Solid state dewetting phenomena of aluminum thin films on single crystalline sapphire

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„To boldly go where no one has gone before“
(Zefram Cochrane)

“Maximum effort“
(Wade Wilson)
Abstract

Thin film technology is used in a variety of applications, whereas a major application field is microelectronics, e.g. with aluminum (Al) and copper thin films as interconnect materials. Miniaturization leads to decreasing film thickness in thin film devices and consequently high surface to volume ratio. Such thin films may degrade at elevated temperatures via dewetting. The process can occur at temperatures below the melting point and is termed in this case solid state dewetting.

This PhD thesis focuses on the solid state dewetting behavior of tetra- and bicrystalline Al thin films on single crystalline (0001) oriented α-Al₂O₃ (sapphire) substrates. Bicrystalline films have the close-packed planes and directions parallel to each other and possess two twin variants resulting in the orientation relationships (OR) OR I a/b. Tetracrystalline films have additionally grains, 30° rotated relative to OR I a/b, which occur also in two twin variants OR II a/b. The films were annealed below the melting point of Al (660°C) to investigate the solid state dewetting behavior and the accompanying microstructural evolution phenomena. The native oxide served as a surface diffusion suppression layer.

In the first part of the thesis the texture evolution and the grain growth of tetracrystalline Al thin films was quantitatively analyzed using large scale electron backscatter diffraction measurements. A detailed scanning electron microscopy plan-view study revealed the formation of faceted voids and their growth behavior with increasing annealing time. High energy grain boundaries were identified as initial points for the void formation. The retraction of the Al thin film below a continuous oxide membrane was found as the underlying dewetting mechanism. Al diffuses primarily via grain boundaries and interfaces.

The void formation and the void growth mechanism within the tetracrystalline films are discussed in the second part of the thesis. The ideal void shape, a hexagon with alternating short and long facets, is described by an inverse equilibrium crystal shape of Al. Site-specific scanning transmission electron microscopy (STEM) investigations of cross sections of the Al|void region revealed atomically sharp interfaces between the retracting Al film and the void. Al is uniformly distributed to the surrounding leading to a homogenous increase in the thickness of the Al film over several µm. Obstacles led to pinning and a subsequently anisotropic retraction of the Al thin film and irregular void shapes. Due to pinning, rim growth at the Al|surface|void triple junction and epitaxial ridge growth at the Al|substrate|void triple junction occurred. The covering surface oxide membrane was increasing in thickness with time, whereby it was still covering both, the film and the void, continuously. A temperature
induced phase transformation of the initial amorphous to $\gamma$-$\text{Al}_2\text{O}_3$ was confirmed by high resolution STEM and electron energy loss spectroscopy. The $\gamma$-$\text{Al}_2\text{O}_3$ surface oxide possesses an orientation relationship with the underlying Al thin film.

The dynamics of the solid state dewetting mechanisms are reported in the third part of the thesis. For this studies, the bicrystalline Al thin film system was used to further reduce grain boundary and texture effects interfering with the solid state dewetting phenomena. In-situ annealing experiments within an environmental scanning electron microscopy enabled for the first time the direct observation of the discontinuous void growth mechanism, as indicated from the ex-situ annealing experiments. Annealing in reducing atmosphere led to a partial removal of the surface oxide and a spontaneous film rupture due to the available surface diffusion path. Experiments in oxidizing atmosphere confirmed that void formation via solid state dewetting occurs below the oxide membrane, but is sluggish due to the suppressed surface diffusion. With increasing annealing time, the void shape deviates from the idealized hexagonal shape due to the increasing complexity of the Al film retraction caused by pinning. The evolution and the interplay of pinning, fingering instabilities, faceting instabilities and straight facets were investigated as a function of time. The time-dependent observation of the solid state dewetting behavior of defined Al thin films on sapphire in-situ allows to manifest the mechanism, postulated from the ex-situ experiments.

This thesis demonstrates the potential of combining in-situ and ex-situ techniques at high spatial resolution to reveal dynamic phenomena in material science.

In dieser Arbeit wird das Festphasenentnetzungsverhalten von Al-Dünnschichten auf einkristallinen (0001) orientierten α-Al₂O₃ (Saphir) Substraten beschrieben. Es handelt sich um bikristalline Schichten, bei denen die dichtest gepackten Ebenen und Richtungen parallel zueinander sind, wobei zwei Zwillingsvarianten auftreten. Zum anderen wurden tetrakristalline Filme untersucht, bei denen zusätzlich Körner, die um 30° rotiert sind (ebenfalls verzwilligt), vorhanden sind. Das Entnetzungsverhalten der Schichten sowie begleitende Veränderungen der Mikrostruktur während des Auslagerns bei Temperaturen unterhalb des Schmelzpunktes von Al (660°C) sind der zentrale Aspekt dieser Arbeit. Die Oberflächendiffusion ist durch das natürliche Oxid unterdrückt.


Im zweiten Teil der Arbeit werden die Bildung der Hohlräume und deren Wachstumsmechanismen im Detail behandelt. Die ideale Hohlraumform kann mittels einer inversen Wulff Konstruktion eines Al Kristalles beschrieben werden. Das sich ausbildende Hexagon wird mit abwechselnden kurzen und langen Facetten gebildet. Rastertransmissionselektronenmikroskopieuntersuchungen (STEM) von Querschnitten der Al|Hohlraum-Bereiche zeigen atomare Grenzflächen zwischen dem sich zurückziehenden Film und dem Hohlraum. Eine gleichmäßige Umverteilung des Materials in die Umgebung sorgt für einen


Diese Arbeit zeigt, wie durch das Zusammenspiel von in-situ und ex-situ Methoden bei hoher Ortsauflösung dynamische Prozesse in der Materialwissenschaft aufgeklärt werden können.
Preface

The following publications contributed to this thesis:

Paper I
Microstructural evolution and solid state dewetting of epitaxial Al thin films on sapphire (α-Al₂O₃)
S.W. Hieke, B. Breitbach, G. Dehm, C. Scheu

Paper II
Annealing induced void formation in epitaxial Al thin films on sapphire (α-Al₂O₃)
S.W. Hieke, G. Dehm, C. Scheu

