the sticking probability for oxygen, thus, significantly promotes the oxygen uptake on the Al surface. Since the facets along the 5f-symmetry directions are the strongest inclined compared to the planar 3f-symmetry facets or the less inclined 2f-symmetry facets, it is suggested that the facets along the 5f-symmetry directions exhibit the largest number of atomic steps and defects. Consequently, oxygen uptake and incorporation into the crystalline Al-oxide matrix is likely to be enhanced along the 5f-symmetry directions of the i-bulk structure, forming a “hill-and-valley” surface morphology, as illustrated in Fig. 4.4b. A similar result was obtained in the case of Al deposition onto the pentagonal surface of i-AlPdMn quasicrystal by Bolliger et al. [104]. The Al films consisted of facets related to fcc crystallites, each oriented with the [1 1 1] direction along the 3f-symmetry direction of the quasicrystal. In the latter case, the epitaxial relationship can be explained by the close structural affinity between the fcc(1 1 1) and the 3f-symmetry surface. However, in general, the crystal sym-
metry and the in-plane lattice constants fall short in the description of crystalline overlayers grown on quasicrystalline substrates. Both, the orientational symmetry of quasicrystals and the aperiodic ordering of the atoms are not compatible with periodicity; therefore, lattice coincidence is not possible. In the present case, the formation of well-ordered growth along the 5f-symmetry direction and the amorphous growth along the other high-symmetry directions can only be accounted for by the kinetics of the oxide growth.
Chapter 5

Oxidation of the 10f-symmetry surface of decagonal AlCoNi

The Al-rich quasicrystals were found to have a similar oxidation behavior compared to Al single crystals and ordered Al–TM alloys [30]. Experimental results have indicated that the local structure of the oxide layers grown on the quasicrystal surfaces is comparable to the common phases of Al$_2$O$_3$ [30,31]. Nevertheless, due to the extreme shallowness of the film and the uncertainty in structure determination usually encountered in quasicrystal–crystal interfaces, the detailed atomic ordering of these oxide layers has not been readily resolved and still presents a substantial challenge to surface science. As discussed in the previous chapters, the oxidation behavior of $i$-AlPdMn quasicrystal facilitates the interpretation of the oxide layer in terms of a hexagonal domain structure, which remains in the nanometer size and locally commensurate with the rotational symmetry of the quasicrystal.

In this chapter, the oxidation behavior of the 10f-symmetry surface of $d$-AlCoNi quasicrystal is presented. Initial observations revealed the elemental adsorption of oxygen, leading to a very thin layer of chemisorbed oxygen [36]. The recent LEED and AES results can be interpreted, similar to the $i$-AlPdMn quasicrystal, as a formation of a thin Al-oxide layer, consisting of domains in hexagonal structure whose global orientations are determined by the rotational symmetry of the quasicrystal. The domains preferentially nucleate on the surface in a way, which is strongly influenced by the topology of the $d$-surface ordering. A structure model based on antiphase domain boundaries is capable of reproducing the LEED patterns. With the results of this study, a new surface phenomenon is presented, which is related in particular to the quasiperiodic atomic ordering.

5.1 The clean decagonal surface of $d$-AlCoNi

Fig. 5.1a shows a LEED pattern of the clean 10f-symmetry surface of $d$-AlCoNi quasicrystal at a primary-electron energy of 55 eV. The structure of $d$-quasicrystals can be interpreted as a periodic stacking of quasiperiodic layers along a 10f-symmetry axis [71,107–111]. Depending on the chemical composition, eight different types of $d$-phases are known to exist, each varying in its structural details [71,108]. The composition of the $d$-AlCoNi quasicrystal used in this study falls in the region of
the Co-rich phase. Thus, its structure can be described by a four-layer periodicity (8 Å) along the $d$-axis [108]. Each layer has 5f-symmetry and is related to the others by a mirror-plane operation. The overall symmetry is $\overline{1}02m$, resulting in a 10f orientational symmetry in diffraction experiments which is clearly observable in Fig. 5.1a. The two sets of 2f-symmetry axes, which are needed to characterize the $d$-surface [71], are superimposed on the pattern. Using the notation according to Fung et al. [112], the [1 0 0 0 0] direction corresponds to the A2P axis and the [0 0 1 T 0] to the A2D axis, respectively. The indices correspond to the five basic vectors $e_i$, which are commonly invoked to describe the (reciprocal) lattice of $d$-AlCoNi (see, e.g., Ref. [109]). The last index refers to the [0 0 0 1] basis vector along the 10f-symmetry axis, while the first four correspond to the four basis vectors found in the quasiperiodic plane plotted at the bottom right-hand side of the pattern. In Table 5.1, a selection of LEED spots observed in Fig. 5.1a are listed as well as the corresponding indices, the experimentally determined components of the scattering vectors parallel to the surface $k_||$, and the real-space values corresponding to $|k_||$. Within an experimental uncertainty of ±0.05 Å, the real-space distances confirm the bulk termination of the $d$-quasicrystal [109, 110]. The length of the [1 0 0 0 0] basis vector agrees with 1.634 ± 0.063 Å$^{-1}$ found by Gierer et al. [109] and 1.668 Å$^{-1}$ found by Gille et al. [111]. The quality of the pattern confirms a well-established quasicrystalline order at the surface [56, 77] with an average terrace size of at least as large as the transfer width of the LEED system (≈150 Å) [113].

| #  | $(n_1n_2n_3n_4n_5)$ | $|k_||$ (Å$^{-1}$) | $a$ (Å) |
|----|---------------------|------------------|--------|
| 1  | (1 0 1 1 0)         | 1.001            | 6.275  |
| 2  | (1 0 0 0 0)         | 1.630            | 3.855  |
| 3  | (0 1 1 0 0)         | 2.011            | 3.124  |
| 4  | (0 0 1 1 0)         | 2.631            | 2.388  |

Table 5.1: Selection of LEED spots observed in Fig. 5.1a. The numbers in the first column agree with those inscribed in the pattern. In the second column, corresponding vectors $(n_1n_2n_3n_4n_5)$ are listed, and in the third and fourth, values of $|k_||$ and $a$, respectively.

### 5.2 High-temperature oxidation

The LEED pattern depicted in Fig. 5.1b is obtained after oxygen exposure to a partial pressure of $3 \times 10^{-8}$ mbar at 930 K for 120 min (≈162 L). The diffraction spots characteristic of the clean quasicrystalline surface are still well-visible at this stage of oxide formation. As the surface is more exposed, the LEED spots from the oxide structure gradually appear and reach their best definition at around 430 L (Fig. 5.1c), while the spots from the quasicrystalline substrate decrease in intensity at a constant spot-profile. Due to the intensity saturation of the electron detector, the LEED spots show a large angular spread for the clean surface, while they become misleadingly “sharper” as the surface is exposed to oxygen. Apparently, the oxidation process does not destroy the quasicrystalline order at the interface. For further exposures (Fig. 5.1d), the diffraction spots due to the quasicrystalline
substrate diminish and the intensity of the spots from the oxide structure lose intensity. From this observation, it is inferred that at this stage of the oxide formation an amorphous oxide layer covers the entire surface. Within the capabilities of this study, there is no evidence that the diffraction spots characteristic of the quasicrystal appear “domain-like”. Thus, one can concluded that the oxide layer, amorphous and crystalline, grows eventually continuously over the entire surface throughout the oxidation process observed here.

The striking feature of the pattern shown in Fig. 5.1b is thirty new diffraction spots (more clearly visible in Fig. 5.1c) located on a polar circle of approx-
Oxidation of the 10f-symmetry surface of decagonal AlCoNi

approximately 40.5° corresponding to a momentum transfer of $2.414 \pm 0.063 \ \text{Å}^{-1}$ and an interatomic distance of $3.01 \pm 0.07 \ \text{Å}$, respectively. This value is very close to 3.00 Å, the interatomic O–O distance in the oxide structure grown on $i$-AlPdMn quasicrystal [35] and NiAl single crystal [24]. In accordance with the local rotational symmetry of the quasicrystal, these spots can be assigned to a 5f repetition of a sixfold-symmetric pattern, each placed in equal azimuthal increments of $72° = (2\pi/5)$. The new diffraction spots are azimuthally locked to the quasicrystalline substrate, as illustrated by the two white arrows in Fig. 5.1b. In the pattern, one hexagon is highlighted and oriented in such a way that the [1 0] basis vector of the hexagonal reciprocal lattice is parallel to the [1 0 0 0 0] 2f-symmetry direction of the d-substrate. SPA of the diffracted beams suggests an average domain size of approximately 35 Å which is a result of the self-size-selecting growth at a quasicrystal–crystal interface [35, 36, 56, 113].

Beside the main hexagonal diffraction feature, additional spots placed on inner as well as on outer rings of constant polar angles are identified in the LEED pattern. The strong diffraction spots from the quasicrystalline sample are still observable. The additional spots are better identified in the pattern presented in Fig. 5.1c. This surface is oxidized using a higher dose of oxygen, while the other parameters are kept the same. An even higher dose, shown in Fig. 5.1d, renders a thicker oxide layer growth that covers the substrate surface effectively, while no spots from the quasicrystal are discernible. The additional diffractions spots are located either on rings of thirty spots being azimuthally aligned in registry with the substrate or on rings, which are aligned azimuthally away by 6° from this direction, as illustrated in Fig. 5.1c. Interestingly, the outer ring shows a distinct two-spot formation with a separation of approximately $3°$.

The interaction of oxygen with the alloy constituents has been monitored by AES. In Fig. 5.2, the spectra of the Al $L_{2,3}VV$ as well as the O $KLL$ Auger transition for the different stages in the oxide formation are shown. The labeling of the spectra corresponds to the LEED pattern in Fig. 5.1. While the Auger TM signals do

![Fig. 5.2: AES results of the clean and oxygen-adsorbed 10f-symmetry surface of d-AlCoNi quasicrystal for the different stages in the oxide formation.](image)
not indicate any change in energy and line shape after the exposure of the clean quasicrystalline substrate to oxygen (not shown), the Al $L_{\text{2,3}}VV$ peak shows all the expected interatomic Auger transitions that arise from the formation of Al–O bonds, as discussed in Section 6.1. This observation is similarly in agreement with the thermodynamic data as found by the oxidation of the pentagonal surface of $i$-AlPdMn [32,35,36,109] and $i$-AlCuFe [34] quasicrystals. Thus, it can be concluded that the features observed in the LEED patterns in Fig. 5.1 arise from an Al-oxide layer. The intensity ratio of the Al $L_{\text{2,3}}VV$ Auger transition grows in favor of the oxidized Al when the surface is gradually exposed to more oxygen. In parallel, the O $KLL$ Auger transition grows in signal, as shown in the inset.

### 5.3 The structure model

The main diffraction features of the LEED patterns shown in Fig. 5.1 can be assigned to a 5f repetition of a hexagonal domain structure, each placed in equal azimuthal increments of 72°. Further information about the interface can be obtained by the analysis of the inner and the outer diffraction rings. A structure model based on antiphase domain boundaries is capable of reproducing the LEED patterns similar to the oxide layers grown on the pentagonal surface of $i$-AlPdMn quasicrystal (Chapter 3). Contributions to the LEED patterns arising from antiphase domain boundaries are known by the existence of several subdomains of the same structure within an area, which is smaller than the coherence width of the LEED system [114]. The result is satellite spots around basic reflections in a direction determined by the domain boundaries.

In Fig. 5.3a, a section of a schematic LEED pattern originating from five (1 1 1) surfaces of a hexagonal structure consisting of antiphase domain components, as illustrated in Fig. 5.3c, is presented. The pattern shows the diffraction features from domains, which are rotated by 72° with respect to the neighboring domains and in accordance with the local rotational symmetry of the quasicrystal. The generated pattern is in good agreement with the experimental LEED pattern from the oxidized $d$-AlCoNi surface, shown in Fig. 5.3b. In Fig. 5.3d an enlargement of the dashed area of the single domain model, shown in Fig. 5.3c, is presented to highlight the details. Each domain contributes hexagonally arranged main spots to the diffraction pattern, indexed with the appropriate reciprocal lattice vectors, while the boundaries between two adjacent domains of the same orientation produce satellite spots in the direction perpendicular to the domain boundary lines, as illustrated in the figure. It is to mention that if the domain boundaries have an irregular shape, the additional diffraction spots will be streaky or enlarged.

In the pattern, three boundary contributions $a_1^*, a_2^*, a_3^*$ can be identified which fully orient the hexagonal antiphase domain components with respect to the main hexagonal diffraction spots. The $a_2^*$ and $a_3^*$ contributions are oriented along the [1 0] direction and the $a_1^*$ is along a direction tilted 30° away, corresponding to the [2 1] direction of the hexagonal structure. The reciprocal lattice distances are given in the inset in Å$^{-1}$. While the $a_2^*$ and $a_3^*$ vectors are parallel to the [1 0 0 0 0] direction of the quasicrystal, therefore, coincide with a 2f-symmetry direction of the
\(d\)-surface, the \(a_1^*\) is along a non-commensurate direction. However, the angle of 30° is given by the fact that the domain boundary walls of a hexagonal domain structure can be created either along the [1 0] or the [2 1] directions. The first one forms high-density atomic rows, the latter atomic rows of reduced density. The splitting of the [1 0] spot is \(|a_2^*| \approx 0.330 \pm 0.009 |a_0^*|\) and \(|a_3^*| \approx 0.531 \pm 0.014 |a_0^*|\), respectively, indicating that the domain-wall structure adopts a periodicity of approximately \(\frac{1}{3}\) and \(\frac{1}{2}\) of the reciprocal lattice vector of the oxygen hexagonal sublattice. The splitting of the [2 1] direction is \(|a_1^*| \approx 0.151 \pm 0.004 |a_0^*|\), therefore, approximately \(\frac{1}{7}\) of the reciprocal lattice vector. With this information, the real-space domain-boundary distances \(|a_i|\) can be calculated resulting in \(|a_1| = 19.80 \pm 0.20 \text{ Å}, |a_2| = 7.80 \pm 0.15 \text{ Å},\) and \(|a_3| = 4.90 \pm 0.15 \text{ Å}.\) The proposed model reproduces all of the observed details giving confidence to adopt this structure for the oxide layer.