Paper III
Dewetting mechanisms and kinetics of epitaxial Al thin films
manuscript in preparation
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Acknowledgement
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Å</td>
<td>Angström (10⁻¹⁰ m)</td>
</tr>
<tr>
<td>A</td>
<td>Ampere</td>
</tr>
<tr>
<td>ABF</td>
<td>Annular bright field</td>
</tr>
<tr>
<td>ADF</td>
<td>Annular dark field</td>
</tr>
<tr>
<td>bar</td>
<td>Bar</td>
</tr>
<tr>
<td>BF</td>
<td>Bright field</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered electrons</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>CCS</td>
<td>Cleaning cross section (in FIB)</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal-oxide semiconductor</td>
</tr>
<tr>
<td>Cs</td>
<td>Spherical aberration</td>
</tr>
<tr>
<td>CSL</td>
<td>Coincidence site lattice</td>
</tr>
<tr>
<td>CTEM</td>
<td>Conventional transmission electron microscopy</td>
</tr>
<tr>
<td>DF</td>
<td>Dark field</td>
</tr>
<tr>
<td>dhkl</td>
<td>Interplanar spacing of the plane (hk(i)l)</td>
</tr>
<tr>
<td>E</td>
<td>Energy</td>
</tr>
<tr>
<td>e⁻</td>
<td>Electron</td>
</tr>
<tr>
<td>f</td>
<td>Lattice mismatch</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>ELNES</td>
<td>Electron energy loss near-edge structure</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron backscatter diffraction</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental scanning electron microscopy</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt (1.60 · 10⁻¹⁹ kg m² s⁻²)</td>
</tr>
<tr>
<td>fcc</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>FEG</td>
<td>Field emission gun</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam microscopy</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier transformation</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>GB</td>
<td>Grain boundary</td>
</tr>
<tr>
<td>HAADF</td>
<td>High angle annular dark field</td>
</tr>
<tr>
<td>h</td>
<td>Hour(s)</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal close-packed</td>
</tr>
</tbody>
</table>
hkl  Miller indices
hkil  Bravais-Miller-indices
HRTEM  High resolution transmission electron microscopy
kV  Kilovolt (1000 V)
mbar  Millibar ($10^5$ Pa)
MBE  Molecular beam epitaxy
min  Minute(s)
mm  Millimeter ($10^{-3}$ m)
nA  Nanoampere ($10^{-9}$ A)
nm  Nanometer ($10^{-9}$ m)
OR  Orientation relationship
pA  Picoampere ($10^{-12}$ A)
Pa  Pascal
r  (Equivalent) Radius
ROI  Region of interest
Sapphire  $\alpha$-Al$_2$O$_3$
SAD  Selected area diffraction
SDD  Silicon drift detector
SE  Secondary electrons
s  Second(s)
SEM  Scanning electron microscopy
STEM  Scanning transmission electron microscopy
t  Time
T  Temperature
Tm  Melting point
TB  Twin boundary
TD  Transverse direction (EBSD)
TEM  Transmission electron microscopy
u  Spatial frequency
UHV  Ultra-high vacuum
V  Volt
x  Power law exponent
X-FEG  Extreme field-emission gun
XRD  X-ray diffraction
YSZ  Yttria-stabilized zirconia
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Z</td>
<td>Atomic number</td>
</tr>
<tr>
<td>°C</td>
<td>Celsius</td>
</tr>
<tr>
<td>α</td>
<td>Coefficient of thermal expansion</td>
</tr>
<tr>
<td>γ</td>
<td>Surface or interface energy</td>
</tr>
<tr>
<td>Δf</td>
<td>Defocus</td>
</tr>
<tr>
<td>θ&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Convergence semi-angle</td>
</tr>
<tr>
<td>θ&lt;sub&gt;w&lt;/sub&gt;</td>
<td>Wetting or contact angle</td>
</tr>
<tr>
<td>θ</td>
<td>Collection semi-angle</td>
</tr>
<tr>
<td>ρ</td>
<td>Density [g/cm³]</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>χ</td>
<td>Aberration function</td>
</tr>
<tr>
<td>W&lt;sub&gt;ad&lt;/sub&gt;</td>
<td>Thermodynamic work of adhesion</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometer (10⁻⁶ m)</td>
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</table>
1 Introduction

Thin films are deployed for various applications ranging from optics as antireflective coatings, chemistry as adhesion layers, diffusion barriers or chemical sensors to mechanics as wear resistant hard coatings or microelectromechanical systems. Thin films are used in magnetic random access memory devices, solar cells, transistors or as electrodes for water splitting [1-10]. The microelectronic technology is the major application field for thin films, whereby aluminum (Al) and copper (Cu) are common interconnect materials [10-12].

Due to a high surface to volume ratio, thin films are usually thermodynamically unstable and prone to degradation if exposed to sufficiently high temperatures that overcome the activation energy for diffusion [13]. The transformation of a dense film to a set of particles, dewetting, can occur well below the melting temperature of the thin film material and is termed solid state dewetting. Solid state dewetting research focused in the past especially on the prevention of the harmful consequences of dewetting. The temperature induced diffusion based degradation processes during processing and operation can ultimately lead to failure of thin film devices [14, 15]. Recent research showed the beneficial potential of solid state dewetting for nanopatterning processes [13, 16-19]. The combination of template techniques, e.g. lithography, selective etching or substrate topography modifications, and controlled solid state dewetting can be used for the production of particle arrays with defined shape, size and composition [20-26]. Subsequent usage of the defined, dewetted particle arrays as catalysts for nanowire growth, e.g. using the well-established vapor-liquid-solid mechanism by Wagner and Ellis [27], demonstrated the potential of dewetting engineering [28]. Nanowire growth can also occur self-catalytically out of the agglomerated, dewetted film [29].

The underlying mechanisms of solid state dewetting are still not fully understood, especially considering single crystalline films [13]. Dewetting initiates typically at defects like grain boundaries by grooving or void formation. Growth of the features may lead to a rupture of the film and the formation of holes. Further film retraction leads to the formation of individual particles [13, 30]. Dewetting is influenced by various properties of the initial thin film system including the film thickness, grain size, grain growth, grain orientation, texture and the type of substrate material [31-34]. For this reason, model systems are generally used to study solid state dewetting mechanisms and to develop strategies to control dewetting [35].

Miniaturization in microelectronics leads to decreasing film thicknesses in thin film devices, whereby solid state dewetting is an undesired degradation process [13, 36, 37]. Surface diffusion has usually been considered as the dominant diffusion process. Thus, the addition
of a capping layer and subsequent suppression of surface diffusion is a possibility to prevent solid state dewetting [13]. Recent works showed that grain boundary and interface diffusion can be of high importance for solid state dewetting as well [38-40]. Niekiel reported solid state dewetting for Au thin films below a capping layer [41]. Temperature induced void formation and growth was also observed for passivated Al thin films on Si [42-44]. Thermal stresses were identified as driving forces and grain boundary diffusion as material transport mechanism. In-situ experiments by optical microscopy were carried out by Sugano et al. to monitor void formation on the µm length scale [45]. Void formation below a continuous oxide layer was reported for Al thin films [46, 47]. However, details of the void formation mechanism are still unclear.