Fig. 5.3: Schematic LEED pattern for the oxide layer on \(d\)-AlCoNi quasicrystal: (a) 5f repetition of the single domain model shown in (c), which can be compared with the experimental LEED pattern in (b). The contribution from the hexagonal domain structure is white. The “+” signs represent the contribution from the quasicrystalline substrate. The domain structure consists of hexagonal antiphase components along the [1 0] as well as the [2 1] direction, as illustrated in (d).
5.4 The interface

In Fig. 5.4, a $150 \times 150 \text{Å}^2$ large section of the interface model between the oxidized $d$-surface of $d$-AlCoNi quasicrystal and the Al-oxide layer with details deduced from the LEED investigation is shown. The coordinates for the atomic arrangement of the $d$-AlCoNi surface is based on the structure model proposed by Deloudi and Steurer [108]. It consists of a four-layer periodicity (8 Å) ordering along the $d$-axis. However, for simplicity, the surface shown in Fig. 5.4 does not make any distinction between the four surface layer terminations, i.e., it shows a superposition of all

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**Fig. 5.4**: A model for the interface between the 10f-symmetry surface of $d$-AlCoNi quasicrystal and the hexagonal structure of the Al-oxide layer. The atomic arrangement of the quasicrystalline substrate is represented by the circles, while the hexagonal structure of the oxide is drawn to scale by the lattice grids. The $150 \times 150 \text{Å}^2$ large section of the surface suggests the nucleation behavior of the Al-oxide domains on the quasicrystalline surface based on the LEED investigations and sets the length scales found in Fig. 5.1d in relevance with some distances of the $d$-surface, as discussed in the text. The size of the section was chosen in accordance with the coherence width of the LEED system.
the layers. The random pentagonal tiling, which is superimposed on the atomic arrangement, is commonly invoked to describe the Co-rich structure of $d$-AlCoNi and chosen such that the vertices coincide with the 10f-symmetry features of the surface [71, 107]. The as-constructed tiling possesses pentagons with an edge length of 19.79 Å [115]. The hexagonal lattice grids represent the Al-oxide and are drawn to scale with a lattice parameter of 3 Å and a diameter of approximately 35 Å, as extracted by LEED and SPA, respectively. The lattice parameter of 3 Å is closely related to the nearest neighbor Al–Al bond length of approximately 2.9 Å found in the $d$-AlCoNi quasicrystal structure [110].

In the figure, the real-space antiphase domain-boundary distances $|a_i|$, obtained from the reciprocal vectors shown in the inset of Fig. 5.3d, are listed. Eight domains are oriented along one of the five distinct high-symmetry directions of the quasicrystal, as discussed in Section 5.3, and are arranged on the surface that the centers of the domains are in the vicinity of high-symmetry sites of the $d$-substrate surface. The interface model is restricted on a schematic illustration, i.e., it only shows one preferential alignment of the Al-oxide domains with respect to the quasicrystalline substrate and only one of the (hexagonal) antiphase domain-boundary contribution. The black arrows indicate the crystallographic orientation of the domains, the black lines represent the relevant domain boundaries, and the white arrows the antiphase domain-boundary distances. In order to elucidate the preferential cluster nucleation behavior and the resulting domain-boundary distances, a section of a random pentagonal tiling is shown in the right hand side of the figure with an edge length of $L = \tau S = 4.67$ Å. $S$ is equal to 2.89 Å and $\tau = 1.618...$, the golden mean. The $L$ and $S$ are fundamental lengthscales found in the $d$-quasicrystal structure. With the aid of this tiling, it was possible to link the domain boundary distances with the surface ordering of $d$-AlCoNi: the domain boundary distance of $|a_1|$ can be related to the length $L_4$, $|a_2|$ to $L_5$, and $|a_3|$ to $L$, respectively. Thus, a nucleation behavior, which is bounded up with high-symmetry sites, is very feasible and the model suggests that the quasicrystalline surface acts as a template for the growth of the Al-oxide domains, a phenomena which is well-known in surface science [88, 116].

From the figure, it appears that the domain boundaries align along the most densely packed rows of atoms within the $d$-surface plane. These can be found along the edges of the pentagons. While the domain boundaries along the [1 0] direction of the hexagonal lattice are in registry with the [1 0 0 0 0] direction of the quasicrystal, the domain boundaries along the [2 1] direction are arbitrary since a 60° rotation of a hexagonal structure exposing its (1 1 1) face is not commensurate with the 5f-symmetry of the $d$-substrate. However, the two symmetries do only differ in an azimuthal rotation of 6° with the consequence that only minor atomic displacements are needed to form an optimum matching at the interface.

In summary, a structure model based on an antiphase domain ordering is capable of reproducing the LEED patterns. Such an interpretation rests on the following assumptions: (i) the domain boundaries need to be well-ordered and of regular shape in order to contribute a sufficiently sharp diffraction characteristic to the LEED pattern and (ii) within the coherence width of the LEED beam, several in-
phase hexagonal Al-oxide domains of equal orientational alignment must favor a surface ordering, which exhibits the extracted domain-wall boundary distances.

The first assumption is likely to be based on a large thermal relaxation rate of the adsorbate in which the adatoms thermally equilibrate with the substrate. The strong adsorbate–adsorbate interaction for oxygen and the dissociative nature of the adsorption process do allow for some surface diffusion [117], thus, the adsorbate tends to occupy the most energetically favorable sites, \( i.e. \), the oxygen atoms are likely to nucleate on high-symmetry sites of the substrate with domain boundaries along high-density atomic rows of the quasicrystalline substrate. On the contrary, a situation in which the adsorbate–substrate interaction dominates over the adsorbate–adsorbate interaction, \( i.e. \), the atoms essentially attach to the surface where they land (generally referred to as \textit{hit and stick}), was found in the case of, \( e.g. \), Al deposition onto the \( d \)-surface of Al\textsubscript{70}Co\textsubscript{15}Ni\textsubscript{15} [113]. As a result, the fcc Al clusters grew randomly distributed on the \( d \)-surface.

The second assumption can be explained by the small extension of the oxide domains with respect to the coherence zone of the LEED beam and the relatively large number of nucleation centers available on the surface. One possible arrangement of the domains is shown in Fig 5.4. The superstructure, which is given by a linear combination of the extracted domain-wall boundary distances, is successfully formed in a limited region of the coherence zone by simply imposing a restriction on the surface ordering to be dominated by high-symmetry sites. Thus, with the above arguments, it is feasible to adapt a surface structure with three different supercells identified by LEED. However, there is to mention that from the LEED investigation alone it is not possible to extract the exact domain ordering on the \( d \)-surface due to the averaging nature of the LEED investigation.
Chapter 6

Al nanoclusters on the oxidized pentagonal surface of \textit{i-AlPdMn}

Metal-oxide surfaces acting as templates for thin metal films have been widely employed as catalyst support \cite{2} as well as in a variety of technological applications in microelectronics \cite{118}. Of particular interest is that Al$_2$O$_3$ was found to be suitable as a substrate for the growth of \textit{self-organized} nanopatterns: for instance, Luo \textit{et al.} \cite{119,120} showed that Co deposited onto $\theta$-Al$_2$O$_3$/NiAl(1 0 0) leads to a preferential alignment of the adsorbate on the surface and to a \textit{self-size-limiting} growth, a behavior, which is in contrast to the usual increase in domain size for MBE growth with deposition thickness. The self-organized nanopatterning on thin Al-oxide films was confirmed in other studies \cite{6,54,55,58–63,118,121–123} with the same observation that the adsorbate grows preferentially aligned on the surface and in clusters. Thus, thin Al-oxide films present an interesting alternative to conventional techniques \cite{124} for the fabrication of nanometer-scale surface structures.

Particularly, systems giving rise to quantum-size effects offer a variety of novel features in surface science and technological applications, which are a consequence of the unusual behavior of matter in the nanometer size \cite{124}. One example is the occurrence of discrete energy levels affecting the electronic properties arising from the confinement of electrons to a reduced volume. The necessary condition for confinement in space is a potential-well formed by the vacuum barrier on one side and the substrate interface on the other side. While this situation is evident for metal deposition onto semiconducting or insulating substrate, confinement can even be accomplished in metal-to-metal junctions with the prerequisite of an energy gap in the substrate for a particular crystallographic direction (usually perpendicular to the surface) \cite{125,126}. This phenomenon of the dependence upon particle-size and \textit{structure} enhances the possibility of tailoring physical properties under various conditions. The reproducibility of the oxide layer, Al-oxide films as wide-gap insulators \cite{127}, and the usual thermodynamically preferred affinity of metal-oxide systems to form three-dimensional clusters on top \cite{128} make oxide-supported metal clusters promising candidates for the study of quantum- and particle-size effects.