Temperature induced processes during film growth or thin film processing occur in parallel and may interfere with the solid state dewetting behavior of thin films [48]. Grain growth is well-known for thin film systems to happen during thermal treatment [49]. Minimization of the total grain boundary area as well as of the grain boundary and interface energies are the driving forces. Therefore, grain growth is also often connected to a change of the grain orientation, or texture evolution as a special case, via the minimization of the total grain boundary energy and interface energy [48]. The out-of-plane orientation of grains is driven by the minimization of the surface as well as of the interface energies. For face-centered cubic metals, the \{111\} surfaces have typically the lowest surface energy [50] which leads to \{111\} out-of-plane orientation for thin films. Interface energies and grain boundary energies determine preferred in-plane orientations. The deposition procedure and further parameters, e.g. the choice and treatment of the substrate, influences the interface (energy) and consequently the texture formation. This was shown for example for Au thin films on amorphous substrates where no preferential in-plane or out-of-plane orientation was observed [36, 51]. In contrast epitaxial orientation relationships and a low number of defined in-plane orientations are often found for thin films on single crystalline substrates [52, 53]. Depending on the substrate treatment or the deposition parameters, polycrystalline thin films with \{111\} out-of-plane orientation and random in-plane grain orientations can also be achieved for single crystalline substrates as shown for example for Au or Cu films on (0001) oriented sapphire substrates [39, 54].

Thin film processing by heat treatments can change the grain size and the grain orientation. Niekiel et al. reported the texture evolution of Au thin films from random orientation to a \{111\} texture with increasing annealing time in-situ using transmission electron microscopy (TEM) [36]. Dehm et al. reported for a bicrystalline \{111\} Al thin film on single crystalline (0001) sapphire the growth of a single twin variant at the expense of the other with increasing
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annealing time [55]. Westmacott et al. carried out an extensive study of the microstructure and texture of various metallic films with face-centered cubic, body-centered cubic and hexagonal close-packed crystal structures on differently oriented Si and Ge [52]. In conclusion, texture control in thin films is complex, but can be achieved by adjusting different experimental parameters before, during and after thin film deposition [52].

As stated above, grain boundaries or grain boundary triple junctions may act as initial points for solid state dewetting. Thus, grain size, grain growth behavior and grain orientation may influence the solid state dewetting behavior. Müller and Spolenak stated that the shape of annealing induced holes is influenced by adjacent grains and void growth may proceed along high angle grain boundaries [51]. Derkach et al. supported the effect of grain boundaries on hole morphology and hole growth during solid state dewetting by numerical simulations [56]. Rabkin et al. reported the dewetting and hole formation of Ni films on single crystalline sapphire in distinct crystal directions, which can be used for targeted film patterning [57]. Thus, defined model systems without or with a reduced number of grain boundary types have often been used to study solid state dewetting mechanisms, like single crystalline Si (100) films on amorphous SiO2 substrates [58] or single crystalline Ni films on MgO substrates [37], as recently reviewed by Leroy et al. [35].

Mechanisms and models are often derived from post mortem analysis [59]. In contrast, in-situ techniques allow the direct observation of the dynamical processes and subsequently refinement or development of new models, demonstrated for various systems ranging from mechanics [60] to phase transformations or catalytic processes like graphene growth [59, 61]. Beside ex-situ studies, solid state dewetting of thin films without capping layers has also been studied by in-situ methods [62]. Applied in-situ techniques included electrical resistance [63], low-energy electron microscopy [64, 65], Auger electron spectroscopy [66], laser light transmission [67, 68], confocal laser microscopy [69, 70], atomic force microscopy [71], X-ray diffraction [51, 72, 73], time resolved differential reflectometry [74], scanning electron microscopy (SEM) [31] and TEM [36, 75, 76]. High spatial resolution is only achieved by SEM or TEM, but for these methods the observed processes are usually limited to high vacuum conditions. In the present work, the solid state dewetting processes below a capping layer were investigated using in-situ techniques at low pressures in a dedicated environmental SEM (ESEM). In-situ as well as ex-situ annealing experiments were combined with state of the art characterization techniques at high spatial resolution including scanning TEM (STEM) and electron energy loss spectroscopy (EELS).
1.1 Aim of the thesis

The aim of this thesis is to discover phenomena occurring during the annealing treatment of two defined model systems. Both systems were grown by molecular beam epitaxy (MBE) and contain Al grains possessing orientation relationships (OR) with the underlying sapphire substrate. For the system, termed bicrystalline, the close-packed planes and directions of the film and the substrate are parallel and the Al grains are twinned resulting in two OR, termed \( OR\ I\ a/b \). A second set of twinned Al grains \( OR\ II\ a/b \) with 30° rotation relative to \( OR\ I\ a/b \) is contained in the second model system, which is termed tetracystalline in the following.

The tetra- and bicrystalline Al thin films on single crystalline \((0001)\ \alpha\text{-Al}_2\text{O}_3\) were annealed at temperatures below the melting point of Al \( (T_m (Al) = 660°C) \), where besides grain growth also solid state dewetting occurred. The native oxide served as the surface diffusion suppression layer during the annealing treatment at 600°C. The as-deposited as well as the annealed Al thin films were characterized using various analytical techniques at different length scales. The microstructure was investigated using SEM, electron backscatter diffraction (EBSD) and X-ray diffraction (XRD). Site-specific cross-sectional specimens were prepared by focused ion beam (FIB) microscopy and characterized in depth by TEM techniques including atomic column resolved STEM, energy-dispersive X-ray spectroscopy (EDS) and EELS. The dynamics of the processes were also studied by in-situ annealing XRD and in-situ ESEM.

The outline of thesis is as follows. After the introduction, the process of solid state dewetting and the Al/Al\(_2\)O\(_3\) model systems are described in chapter 2. The experimental details of the thin film growth, thermal treatments and the characterization techniques are reported in chapter 3. Chapter 4 focuses on the synthesis of a defined epitaxial, tetracystalline model system and its microstructural evolution with annealing time. The underlying diffusion mechanisms leading to void formation and the corresponding interfaces are investigated in depths in chapter 5. The dynamics of the solid state dewetting mechanisms are studied in-situ in chapter 6. The thesis ends with a summary in chapter 7 and an outlook is given.
2 Theoretical background

2.1 Solid state dewetting

Dewetting is generally used to describe the temperature induced fragmentation of thin films into particles (Figure 2-1) [13, 30]. The driving force for dewetting is the minimization of the total energy. The process can occur below the melting temperature of the material in the solid state, which is in that case termed solid state dewetting.

Dewetting can be beneficial for targeted patterning or a disadvantageous degradation mechanism of thin film devices [13, 23, 35]. Due to the miniaturization of microelectronic components where interconnects decrease in thickness the importance of dewetting research raises. The excess surface energy is high for thin films due to their large surface area to volume ratio. Thus, the capillary driving forces increase and consequently the needed dewetting temperature decreases with decreasing film thickness [13, 77]. Thompson reviewed the solid state dewetting phenomena for thin film systems recently [13].