In this chapter, the results obtained for the deposition of Al onto the oxidized pentagonal surface of \textit{i-AlPdMn} quasicrystal is discussed. Al as an adsorbate was not only chosen due to its wide application in microelectronics but also due to simple
structural reasons: Al as an fcc metal does well match the close-packed O ions of the Al-oxide domains, therefore, is likely to reduce any additional thermodynamic driving forces which alters the interface quality and possibly masking effects that solely arise from the substrate topology as mentioned above. It was found that the Al crystallites grow in an fcc structure exposing its (1 1 1) face parallel to the pentagonal surface of the quasicrystal, while the in-plane orientations of the crystallites are random. With increasing deposition thickness, no coalescence of the 3 nm large Al domains can be observed.

6.1 AES

The stoichiometry at the surface was confirmed by means of AES for several steps of the deposition process, as presented in Fig. 6.1. In this figure, only low-energy spectra are shown since they are suitable to obtain information about the oxygen take up and the deposited overlayer, considering the high surface sensitivity of electrons in this energy region [77] and the fact that AES transitions including valence electrons are likely to reflect electronic changes in the sample. After exposure of the clean quasicrystalline substrate to oxygen, the interatomic Auger transitions at approximately 40, 46, and 54.5 ± 1.5 eV are observable, which can be assigned to the formation of Al–O bonds involving Al(L2,3)O(L2,3)O(L1)' , Al(L2,3)O(L2,3)O(L2,3), and Al(L2,3)O(L2,3)O(L2,3)' transitions, respectively, as thoroughly described by Citrin et al. [8]. The ' -sign stands for the degree of localization of the final hole states of the Auger transition, i.e., it describes whenever hole filling and electron ejection from nearest neighbor sites (around the initial hole site) in the Auger transition are involved. The labeling of the peaks in Fig. 6.1 and their experimental uncertainties of ± 1.5 eV, was adopted from Ref. [8]. The oxidation of the quasicrystalline surface is confirmed by observing the typical Auger transitions arising from the interaction with oxygen. After the deposition of 3 ± 0.1 monolayers

<table>
<thead>
<tr>
<th>E_k (eV)</th>
<th>Label</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>84</td>
<td>C</td>
<td>Al^{2+}</td>
</tr>
<tr>
<td>68</td>
<td>A</td>
<td>Al L_{2,3}VV</td>
</tr>
<tr>
<td>54.5</td>
<td>B</td>
<td>Al plasmon</td>
</tr>
<tr>
<td>42</td>
<td>D</td>
<td>Al L_1 L_{2,3}V</td>
</tr>
<tr>
<td>54.5</td>
<td>P_1</td>
<td>Interatomic</td>
</tr>
<tr>
<td>46</td>
<td>P_2</td>
<td>Interatomic</td>
</tr>
<tr>
<td>40</td>
<td>P_3</td>
<td>Interatomic</td>
</tr>
</tbody>
</table>

Fig. 6.1: AES spectra of the pentagonal surface of i-AlPdMn during high-temperature oxygen exposure and RT deposition of Al films of different thickness. The lower two spectra represent the substrate before Al deposition. The peak positions found in the AES spectra and their assignments are shown in the table.
6.2 LEED

Fig. 6.2: LEED patterns obtained (a) at 64 eV from the oxidized pentagonal surface of \( i\)-AlPdMn quasicrystal and (b) at 270 eV after a 10 ± 0.1 ML Al RT deposit onto the surface shown in (a). The diffraction-ring radii can be compared with the distances found in the reciprocal-lattice of an fcc(1 1 1) surface with a lattice parameter of \( a_{Al} = 4.05 \) Å, as shown in (c).

(ML)\(^1\) Al, the spectrum shows a peak at 68 ± 1.5 eV, which can be assigned to an Al metal \( L_{2,3}VV \) Auger transition [74]. With increasing deposition thickness, this peak becomes larger and the contributions from the oxidized surface to the spectra decreases. After 37 ± 0.1 ML of Al deposition, the interatomic Auger transitions involving oxygen atoms are hardly detectable, instead, the bulk plasmon satellite peak for the \( L_{2,3}VV \) Auger transition and the \( L_1L_{2,3}V \) transition are detectable. Thus, the spectrum has evolved towards metallic Al allowing for the conclusion that the deposited Al film solely consist of a homogenous (connected) metallic film.

6.2 LEED

In order to determine the structure of the Al crystallites and their orientation with respect to each other and to the substrate, LEED and SEI have been applied. Fig. 6.2a shows a typical LEED pattern of the oxidized pentagonal surface of \( i\)-AlPdMn quasicrystal obtained after oxygen exposure of several hundreds of L. As discussed in Chapter 3, this LEED pattern can be interpreted as an Al-oxide layer consisting of five nanometer-size domains in hexagonal structure. In a subsequent experiment, the small lateral extension of the Al-oxide domains, which have been estimated to be 35 ± 2 Å [35, 44], have been used for nanometer-scale epitaxy to form small crystalline Al particles in the same size-region.

In Fig. 6.2b, a LEED pattern for a 10 ± 0.1 ML Al deposit is shown. The LEED pattern exhibits four concentric rings (one is very faint) without any fine structure consisting of individual spots. Similar observations have been reported by the evaporation of the semiconducting materials CdTe as well as PdTe onto the same Al-oxide layer [57]. A diffraction ring characteristics in LEED can be attributed to the formation of crystallites on the surface with a random in-plane epitaxial rela-

\(^1\)1 ± 0.1 ML corresponds to a film thickness of 2.33 Å, considering the structure and orientation of the growing film. The uncertainty of ± 0.1 ML is mainly given by the experimental error of the deposition rate, as described in Chapter 2.
Al nanoclusters on the oxidized pentagonal surface of \( i \)-AlPdMn

6.1 Relationship with the substrate. Naturally, Al crystallizes in the fcc structure with a lattice parameter of \( a_{\text{Al}} = 4.05 \text{ Å} \) [129]. By comparing the observed diffraction-ring radii \(|k_i|\), presented in Fig. 6.2b, with the distances found in an fcc(1 1 1) reciprocal surface mesh, as presented in Fig. 6.2c, it is found that \(|k_1|\) corresponds to (1 0), \(|k_2|\) to (2 1), \(|k_3|\) to (2 0), and \(|k_4|\) to the (3 1) diffraction reflex, respectively. The distances only agree with the proposed fcc(1 1 1) structure giving confidence to adopt this structure for the grown Al overlayer. From the pattern, a lattice parameter of \( a = 4.04 \pm 0.04 \text{ Å} \) is extracted, which agrees well with the bulk equilibrium lattice parameter for fcc Al.

In Fig. 6.3, the dependence of the average domain diameter on the deposition thickness is presented. The uncertainties of the domain diameters are given by the error bars, while they fall within the black squares for the deposition thickness. The domain diameters are extracted by SPA of the diffraction rings and do not show any broadening with deposition thickness for a coverage of more than approximately 6 ML. The data suggests an average domain size of \( 30.5 \pm 2 \text{ Å} \) up to a thickness of 51 ML, the highest deposition thickness examined, confirming the feasibility of the Al-oxide surface for growing metal particles in the nanometer-size regime.

6.3 SEI

In Figs. 6.4b–c, SEI patterns of a \( 51 \pm 0.3 \text{ ML} \) Al deposit onto the Al-oxide domains is presented. From the patterns, it is observable that the detected secondary electrons form a circular diffraction feature, while each diffraction ring appears at a polar angle as listed in the second column of Table 6.1. For comparison, an SEI pattern from the clean quasicrystalline substrate is shown in Fig. 6.4a. The pattern of the bare substrate clearly shows a bright central pentagon with five equilateral triangles adjacent to each side, in accordance with the 5f-symmetry of the substrate (see also Section 4.1). It is to mention that the SEI pattern of the oxidized surface does not present any change due to the large mean free path of electrons in the keV range in the Al-oxide layer and the thickness of the Al-oxide domains of only one or two atomic layers. However, the comparison of the patterns indicate that unlike the...
preferential growth of the oxide domains on the quasicrystalline substrate [35, 44], the alignment of the Al crystallites in registry with the Al-oxide domains and to the quasicrystalline surface, respectively, is random.

In Fig. 6.4d, a single-domain fcc(1 1 1) surface structure is presented as a central projection for direct comparison. The black points represent the main crystallographic directions, while the grey thick lines are low-index lattice planes, which account for the Kikuchi bands [76]. The superimposed arrows are in agreement with those shown in Fig. 6.4b. The grey circle labeled $45^\circ$ corresponds to the rim of the collector screen, therefore, only a section of the central projection is presented. The two black circles represent polar angles of 20 and 40° and are guides for the eye. The central projection can be compared with the SEI pattern taken from an Al(1 1 1) surface as shown in the inset. In the pattern, the main diffraction char-

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Fig. 6.4: SEI patterns obtained from (a) the pentagonal surface of $i$-AlPdMn, (b) a $51 \pm 0.3$ ML Al deposit onto the oxidized surface, and (c) the same surface shown in (b) but with the sample tilted by $35^\circ$. The features in (b), indexed with arrows and labeled by $r_i$, are in accordance with Table 6.1 and discussed in the text. (d) For comparison, a central projection (large) of an fcc(1 1 1) structure and an SEI pattern (small) taken from an Al(1 1 1) surface are displayed.
Table 6.1: List of radii \( r_i \) of diffraction rings observed in Fig. 6.4a. In the second column, the corresponding polar angles \( \alpha_i^{\text{exp.}} \) are listed. In column three, the main crystallographic directions of the fcc structure are assigned to the observed rings. The angles \( \alpha_i^{\text{calc.}} \) are the calculated values between the crystallographic directions in column three and the \([1 1 1]\) direction.

<table>
<thead>
<tr>
<th>( r_i )</th>
<th>( \alpha_i^{\text{exp.}} ) (deg.)</th>
<th>( [h k l] )</th>
<th>( \alpha_i^{\text{calc.}} ) (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.95 ± 0.55</td>
<td>[1 1 2]</td>
<td>19.47</td>
</tr>
<tr>
<td>2</td>
<td>27.00 ± 0.70</td>
<td>[1 4 5]</td>
<td>27.02</td>
</tr>
<tr>
<td>3</td>
<td>29.20 ± 0.70</td>
<td>[1 1 3]</td>
<td>29.50</td>
</tr>
<tr>
<td>4</td>
<td>35.60 ± 0.90</td>
<td>[0 1 1]</td>
<td>35.26</td>
</tr>
<tr>
<td>5</td>
<td>39.95 ± 1.25</td>
<td>[0 1 2]</td>
<td>39.23</td>
</tr>
<tr>
<td>6</td>
<td>43.35 ± 2.20</td>
<td>[0 1 3]</td>
<td>43.09</td>
</tr>
</tbody>
</table>

The combination of AES, LEED, and SEI shows that the Al overlayer crystallizes in domains of about 30 Å lateral extension. The domains possess an fcc structure with the \((1 1 1)\) faces aligned parallel to the pentagonal surface of the substrate, while their azimuthal orientation is random in the surface plane. The size and orientation of the Al crystallites did not change by annealing at elevated temperatures \((\leq 500 \text{K})\) and were found to be stable up to a \(51 \pm 0.3\) ML deposit, the highest deposition thickness examined.

### 6.4 Interface formation

Epitaxy of several fcc metals, including Al, onto \((0 0 0 1)\) sapphire (\(\alpha-\text{Al}_2\text{O}_3\)) have been investigated and identified with the expected orientational relationship of \([\overline{T 1 0}]_{\text{fcc}} \parallel [1 0 \overline{T} 0]_{\text{Al}_2\text{O}_3}\) and \([1 1 1]_{\text{fcc}} \parallel [0 0 0 1]_{\text{Al}_2\text{O}_3}\) [130,131]. Expected means that this particular orientational relationship fulfills ideal epitaxial growth conditions like relatively low lattice mismatch at the interface, low surface energy of the \((1 1 1)\) layer, and best structural similarities due to the common symmetry elements of the substrate and the adsorbate structure. Two additional configurations were observed by Medlin et al. [130] but likewise a well-defined azimuthal and polar orientational relationship was predominate. A similar result of a random in-plane fcc growth was found in the literature reported by Vermeersch et al. [131], however, with the following observations: \((i)\) the random growth characteristics was only obtained for a coverage greater than 40 ML and \((ii)\) with a substrate temperature as high as 740 K. \((iii)\) RT deposition resulted in an amorphous growth of the adsorbate. \((iv)\) A reaction involving the first anion ML of the substrate, which lead to a \(\sqrt{3}T(1 \times 1)R \pm 9°\) surface reconstruction up to 5 ML, was observable.
In the case of Al deposition onto the oxidized $i$-AlPdMn quasicrystal, the random in-plane orientation of the nanocrystallites emerges already from the first couple of ML deposits. Wallin et al. [132] have found in a first-principles computational study that the interface interaction between the Al atoms and the O-terminated surface of $\alpha$-Al$_2$O$_3$ is predominantly ionic. This is comprehensible regarding the rather large difference in electronegativity of O (3.44) and Al (1.61). The same situation can be expected from Al deposition onto the oxidized quasicrystal since this surface was found to be O-terminated as well [30, 35]. An ionic bonding is characterized by interatomic electron exchange without orbital mixing resulting in typically non-directional bonding forces [133]. The non-directional character tends to maximize packing efficiency and to a large coordination number which is in fact observed in the experiment: the adsorbate grows in domains possessing a close packet fcc(1 1 1) structure, as illustrated in Fig. 6.5. In this figure, a top and a side view of a section of the interface is shown. The domains are simplified shown in hexagonal shape. The antiphase domain ordering as well as the reconstruction of

Fig. 6.5: Schematic illustration of the Al nanoclusters grown on the oxidized pentagonal surface of $i$-AlPdMn: (a) top view of a 130 × 70 Å$^2$ large section of the interface and (b) its side view. The adsorbate grows in nanometer size, randomly in-plane oriented domains in hexagonal structure on the oxide layer.
the oxide surface layer, which are observed under certain conditions, are neglected. The domain orientations are indicated by the black and white arrows.

While the Al domains are randomly oriented with respect to each other, the Al-oxide domains are rotated by 72°. These orientations can be compared with the four basic vectors \( e_i \) found in the quasiperiodic pentagonal plane, plotted at the top right-hand side of Fig. 6.5a. The LEED investigations reveal that the domains grow in height up to \( 51 \pm 0.3 \) ML. As extracted from Fig. 6.3, the average domain diameter does not show any broadening with deposition thickness for a coverage of more than approximately 6 ML. Thus, it can be concluded that the Al adsorbate wets the oxide and grows in nanometer-size domains, each domain exposing its \((111)\) surface and being randomly oriented in azimuth. A growth mode in form of “towers” is improbable since they would coalesce for a deposition thickness as much as 51 ML.