![Figure 2-1 Idealized scheme of the solid state dewetting process of a dense thin film with an isotropic surface energy into isolated particles.](image)

2.1.1 Thermodynamics

Thin films are usually in non-equilibrium in the as-deposited state and tend to dewet at elevated temperatures with time. The process is driven by the reduction of the total energy, whereby different energy terms contribute. The reduction of surface energies and interfaces energies dominates due to the high surface to volume ratio of the as-deposited film compared to a set of particles with a much lower total surface and interface area after dewetting. Grain boundary energy and defect energy reduction are further driving forces. Depending on the film material, substrate material (and crystallography), film thickness and e.g. annealing parameters texture evolution and grain growth can take place [13, 55]. The equilibrium shape of a liquid particle/droplet, formed during (de)wetting on a rigid substrate surrounded by a
vapor phase (Figure 2-2) for an isotropic surface energy, can be described by the Young-Laplace equation (Equation 2-1).

\[
\gamma_{SV} = \gamma_{LS} + \gamma_{LV} \cos(\theta_w)
\]

(Equation 2-1)

Here \(\gamma_{SV}\) is the solid-vapor interface energy (solid-vapor interface energies are generally termed surface energies), \(\gamma_{LS}\) is the liquid-solid interface energy, \(\gamma_{LV}\) is the liquid-vapor interface energy and \(\theta_w\) is the contact angle. The contact angle can have values between 0° and 180°, whereby 0° means complete wetting (spreading of the liquid) and 180° means non-wetting. In most cases, partial wetting with a contact angle between 0° and 180° is found [30]. Thermodynamic data, such as the thermodynamic work of adhesion \(W_{ad}\) or interfacial energies, can be derived from high temperature wetting experiments [78, 79] like e.g. sessile drop experiments [80, 81].

![Figure 2-2 2D presentation of a liquid drop with an isotropic surface energy on a solid substrate in its equilibrium shape according to Young’s equation.](image)

The surface energy of a crystal is generally anisotropic leading to a faceted equilibrium shape of a dewetted solid particle instead of a rounded shape for an isotropic surface energy. For a given volume, the equilibrium crystal shape of an isolated particle can be obtained using the Wulff construction [30, 82-84] and is exemplary shown for Al in Figure 2-3a. The following surface energies of Al, calculated by Vitos et al. [50], were used: \(\gamma_{(111)} = 1.199\) J/m², \(\gamma_{(110)} = 1.271\) J/m² and \(\gamma_{(100)} = 1.347\) J/m². For the Wulff construction, a polar plot of the surface energies depending on their orientation (\(\gamma\)-plot) is drawn. The Wulff shape with the minimal surface energy is determined by the convex inner shape all surface normals while the vector length is proportional to the surface energy of the corresponding facets. The influence of a substrate on the equilibrium shape of a particle is taken into account in the so-called Winterbottom construction [85]. This approach can be used for the determination of the substrate-particle interface energy \(\gamma_{SP}\) (replacing \(\gamma_{LS}\) in the Young-Laplace equation), which is correlated to the distance of the center of the Wulff shape from the substrate, as indicated in Figure 2-3b [30, 78]. Liquid or solid state dewetting can be utilized to study surface energy
anisotropy by analysis of the equilibrium crystal shape, demonstrated e.g. for Ni on Al₂O₃ substrates by Meltzman et al. [86] or for Cu on Al₂O₃ substrates by Chatain et al. [87].

![Equilibrium Wulff shape of an Al crystal in a vapor phase](image1) ![Schematic drawing of the Winterbottom construction](image2)

*Figure 2-3 a) Equilibrium Wulff shape of an Al crystal in a vapor phase (Wulff construction performed using the WulffMaker code by Zucker et al. [84]. b) Schematic drawing of the Winterbottom construction of a particle equilibrated on a rigid substrate including the particle-substrate interaction (adapted from Sadan et al. [78]).*

### 2.1.2 The process of solid state dewetting

Annealing of thin films below the melting point may initiate solid state dewetting by overcoming the activation barrier. In addition, further microstructural changes may occur concurrently and might influence the dewetting behavior. Especially, grain growth and texture evolution are well-known phenomena induced by temperature [35, 48]. The process of solid state dewetting can be sectioned into different stages. Voids nucleate and grow until the film ruptures and holes form. Subsequent hole growth via edge retraction due to capillarity forces finally leads to the formation of islands [13, 30].

For polycrystalline systems, grain boundaries or grain boundary triple junctions are considered as initial points for void formation (Figure 2-4a) [13, 88]. For single crystalline thin films no mechanism has been established yet [13], but existing holes or defects like e.g. impurities or substrate steps are considered as initial points for dewetting [89]. Void nucleation is often described by grain boundary grooving from the film surface towards the substrate and dominated by surface diffusion [13, 88, 90]. The group of Rabkin et al. recently addressed that grain boundary and interface diffusion need to be considered for solid state dewetting processes [40]. Grain boundary and interface diffusion are the only relevant diffusion pathways if a continuous capping layer on top of the film surface prevents surface diffusion. Void nucleation may also be initiated at the film|substrate interface (voids inside...
the film are also termed pinholes or pores [91]) and void growth towards the film surface may break the film up (Figure 2-4b) [91-93]. In both cases, growth of voids or grooving might occur preferentially along grain boundaries towards the surface and as such the growth speed depends on the type of grain boundary [91]. Simrick et al. studied the dewetting of Ag thin films on yttria-stabilized zirconia (YSZ) and observed a combination of grain boundary grooving from top and void growth from the Ag|YSZ interface towards the surface [94]. Void formation was reported in literature for different systems, e.g. Au films on passivated Si or SiO$_2$ [91, 95], Au films on YSZ [93], Pt films on YSZ [96, 97], Au/Ni bilayer films on passivated Si [98] and Ni films on SiO$_2$ substrates [99].

Void/pore formation and growth at the film|substrate interface can only be explained by sufficient fast diffusion pathways along grain boundaries and/or interfaces. Details of the void formation mechanism at the film|substrate interface are still unclear. However, grain boundary|substrate triple junctions and substrate defects seem to play an important role here [13, 30].

![Figure 2-4 Schematic drawings of initial steps of solid state dewetting: a) Grain boundary grooving from the free, top surface down towards the substrate (adapted from Amram et al. [40]). b) Void (or pore) formation at a grain boundary at the substrate-film interface and subsequent growth towards the free surface (adapted from Rabkin [100]).](image)

Void growth occurs via edge retraction due to capillary forces. In general, the formation of a rim and a valley at the edge retraction front is observed (Figure 2-4a) [13, 39, 40, 51, 101, 102]. Valley deepening until the film|substrate interface is reached may lead to a film break-up [13, 35]. In contrast, solid state dewetting without rim formation was observed for a few thin film systems as well [31, 38, 40].
2.2 Al thin films on (0001) α-Al$_2$O$_3$ substrates

2.2.1 Material properties

Al is the third most abundant element from the earth crust and is highly oxophilic. Thus, it is prone to oxidation, whereas the oxide scale often acts as a passivating layer [103, 104]. Al crystallizes in a face-centered cubic Bravais lattice (fcc; space group no. 225: $Fm\overline{3}m$ [105]) and its most stable oxide [106] α-Al$_2$O$_3$ is rhombohedral, but is commonly described as hexagonal Bravais lattice (hcp; space group no. 167: $R\overline{3}c$ [107]). Within the crystal structure, the O$^2-$ anions form the hcp lattice, in which Al$^{3+}$ cations occupy two thirds of the octahedral sites [107]. A brief summary of the properties of Al and sapphire is given in Table 2-1 [103, 105, 107-109].

Table 2-1 Selected properties of Al and α-Al$_2$O$_3$

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>α-Al$_2$O$_3$ (sapphire/corundum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point [°C]</td>
<td>660</td>
<td>2050</td>
</tr>
<tr>
<td>Bravais lattice</td>
<td>fcc</td>
<td>hcp</td>
</tr>
<tr>
<td>Lattice constant [Å]</td>
<td>$a_0 = 4.0496$</td>
<td>$a_0 = 4.7589$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c_0 = 12.991$</td>
</tr>
<tr>
<td>Density $\rho$ at 25°C [g/cm$^3$]</td>
<td>2.70</td>
<td>3.99</td>
</tr>
<tr>
<td>Coefficient of thermal expansion at 25°C [K$^{-1}$]</td>
<td>$\alpha_a = 23.1 \cdot 10^{-6}$</td>
<td>$\alpha_a = 5.22 \cdot 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_c = 5.92 \cdot 10^{-6}$</td>
</tr>
</tbody>
</table>

2.2.2 Defined model systems for solid state dewetting

Temperature induced failure of aluminum thin film interconnects has always been an object of research, where void formation below a passivation layer was reported [110, 111]. Void formation was reported for solid state annealing of polycrystalline or {111} textured Al thin films on single crystalline (0001) sapphire by Dutta et al. [46, 47]. In contrast in the present work, well-defined bicrystalline and tetracrystalline Al thin films were chosen to reduce the influence of grain boundaries and texture [56]. It is well-known from literature that Al thin films can be grown epitaxially on single crystalline sapphire using MBE [53]. A heteroepitaxial orientation relationship ($OR\ I\ a/b$) has been reported for Al thin films on sapphire with the close-packed planes and directions of Al and sapphire parallel to each other and with two twin related growth variants [55]. The (0001) plane of sapphire, termed the basal plane or c-plane [112], and the Al (111) plane with the in-plane orientation of one twin variant are shown in Figure 2-5. A second twinned orientation relationship $OR\ II\ a/b$, with 30° rotation relative to $OR\ I\ a/b$, has also been reported in literature [53]. These orientation relationships will be referred to as:
Theoretical background

\[ \text{OR I } a/b \{111\} \pm \langle \text{110} \rangle_{\text{Al}} \parallel (0001) \langle 10\overline{1}0 \rangle_{\text{Al}_2\text{O}_3} \quad (\text{Equation 2-2}) \]

\[ \text{OR II } a/b \{111\} \pm \langle 2\overline{1}\overline{1} \rangle_{\text{Al}} \parallel (0001) \langle 10\overline{1}0 \rangle_{\text{Al}_2\text{O}_3} \quad (\text{Equation 2-3}) \]

The “±” indicates the two symmetrically equivalent twin variants \( a \) and \( b \), which differ by a 180° rotation around the \( \langle 111 \rangle \) surface normal.

In this work, mazed bicrystalline Al thin films on sapphire possessing only \( \text{OR I } a/b \) and tetracryalline Al thin films on sapphire containing \( \text{OR I } a/b \) and \( \text{OR II } a/b \) have been used as defined model systems, whereby surface diffusion is suppressed for both by the surface oxide. Solid state dewetting phenomena and the microstructural evolution induced by annealing below the melting point of Al were investigated using ex-situ and in-situ techniques.

Figure 2-5 The basal plane of sapphire viewed in [0001] direction with the underlying hexagonal close-packed anion sublattice, where the large open circles represent the \( O^{2-} \) ions, small filled circles \( Al^{3+} \) ions and small, open circles unoccupied octahedral interstices (modified from Kronberg [113]). b) The \( \{111\} \) plane of fcc Al with the \( \langle 1\overline{1}0 \rangle \) direction parallel to \( \langle 1\overline{0}\overline{1}0 \rangle \) of \( \text{Al}_2\text{O}_3 \) as in \( \text{OR I } b \) (crystal lattice created using EjeZ [114, 115]).
3 Experimental details and characterization methods

In the following chapter, the experimental details for the thin film growth and the annealing conditions are given. Furthermore the applied characterization techniques are briefly explained. The parts describing the used experimental parameters and conditions are based on publications [73, 116, 117].

3.1 Thin film growth conditions

Thin film growth was carried out in two customized MBE systems, both operated under ultra-high vacuum (UHV) conditions (base pressure $\approx 10^{-9}$ mbar), located at the Max-Planck-Institut für Eisenforschung GmbH in Düsseldorf and the Max Planck Institute for Intelligent Systems in Stuttgart (DCA instruments, Finland), respectively.

(0001) oriented $\alpha$-Al$_2$O$_3$ two inch wafers (miscut of $<$0.25°, one side polished, thickness 330±25 µm, CrysTec Kristalltechnologie, Berlin, Germany) were used as substrates for thin film growth. Different substrate treatments were applied which will be described below.

The MBE system in Düsseldorf is equipped with a thermal evaporator loaded with Al (Al purity: 99.999 %, Kurt J. Lesker Company, England and Wales) which was used for thin film deposition. The wafers were ultrasonically cleaned in water, acetone and ethanol (3 times 5 min for each solvent). Before film deposition, the substrates were annealed under UHV conditions within the MBE chamber at 1000°C for 30 min to remove structural defects and contaminants. The background pressure of the chamber stayed below $2\cdot10^{-8}$ mbar, except during the first shutter opening of the thermal effusion cell, which led to a rise to $1.6\cdot10^{-7}$ mbar. The nominal film thickness and deposition rate were chosen to be 250 nm and 17.1-29.0 Å/min, respectively. The sapphire substrate was kept at nominally room temperature during the growth. However, since the deposition system setup did not allow for substrate cooling, radiation heating caused by the effusion cell led to an increase in the substrate temperature up to 82°C. Thin films deposited using this system were used for the experiments and results reported in the chapters 4 and 5.

The MBE system in Stuttgart is equipped with an electron beam evaporator loaded with Al (Al purity: 99.999 %) and allows substrate cleaning by Ar$^+$-sputtering. Within the MBE system, carbon and calcium surface contaminants on the substrate were removed by Ar$^+$-bombardment (kinetic energy 200 eV, 5 min) and structural defects were healed by subsequent annealing at 1000°C for 60 min [55]. The background pressure before deposition
Experimental details and characterization methods

stayed below $4 \cdot 10^{-9}$ mbar. The nominal film thickness and deposition rate were chosen to be 50 nm and 0.3 Å/s, respectively. During deposition, the sapphire substrate was rotated and kept with active cooling at nominal room temperature during the growth. The films, deposited with this system, were used for in-situ annealing experiments summarized and discussed in chapter 6.