Upon thermal treatment at temperatures up to 500 K, no measurable enlargement of the domain size was observable. Annealing at higher temperatures lead to a significantly enhanced diffusion through the Al-oxide, resulting in a gradual loss of the deposited Al films, as monitored by means of AES and LEED. The thermal stability of the Al nanocrystallites indicates a strong metal–support- and metal–metal-interaction in the adsorbate and to the substrate. This result is surprising and is in contrast to the expected growth behavior for vapor deposition onto an oxide surface, which usually results in a low adsorbate–substrate interaction.

### 6.5 Random in-plane growth

One striking difference between the layers grown on the oxidized quasicrystals and those grown on crystalline substrate is the random in-plane ordering of the adsorbate (Table 1.1). Vermeersch et al. [131] have suggested that the deposition and sample preparation conditions account for the different surface structures observed from Al deposition onto \( \alpha\)-Al\(_2\)O\(_3\)(0 0 0 1). Likewise, it is conjectured that (i) the defect-rich Al-oxide layer grown on the pentagonal surface of \( i\)-AlPdMn quasicrystal and (ii) its structural deviation from a perfect hexagonal lattice plane (Chapter 3) is essential for the observations of a random in-plane oriented growth of the Al adsorbate.

(i) It is helpful to attribute the film growth to atomistic processes: the growth dynamic is always a consequence of the minimization of the total (free) energy at the interface. Consequently, under the assumption of equilibrium conditions, any additional adatom will find its configuration on the surface, which is the least energetic with respect to its position within the compound. The final configuration is given by the surface potential energy, which can be significantly modified by surface defects since they account for strong attractive interactions, therefore, likely trap adatoms. It has been found that although the oxidation of Al-based ordered binary alloys results in almost perfect atomically thin Al-oxide layers with an exceptionally high degree of long-range order, thin Al-oxide films exhibit a large number of defects [1, 10, 20, 64]. The adatoms are even more favorably attracted by defects, if the average distance of two separated defects is smaller than the separation of nucleation centers predicted by homogenous nucleation theory [1]. Thus, a surface...
6.5 Random in-plane growth

texture whose growth is highly affected by defects is not likely to form a uniform (connected) surface film and surface defect nucleation is the dominating factor in the early stage of interface formation. The observation of a random in-plane growth of the Al nanocrystallites, which can be assigned to many domains on the surface that grow independently, fits well into a picture of a defect nucleated surface structure. A possible explanation for the existence of a large number of surface defects is the difference in surface preparation for the oxidized $i$-AlPdMn with respect to bulk sapphire and thin oxide layers grown on Al-based ordered binary alloys. The surface preparation of such samples can be carried out at much higher temperatures of around 1000 K [1,58,64,119,120,127,128,134] as a consequence of the much higher surface melting temperatures$^2$. Studies on the influence of the annealing temperature on the surface morphology and ordering resulting in atomically flat and defect free surfaces, are reviewed in detail by Sharma et al. [71].

$^{(ii)}$ The geometrical structure of the Al-oxide surface is expected to be similar to (1 1 1) $\gamma$-Al$_2$O$_3$, therefore, does most likely not represent a perfect hexagonal atomic mesh. Consequently, the atomistic interface model between the local atomic arrangement of the Al(1 1 1) texture and the atoms of the oxide layer allows for some azimuthal rotational freedom. This additional degree of freedom during the interface formation and the non-directional character, which allows to accommodate the bonding requirements at the interface more easily, are expected to result in a random in-plane growth of the adsorbate.

In summary, the deposition of Al films onto the oxidized pentagonal surface of $i$-AlPdMn quasicrystal results in an fcc domain growth of the adsorbate with the (1 1 1) faces aligned parallel to the pentagonal surface of the substrate while their azimuthal orientations are randomly oriented in the surface plane. Although, the epitaxial growth conditions are satisfied on a global scale, nanometer-size domains are formed as a consequence of the small lateral extension of the oxide domains. The nanocrystallites grow in domains and arrange themselves on the surface in a way, which is predetermined by the defect-rich surface structure of the oxide. The non-directional bonding forces as well as the freedom in azimuthal alignment of the Al(1 1 1) crystallites on the Al-oxide domains are expected to account for the random in-plane growth.

$^2$e.g., a NiAl crystal has a bulk melting temperature of approximately 1400 K, an $i$-AlPdMn quasicrystal melts around 1100 K.
Chapter 7
Conclusions and outlook

In this dissertation, the oxidation process of $i$- and $d$-quasicrystals has been discussed. In particular, the structural properties of the oxide layers grown upon high-temperature oxygen exposure on the 5f- and the 3f-symmetry surface of $i$-AlPdMn as well as the 10f-symmetry surface of $d$-AlCoNi quasicrystal have been a main focus and investigated by means of LEED.

The results indicate the growth of thin Al-oxide layers comparable to the Al-based binary alloys. However, while the oxide layers grown on periodic crystals represent typical epitaxy-stabilized interfaces, the quasicrystalline substrate, while containing Al, has an aperiodic structure on which the crystalline oxide layers assemble. A natural question arises as to what extent this aperiodicity contributes to novel surface phenomena that may be observed for such oxide compounds. Due to the lack of commensurability between a crystalline overlayer and the aperiodic ordering of the substrate, lattice coincidence is not possible. As a consequence, the oxide layers break up into small domains in order to reduce the large interfacial strain. Hence, the oxide layers that form on the different high-symmetry surfaces of the quasicrystals have in common that they are composed of nanometer-size domains possessing an oxygen sublattice in hexagonal structure, which is locally commensurate and in registry with the substrate. Differences arise on each surface from the exact arrangement and the registry of the domains with the substrate.

The growth of an Al-oxide layer is controlled by diffusion of Al and O ions towards the metal-oxide interface involving predominantly the formation of Al–O bonds. Depending on the oxidation pressure, temperature, exposure time, as well as the sample preparation prior to oxidation, different oxide layers can be observed. At low temperatures, an Al-deficient oxide film of self-limiting thickness grows which prevents Al to diffuse to the interface to further react with oxygen. A stoichiometric $\text{Al}_2\text{O}_3$ may form if the exact amount of Al is available for a given oxygen dose. At the high-temperature limit, the diffusivity does not prevent the supply of Al and O, thus, the surface film establishes a stoichiometric condition, which favors crystallization. Correspondingly, the oxidation of the clean pentagonal surface of $i$-AlPdMn quasicrystal leads to the growth of an amorphous oxide layer at RT. In contrast, five distinct and few-nanometer-large domains possessing hexagonal long-range properties grow at 700–800 K. Due to a domain size, which is significantly smaller than the coherence width of the LEED system, the diffraction patterns disclose the presence
and interactions of antiphase domain boundaries. This oxide structure is observed for small and large coverage and forms a new kind of quasicrystal–crystal interface. Its formation can be explained by the dissociative nature of the (molecular) adsorption process: Brune et al. [117] have shown that some of the excess energy release associated with the Al–O bond formation gives rise to translational motion parallel to the surface. Consequently, the dissociated oxygen atoms scatter apart from each other for at least 80 Å before the Al–O bond is formed, therefore, are allowed to occupy the most energetically favorable surface sites. On the contrary, with atoms directly arriving from the gas phase, the excess energy is essentially transferred into motion along the surface normal, i.e., the atoms attach to the surface at the point of their impact. Beside the antiphase domain ordered surface films, in an intermediate range, the diffraction patterns indicate a reconstruction of the surface layer characteristic of \(2\sqrt{3}(1 \times 1)R \pm 30^\circ\), which is twelve times larger than the unreconstructed unit cell. The driving force for the reconstruction is the commensurability of the hexagonal Al-oxide superstructure with the aperiodic atomic ordering in real space, i.e., the interface is additionally stabilized due to the minimization of the interfacial strain energy. Similar observations have been reported from the oxide layers grown on NiAl(1 1 0) [7,10,20–29]. These layers reconstruct with a unit cell, which is approximately 16 times larger, and the real- and reciprocal-space images are dominated by an antiphase domain ordering of the reflection domains.