3.2 Annealing treatment conditions

Following the deposition, the coated wafers were cut in several pieces for subsequent annealing experiments. Ex-situ annealing for varying times was carried out for several samples to investigate the solid state dewetting behavior. The annealing time of the samples was varied between 1 h and 45 h. A ~1.10 m long pipe furnace (diameter 0.055 m) equipped with a custom made quartz pipe was used for annealing treatments in Ar protective atmosphere ($p = 1.1 \cdot 10^5$ Pa, Ar purity: 99.999%, two times purging with Ar before sample loading by pumping with a vacuum pump down to $< ~10$ Pa). The Al thin film samples were loaded to an Al₂O₃ boat which was inserted under Ar flow in the preheated furnace at the annealing temperature (600°C for the experiments described in the chapters 4 and 5). The samples were retracted under Ar flow and quenched in the cold zone of the furnace (the estimated cooling time down to 200°C was roughly 2 – 3 minutes). The partial pressures of residual gases (e.g. O₂ or H₂O) could not be determined in the pipe furnace. A flow in of oxygen containing gases could have occurred during sample insertion and retraction despite the Ar flow.

3.3 Characterization techniques

The micro- and nanostructure of the Al thin films and the texture was characterized using light microscopy, XRD, SEM, FIB and TEM techniques. In the following a basic description of the methods and a summary of the applied experimental parameters will be given. More details about the techniques can be found in various textbooks [59, 118-129].

3.3.1 X-ray diffraction

XRD is a frequently used technique to investigate the crystal structure and orientation relationships. XRD measurements were carried out to obtain information about the phases and the texture of the films. A Seifert diffractometer operating with Cu Kα radiation
Experimental details and characterization methods

(\(\lambda = 1.54\) Å) and equipped with parallel beam optics (polycapillary), a four-circle Eulerian cradle and point detector was used for collection of the X-ray diffraction data. The XRD patterns were recorded in the conventional \((\theta/2\theta)\) mode with a \(2\theta\) scan range from 20° to 120°, a \(2\theta\) step size of 0.05°, and a counting time of 0.5 s/step. The in-plane orientation and the \{111\} texture were determined using pole figures by tilting the normal of the sample out of the plane defined by the X-ray source and the detector to an angle \(\Psi\), which was varied from 0° to 85° in 5° increments. The intensities of the \{111\} Al reflections were then measured while the sample was rotated about the normal through an angle \(\Phi\) from 0° to 360° in 5° increments.

In-situ XRD annealing experiments were performed to study the texture evolution with the annealing time. A Bruker D8 GADDS diffractometer operating with Co K\(\alpha\) radiation (\(\lambda = 1.79\) Å) and equipped with parallel beam optics (polycapillary), a four-circle Eulerian cradle, an area detector and an Anton Paar DHS 1100 heating attachment was used for the in-situ study. The \{111\} pole figures used to determine the texture evolution were measured according to the procedure described above, where the angle \(\Psi\) was varied only from 0° to 70° in 5° steps. Pole figures were measured before annealing, during annealing at the target temperature of 600°C and after the annealing experiment in nitrogen atmosphere (cooling and heating rate 25 K/min) using a Bruker HIGHSTAR area detector (20 s/frame, approx. 90 min/pole figure). Quantitative pole figures were measured before and after heating using the Seifert diffractometer. The \{111\} peaks were grouped into three sectors and the corresponding intensities of the three sectors were averaged. The results are represented by the mean ± error, where the error is described by the standard deviation.

3.3.2 Electron microscopy

Electron microscopy allows the analysis of materials at different length scales by the usage of electrons as source of illumination. Different elastic and inelastic scattering processes occur during the interaction between electrons and matter within the so-called interaction volume, which size varies depending on the material and the energy of the electrons. Different signals can be collected by specialized detectors (selected signals are shown in Figure 3-1) and then used for imaging or chemical analysis. SEM covers the range from mm down to a few nm, whereby with TEM transmitted electrons allow to obtain information of even smaller features. For elastic scattering, the energy of the incident electron remains constant, whereby energy losses occur for inelastic scattering processes.
**3.3.3 Scanning electron microscopy**

In a SEM, a focused electron beam is scanned over the sample, signals are emitted due to the electron-sample interaction (Figure 3-1) and for each point a chosen, particular signal is collected. The most used signals for imaging are secondary electrons and backscattered electrons. Secondary electrons (< 50 eV by definition) are emitted from the surface-near region and result in topographical contrast. Strongly deflected, high energy electrons (backscattered electrons, BSE, >50 eV) can be utilized for images where a strong atomic number contrast occurs. Inelastic scattering can lead to the ionization of target atoms by exciting inner-shell electrons. The ionized atom can return to its ground state by filling of the empty state by outer-shell electrons. The transition can lead to the emission of an X-ray or an Auger electron with a defined energy, characteristic for the energy shell difference and unique for each element. X-ray and Auger emission are competing processes which are strongly depending on the atomic number, where X-ray emission dominates for heavy elements and Auger emission for light elements. For more details about SEM and correlated signals, see the book by Brandon and Kaplan [119] as well as the book by Goldstein [124].

SEM techniques were used for the characterization of the morphology and the composition of the as-deposited as well as the annealed Al thin films. Field emission gun (FEG) SEMs (a Jeol JSM 6500F and a Zeiss Merlin) operated at various accelerating voltages were used. For improved conductivity, the surface of the samples was coated with a thin layer of carbon (thickness ~1-1.5 nm) to avoid charging of the samples. The size distribution of the voids was determined using SEM micrographs at low magnification acquired using the in-lens detector of the Zeiss SEM. The micrographs were binarised and analyzed by ImageJ [130].

*Figure 3-1 Scheme of the interaction between an electron beam with a thin specimen. Different signals can be utilized for analysis.*
equivalent circle radius was calculated using the void area. The resulting size distribution histogram was analyzed using MatLab and Origin. The major peaks of the void size distribution data was fitted with a Gaussian fit and error bars were determined by the standard deviation.

3.3.3.1 Electron backscatter diffraction

Incoming electrons can be scattered multiple times within a thicker sample. The incoherently scattered electrons can act as an electron point source within the sample. The electrons of this virtual electron point source can then be coherently, elastically diffracted at lattice planes of the sample and form so-called Kossel cones. The intersection of the Kossel cones and a detector leads to an EBSD pattern which reveal information about the orientation and crystal structure of the samples [122].

Crystal orientation microscopy was performed by EBSD measurements to investigate the grain size distribution, grain growth, grain boundary type and the coincidence site lattice (CSL) boundary distribution, orientation within the film and orientation relationships relative to the substrate of the as-deposited as well as of the annealed Al thin films. A high-speed charge-coupled device (CCD) camera (DigiView) at the Jeol JSM 6500F SEM was used for pattern acquisition and TSL orientation imaging microscopy (OIM) was used for data analysis.

EBSD is a near-surface sensitive technique [122] where the lateral resolution is determined by the interaction volume between the electron beam and the sample using an incident electron beam being typically inclined by 20° [131]. To obtain high quality EBSD patterns for the quantitative analysis, high voltages of 20 kV (for 45h annealed films up to 30 kV) had to be used so that the native oxide layer covering the Al thin film is penetrated and the main signal is generated within the Al layer. In addition, high resolution EBSD measurements of smaller regions were carried out at 15 kV.