Upon formation of the Al-oxide layer, the lack of Al atoms in the alloy can adversely affect the stoichiometry of the quasicrystal surface and hence the structure of the quasicrystal. In fact, the reduction of the Al concentration on the surface was found to shift the structural stability towards the cubic crystal identified as \(\text{Al}_{50}(\text{PdMn})_{50}\). In order to obtain a proper quasicrystal–oxide interface, Al segregation from the bulk to the surface is required that first restores the quasicrystalline order and (only) then binds to oxygen to form the oxide layer. The high heat of formation for \(\text{Al}_2\text{O}_3\), however, favors most likely the oxide formation on the crystalline AlPdMn surface before the quasicrystalline stoichiometry and order is restored. In this case, the oxide layer is surprisingly similar to that observed on the (1 1 0) surface of the ordered NiAl alloy. In order to avoid this formation, oxidation is performed at high-temperatures that promotes segregation of Al from the bulk to the surface and maintains the quasicrystalline stoichiometry. Yet, in some oxide structures, traces of a cubic overlayer can be identified underlining the sensitivity of the oxide formation on the segregation process. Similar to the temperature effect, any improper treatment of the surface, e.g., ion bombardment during or after the oxidation process, or improper surface preparation of the quasicrystal prior to oxidation both result in oxide layers typical of those on crystalline surfaces. Consequently, the oxide layer formed after sputtering the pentagonal surface was found to be almost identical to the oxide grown on the (1 1 0) surface of the NiAl alloy. Its identification is primarily based on the analogy between the \(i\)-structure of AlPdMn and the CsCl structure of the NiAl alloy.

The influence of the balance between the diffusion of Al and O to the interface on the resulting atomic structure was also demonstrated by the oxidation of the 3f-symmetry surface of \(i\)-AlPdMn quasicrystal. This high-symmetry surface represents a termination of higher surface energy, thus, is prone to reconstruct and likely to
possess a rougher terrace fine structure compared to the pentagonal surface, the most stable high-symmetry termination of $i$-AlPdMn. Consequently, the sticking probability for oxygen is increased which significantly promotes the oxygen take up. The driving force of energy minimization supports the growth of facets along the high-symmetry directions of the $i$-bulk structure. Furthermore, it was found that the incorporation of Al and O into the Al-oxide matrix favors an environment, which only crystallizes the oxide layer along the 5f-symmetry directions. This may be explained by the most pronounced bulk diffusion of Al in the $i$-quasicrystal structure along these directions, as observed by Lüscher et al. [81]. Since the surface was initially planar, it can be deduced that the oxidation process is responsible for the formation of the facets.

The Al-oxide layer formed on the 10f-symmetry surface of $d$-AlCoNi quasicrystal is comparable with that grown on the pentagonal surface of $i$-AlPdMn. The LEED investigations are consistent with five distinct Al-oxide domains with hexagonal long-range properties. Each domain exposes its (1 1 1) face parallel to the surface and is rotated by $2\pi/5$ with respect to the others, reflecting the local rotational symmetry of the $d$-substrate. Besides the main hexagonal feature, the details of the diffraction pattern can be ascribed to antiphase domain boundaries along the high-symmetry directions of the $d$-surface. These domain boundaries are the main dislocations in the oxide layer, while the size of the domains comply with self-size-selecting arguments. Furthermore, the distances between the domain boundaries can unambiguously be related to the $d$-surface ordering, suggesting that the quasicrystalline surface acts as a template for growth of the Al-oxide domains. In contrast to the pentagonal surface of $i$-AlPdMn, only the antiphase domain ordering of the oxide layer is observed. The significantly higher sample temperature, which is needed for the growth of well-ordered oxide layers on $d$- compared to $i$-quasicrystals, results in a superior quality of the (antiphase) domain ordering.

The growth of ordered Al-oxide layers on aperiodic substrate is now well-established. However, the understanding of the oxide growth kinetics and structure is still lacking on several points. In particular, the characterization of the oxide layers at the atomic level and the details about the oxide formation, which involves dissociation of diatomic molecules with subsequent adsorbate–substrate bond formation, have so far not been successful. To date, the conceptual framework has been limited to dissociative adsorption of O$_2$ on Al-based substrate. Conducting the oxidation process with more complex molecules like methanol (CH$_3$OH), ethanol (CH$_3$CH$_2$OH), or acetic acid (CH$_3$COOH) is promising for obtaining further information about the bond mechanism, which is responsible for the formation of a stable interface. In general, understanding the energetics of molecular dissociation may shed light on the several still unclear points, for instance, the reason for the very low dissociative sticking coefficient for O$_2$ or the exact nature of the dissociation process (existence of an activation barrier or possible precursor mediated state). Further, in spite of the efforts, quantitative information on the metal–oxide interface such as adhesion, interface energies, electronic as well as chemical properties are still very basic or not known at all. Understanding these properties in more detail is a prerequisite for oxidized quasicrystals to achieve serious considerations for future applications. The results of this dissertation have also shown that the ordered Al-
oxide islands generated by the oxidation of the quasicrystal surfaces can be used as substrates for the formation of ordered, nanometer-size Al particles. The natural growth mechanism of the oxide layer leads to an overlayer structure in the same size-region. Since the substrate and the adsorbate are structurally well-matched and no coalescence of the domains can be observed, the results found in this study are encouraging for investigating and tuning size effects without the influence of epitaxial strain in the growing film.


Appendix

A Determination of the domain size using LEED

The profiles of the diffraction spots in LEED can be used to obtain information about the lateral size of the surface area, which contributes coherently to the diffraction characteristics [135, 136]. For a perfect infinite surface, the diffraction pattern consists of sharp spots, which are only broadened by the instrumental resolution, thus, the domain size is equal to the transfer width\(^1\) of the LEED system [137]. In the experiment, additional broadening is observed if the surface structure lacks periodicity, or due to domain formation.

The angular spread of the spot profiles is directly related to the domain size and can be converted into a real-space length in the same way using (Fraunhofer) diffraction at a single slit geometry. This method is the simplest approach to the problem and will be discussed further\(^2\). Under the Fraunhofer assumption, the wave impinging the crystal arrives as a plane wave. As illustrated in Fig. A.1, each surface atom can be regarded as a point source for a spherical wave, dividing the slit into segments of constant phase displacement. The intensity from this geometry can be calculated in a standard way (see, e.g., Ref. [139]). We obtain

\[
I = I_0 \frac{\sin^2(\delta/2)}{(\delta/2)^2}
\]

with a phase difference of

\[
\delta = \frac{2\pi}{\lambda} N d \sin \theta
\]

with \(\delta\) being the phase difference between the outermost left and the outermost right array of light. This functions is shown in the upper part of Fig. A.1. In this geometry, the total path length difference for \(N\) scatterers is \(N d \sin \theta\). The first minimum occurs when \(\delta/2 = \pm \pi\), which can also be written as \(\lambda = \pm N d \sin \theta\). Thus, in other words, the first minimum can be found if the total path length difference equals \(\lambda\). From \(\lambda = N d \sin \Delta \theta_{HW} \approx N d \Delta \theta_{HW}\), where \(\Delta \theta_{HW}\) is the half-width angle of the first minimum, we obtain that the spot-profile width to the first minimum is approximately \(\Delta \theta_{HW} = \frac{\lambda}{Nd}\). The half-width angle \(\Delta \theta_{HW}\) of the \(n^{th}\) maximum, found at \(\theta_n\), depends on the location relative to its central axis. Since its adjacent minimum is located at \(\frac{n+1}{N}\), we obtain from \(d \sin (\theta_n + \Delta \theta_{HW}) = (\frac{n+1}{N}) \lambda\) and the

\(^1\)This distance, which is also called the coherence length, is usually between 100–150 Å [84].