The mistilt of the sample normal was corrected for all EBSD datasets using the center peak of the Al \{111\} pole figure. The following parameters were used during EBSD analysis: grain tolerance angle 5°, minimum grain size 3 times step size of scan and removal of data points with a confidence index below 0.1. All EBSD datasets were aligned by in-plane rotation using the Al \{110\} and the sapphire \{10\bar{1}0\} pole figure for comparison and prevention of analysis artefacts by the sample misorientation. CSL grain boundary ratios were calculated using the corresponding boundary length ratios normalized to the sum of all CSL boundaries. Grain
size distribution data was generated for OR I and OR II using TSL OIM. For OR II grains, the equivalent circle diameter was calculated using the grain area. Due to the maze-like microstructure of OR I, the average grain width was determined by the line interception method instead of the equivalent diameter using TSL OIM or analyzing color coded orientation maps by ImageJ [130]. The subsequent histogram of the grain width (OR I) or the equivalent grain diameter (OR II) was analyzed using MatLab and Origin. For the grain width and the grain size, a log-normal fit was used and the data compared by the median value of each grain size distribution dataset. The error is represented by the 68% confidence interval [132] and the lower as well as the upper threshold is given in brackets after the median.

3.3.3.2 In-situ environmental scanning electron microscopy

Dedicated environmental electron microscopes enable the study of the dynamical processes in-situ during different stimuli [41, 59]. SEMs are usually operated at high vacuum conditions (~10^{-3} Pa), whereas environmental SEMs can be operate at higher pressures (up to 3000 Pa for the ESEM used in this thesis) which are closer to the conditions of e.g. ex-situ annealing treatments (1.1 \cdot 10^5 Pa, see chapter 3.2). In combination with a heating stage, the dynamics of solid state dewetting processes can be studied in-situ at high spatial resolution.

In-situ isothermal annealing experiments at 500°C respectively 550°C were carried out in a FEG ESEM FEI Quantum 200 equipped with a heating stage (up to 1000°C) and a gas supply unit (mass flow controllers from Bronkhorst) at the Fritz Haber Institute of the Max Planck Society in Berlin. The solid state dewetting experiments were performed in oxidizing (O_2, ~30 Pa) and reducing (67% H_2/33% N_2, ~50 Pa) atmosphere for time intervals of ~1 h up to ~15.3 h. The initial base pressure within the ESEM chamber prior the annealing experiments was below 5 \cdot 10^{-3} Pa. Temperatures were measured with a K-type thermocouple, spot-welded to a thin copper sample holder with an accuracy of target temperature ± 50°C. Secondary electron micrographs were acquired at 5 kV acceleration voltage using an Everhart-Thornley detector. Heat-up to the target temperature and selection of the region of interest for isothermal annealing experiments took up to 15 min. Representative areas were chosen as controlled by further micrographs at different locations. No electron beam induced effects influencing the dewetting phenomena were observed by comparing irradiated and non-irradiated regions. In-situ obtained SEM micrographs were processed using ImageJ [130] including the plugin suite FeatureJ [133] and the plugin Template Matching and Slice Alignment [134]. Individual voids were tracked during the in-situ experiment. The perimeter and the equivalent void radius was extracted from the in-situ SEM datasets by image
processing as a function of time. Facet velocities were determined by measuring the distance between the positions of the facet within a specific time interval. Prior to the in-situ experiment and post mortem the samples were characterized by XRD, SEM, EBSD, FIB and (S)TEM as described in the corresponding chapters.

### 3.3.4 Focused ion beam microscopy

The usage of Ga⁺ ion sources instead of electron sources allows besides imaging the local sputtering and thus machining of micro- or nanometer sized samples. In addition to local removal of materials, the combination of a FIB and a gas injection system (GIS) allows the deposition of different materials, depending on the precursor gas which is cracked by the FIB beam. Typically used materials are carbon, Pt and W. More general details about FIB can be found in the review article by Volkert and Minor [135] as well as in the textbook by Brandon and Kaplan [119].

Site-specific cross-sectional TEM specimens were prepared in dual beam focused-ion-beam systems (FEI Helios Nanolab 600 or 600i dual beam SEM/FIB, FIB gun 52° tilted relative to electron gun) using the lift out technique [136, 137]. A modified procedure according to Baram et al. [138], Schaffer et al. [139] and Langford et al. [140, 141] was applied. Schaffer et al. listed the detailed parameters for various material systems [139] which were modified in this thesis. Wedge pre-milling was applied because the interesting features are close to the surface as well as close to the Pt protection layer [139]. The main steps are shown in Figure 3-2 (6 h annealed sample, corresponding STEM investigations in chapter 5.2.1, Figure 5-4) and the procedure is described below. The used accelerating voltages and beam currents of the FIB varied depending on each sample. In principal, for coarse milling/coarse thinning the FIB was operated at 30 kV, for gentle thinning at 16 kV, and for final polishing at 5 kV.

The main steps of the FIB machining are described as follows. A protective Pt layer was deposited on top of the region of interest (ROI) using the gas injection system to protect the surface during the subsequent Ga ion milling. The Pt layer had dimensions of 10 to 15 µm in length and 1.5 to 2.5 µm in width (Figure 3-2a). The first 0.3 – 0.5 µm were deposited using the electron beam (3 kV, 1.4 nA), while the final Pt layer thickness of 1.5 – 3 µm was achieved by ion beam assisted Pt growth (30kV, ~40 to ~240 pA ion beam current). Afterwards, trenches around the Pt protective layer were milled using the regular cross section pattern using the stair step variant. The dimensions of the side trenches ① and ③ were up to ~25 µm in length, 10 µm in width and ~25 µm depth, the front trench ② was variable chosen to ensure tolerance during the lift out procedure (see Figure 3-2a). High ion currents
in the range from 9 to 47 nA were used. The decreasing milling accuracy due to the increasing ion beam blur [139] had to be considered to avoid milling of the region of interest, thus the wedge approach was also applied during trench milling (±2° tilt).

An undercut and a side cut were milled at low currents (~1 – 2 nA, tilt 0°, rectangle pattern) to separate the lamella from the specimen except of the remaining bridge above the side cut. The SEM micrograph in Figure 3-2b shows the resulting freestanding lamella with the free space at the bottom between lamella and specimen. The subsequent lift out procedure was usually carried out at a stage tilt of 0°. The micromanipulator was positioned close to the lamella (Figure 3-2c) and Pt was deposited (30kV, ~40 or ~80 pA) using the gas injection system to weld the lamella and the micromanipulator. The bridge to the specimen is disconnected by a freecut (~1 – 2 nA, tilt 0°, rectangle pattern).

After retraction of the micromanipulator and the attached lamella, the lamella was transferred to a TEM half grid (Figure 3-2d). The lamella was connected to the Cu post of the TEM half grid with Pt welding (30kV, ~40 respectively ~80 pA) and cut free from the micromanipulator. The Pt welding leftover (Figure 3-2e) was removed prior the thinning of the lamella (~1 – 2 nA, tilt 0°, rectangle pattern).