\(^2\)Alternative discussions can be found in Refs. [137, 138].
Fig. A.1: The domain size can be extracted from the spot profiles in the same way light is scattered at a single slit diffraction geometry (bottom). According to Huygens principle, each surface atom acts as a point source for a spherical wave. The intensity calculated from this geometry (top) can be compared with the intensity recorded at the LEED screen, as discussed in the text.

**small-angle approximation** the general form:

\[
\Delta \theta_{HW} \approx \frac{\lambda}{Nd \cos \theta_n}.
\]  

(1)

As an example, a spot-profile line scan of the hexagonal diffraction characteristics obtained from the oxidized 10f-symmetry surface of \(d\)-AlCoNi quasicrystal is shown in Fig. A.2. In this figure, the normalized radial intensity plot of the (1 0) diffraction spot is drawn for \(q \approx 2.40 \text{ Å}^{-1}\), which corresponds to a polar angle \(\theta \approx 40^\circ\) for a primary-electron energy of 55 eV. From the plot, the full-width at half-maximum (FWHM) angle \(\Delta \theta_{FWHM}\) of the spot profile is deduced to be approximately 0.05 rad. If a Gaussian shape of the spot profile is assumed, then \(\Delta \theta_{FWHM} \approx 0.9 \Delta \theta_{HW}\). Consequently, with the above values, Eq. 1, and considering the inner potential in LEED [140], an average domain size of approximately 35 Å is obtained.

Fig. A.2: Normalized radial (1 0) intensity plot of the hexagonal domain diffraction characteristics from the oxidized 10f-symmetry surface of \(d\)-AlCoNi quasicrystal. The spot profile is obtained at a polar angle of \(\theta \approx 40^\circ\) for a primary-electron energy of 55 eV.
The above examination of the spot profiles using LEED patterns gives quantitative information about the domain size with ease. However, it is to mention that this method renders difficult in several points [141]: (i) a direct inversion of the spot profiles into a real-space length is only possible if just one single domain diameter is present on the surface. But this is a rather unrealistic and simplified assumption. (ii) The exact spot profile can have a severe influence on the extracted value. Usually, the FWHM is the easiest quantity to describe a spot profile by just one parameter, but this holds true only for Gaussian or well-defined profiles. (iii) The arrangement of the domains on the surface and their interaction can also significantly contribute to the broadening of the diffraction spots. (iv) The accuracy in determining the domain size is not only given by the half-width \( h_D \) produced by the domains, it also depends on the instrumental limitation, which produces a half-width \( h_I \). The measured half-width angle is then \( h_M = \sqrt{h_D^2 + h_I^2} \) if both profiles are Gaussian.

Nevertheless, the above method gives an upper limit of the average domain size, which is usually sufficient for drawing conclusions about the size and the arrangement of the domain structure as well as details of the growth mode.
## B Acronyms

<table>
<thead>
<tr>
<th>2f</th>
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<tr>
<td>3f</td>
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<tr>
<td>5f</td>
<td>fivefold</td>
</tr>
<tr>
<td>10f</td>
<td>tenfold</td>
</tr>
<tr>
<td>i-</td>
<td>icosahedral</td>
</tr>
<tr>
<td>d-</td>
<td>decagonal</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
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<tr>
<td>LEED</td>
<td>low-energy electron diffraction</td>
</tr>
<tr>
<td>SEI</td>
<td>secondary-electron imaging</td>
</tr>
<tr>
<td>SPA</td>
<td>spot-profile analysis</td>
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<tr>
<td>MBE</td>
<td>molecular-beam epitaxy</td>
</tr>
<tr>
<td>bcc</td>
<td>body-centred cubic</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centred cubic</td>
</tr>
<tr>
<td>ML</td>
<td>monolayer(s)</td>
</tr>
<tr>
<td>L</td>
<td>Langmuir(s)</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>TM</td>
<td>transition-metal</td>
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<tr>
<td>FWHM</td>
<td>full-width at half-maximum</td>
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Publications

The quasicrystal-crystal interface between icosahedral Al-Pd-Mn and deposited Co: evidence for the affinity of the quasicrystal structure to the CsCl structure
Y. Weisskopf, S. Burkardt, M. Erbudak, J.-N. Longchamp

Formation of a well ordered ultrathin aluminum oxide film on icosahedral AlPdMn quasicrystal
J.-N. Longchamp, S. Burkardt, M. Erbudak, Y. Weisskopf

CdTe and PbTe nanostructures on the oxidized pentagonal surface of an icosahedral AlPdMn quasicrystal
J.-N. Longchamp, S. Burkardt, M. Erbudak, Y. Weisskopf

Co nanocrystallites on an icosahedral Al-Pd-Mn quasicrystal
S. Burkardt, M. Erbudak, J.-N. Longchamp, Y. Weisskopf

Bulk and surface structure of the clean and adsorbate-covered decagonal Al–Co–Ni quasicrystal
S. Burkardt, S. Deloudi, M. Erbudak, A.R. Kortan, M. Mungan, W. Steurer

Structure of Al deposits on nanometer-size islands of aluminum-oxide
S. Burkardt, M. Erbudak

High-temperature surface oxidation of the decagonal AlCoNi quasicrystal
S. Burkardt, M. Erbudak, R. Mäder

Oxygen-induced surface faceting of the threefold-symmetry surface of icosahedral AlPdMn quasicrystal
S. Burkardt, M. Erbudak
Nanoepitaxy on quasicrystal surfaces
M. Erbudak, M. Mungan, S. Burkardt

Ordered oxide layers on the pentagonal surface of AlPdMn quasicrystal
S. Burkardt, M. Erbudak
Submitted to Phys. Rev. B.
Curriculum Vitae

Last and first name  Burkardt Sven  
Date of birth  December 16, 1976  
Citizen of  Sirnach, TG, Switzerland  

Education  
1983 – 1989  Primary school in Strass, TG  
1989 – 1992  Secondary school in Frauenfeld, TG  
1992 – 1996  Apprenticeship as a technical designer  
1996  Graduation as a technical designer  
1996 – 2000  High school at TSME in Frauenfeld, TG - emphasized on physics and applied mathematics  
2000 – 2006  Studies of physics at the Swiss Federal Institute of Technology Zurich  
2006  Diploma thesis on growth mode of Co deposited on AlCo domains formed on the pentagonal surface of an icosahedral AlPdMn quasicrystal in the group of Prof. Dr. M. Erbudak, Institute for Solid State Physics, Department of Physics, Swiss Federal Institute of Technology Zurich  
2006 – 2009  PhD student in the research area of oxide and oxide-supported nanoclusters on quasicrystals in the group of Prof. Dr. M. Erbudak, Institute for Solid State Physics, Department of Physics, Swiss Federal Institute of Technology Zurich
Dank