The thinning of the lamella was carried out using the wedge milling approach as described by Schaffer et al. [139]. Exact milling parameters depend on each sample, the settings listed in Table 3-1 reflect a typical thinning procedure. In general, coarse thinning at 30 kV down to a thickness of ~ 0.5 – 1 µm and subsequent gentle thinning at 16 kV down to ~200 nm was used. For both, coarse and gentle milling, the CCS (cleaning cross section) pattern was used iteratively, whereby the beam current was varied from high to low currents.

Each milling step was repeated on both sides of the lamella indicated by ± for the value of the relative tilt. In the FIB micrograph in Figure 3-2f an intermediate step during the coarse thinning is shown, whereby the thickness of the lamella decreased relative to the thickness after the lift out (Figure 3-2e). Additionally, the relative tilt was varied from high (~±3 to 4°) to low (~±1.2°) to avoid removal of the Pt protection layer and subsequent damage of surface near regions at higher beam currents. Due to the relatively large thickness of the sapphire substrate, low depth values were used for the CCS pattern during fine thinning to obtain a thin region of interest while considering time constraints (see STEM image in Figure 3-2j). The SEM micrograph in Figure 3-2g shows that the Pt protection layer was still intact after coarse milling. The wedge approach is schematically shown in Figure 3-2i which leads to a lamella with uniform thickness and intact Pt protection layer.
Figure 3-2 SEM and FIB micrographs illustrating the different steps of the site-specific FIB machining of a TEM lamella: a) Choice of the ROI and Pt deposition. b) TEM lamella after undercut. c) Welding of the lamella to the micromanipulator and freecut. d) Intermediate step during lift out. e) Lamella with the ROI for TEM (dashed line) after welding to the Cu post. f) Intermediate step during thinning. g) Lamella after coarse thinning. h) Lamella during final low-kV thinning. i) Scheme of the wedge pre-milling approach (modified after Schaffer et al.[139]). j) STEM micrograph of final lamella.
Final thinning of the lamella was carried out at 5 kV (16 pA, rectangle pattern) to minimize beam damage. The lamella thickness was estimated using live imaging at 3 kV in the SEM during the final milling process. The SEM micrograph in Figure 3-2h shows an intermediate step during thinning very close to the final thickness. High contrast at the ROI indicates a low thickness of the lamella. The STEM micrograph in Figure 3-2j of the corresponding region confirms that the Pt protection layer decreased in thickness, but is still intact and covers the specimen surface. The lower part of the lamella is thicker because thinning was only applied in the ROI close to the surface respectively Al|substrate interface due to time constraints. For the exemplary shown lamella relative thicknesses down to 0.1 thickness/inelastic mean free path (determined using EELS) could be reached using the described preparation approach.

<table>
<thead>
<tr>
<th>Table 3-1 Exemplary FIB settings applied for the thinning of TEM lamellae</th>
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<tbody>
<tr>
<td>Down to lamella thickness of (estimated by FIB imaging)</td>
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<tr>
<td>~1200 nm</td>
</tr>
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</tr>
<tr>
<td>~800 nm</td>
</tr>
<tr>
<td>~200 nm</td>
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3.3.5 Transmission electron microscopy

TEM enables high spatial resolution by detecting selected electrons after transmission of electron transparent samples. Due to the electron-specimen interaction (schematically shown in Figure 3-1), various signals are produced caused by different elastic and inelastic scattering processes. The concepts and methods applied in this thesis are briefly described below. For a detailed explanation of fundamental concepts of TEM and the correlated techniques, readers are kindly referred to [120, 121, 123, 127].

In conventional TEM (CTEM), scattering phenomena are utilized to obtain image contrast. The usage of apertures in the back focal plane, where the diffraction pattern forms, enables different imaging modes enhancing the contrast, where bright field (BF) and dark field (DF) are the most common. In BF imaging, the objective aperture is centered around the primary beam allowing only non-scattered or forward scattered beams to contribute to the image. Scattered beams are blocked by the aperture and the strong scattering regions appear dark in BF micrographs. Strong scattering can be caused by thick regions or regions containing heavy elements with large atomic numbers (incoherent scattering, Rutherford scattering) and for
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crystalline regions in the specimen mainly by Bragg diffraction (coherent, elastic scattering). For DF imaging, one diffracted beam is selected by centering of the objective aperture around certain reflections. Crystal(s) which scatter in the specific direction appear bright in the DF image. To minimize aberration effects, the incident beam is tilted on the optical axis of the microscope.

High resolution TEM employs the wave nature of electrons and the interference of transmitted and diffracted waves to achieve atomic resolution. For thin TEM samples, the weak phase object approximation (WPOA) can be applied which means that the interaction of the incident, plane electron wave is mainly altered in phase due to the projected potential of the specimen while the amplitude stays constant. After passing the sample, the electron wave, now called exit wave, is further modified by additional phase shifts due to aberrations of the lens systems and the distance the wave is traveling. The contrast transfer function (CTF) describes the transformation of spatial frequencies $u$ into an image wave and is exemplary shown in Figure 3-3.

![Figure 3-3 Plot of the CTF as function of the spatial frequency $u$ (modified from [142]). The information limit $1/e^2$ is represented by the purple, horizontal line.](image)

The CTF can be described with

$$CTF = A(u)E(u)B(u)$$

(Equation 3-1)

Here is $A(u)$ the aperture function, $E(u)$ the envelope function and $B(u)$ the aberration function, which can be approximated by $2 \sin \chi(u)$ for weak phase objects. The cut off of spatial frequencies due to the finite size of the aperture is described by $A(u)$. The spatial coherence of the source and chromatic effects limit the resolution due to damping of higher spatial frequencies and are described by $E(u)$. 

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If considering only the spherical aberration $C_s$ and the defocus $\Delta f$ the simplified aberration function $\chi(u)$ is:

$$\chi(u) = \frac{2\pi}{\lambda} \left( \frac{1}{4} C_s \lambda^2 u^4 - \frac{1}{2} \Delta f \lambda^2 u^2 \right) \quad \text{(Equation 3-2)}$$

Here $\lambda$ is the wavelength of the electron determined by the accelerating voltage.

The point resolution is defined as the first zero-crossing of the CTF above whereas a contrast inversion occurs. For a given spherical aberration $C_s$, the maximum point resolution is achieved at the so called Scherzer defocus:

$$\Delta f_{\text{Scherzer}} = -1.2\sqrt{C_s \lambda}$$

The resulting phase contrast images are directly interpretable until the point resolution, where all atomic positions appear dark on a bright background. However, a careful, detailed interpretation of high resolution TEM (HRTEM) micrographs includes comparative image simulations to avoid misleading interpretation due to contrast inversions. The usage of $C_s$ correctors improves the point resolution until it equals the information limit, which is defined as the spatial frequency where the CTF is damped by the factor $1/e^2$ compared to the undamped CTF.

STEM is carried out by scanning a convergent electron beam across the specimen and detecting a selected signal point by point. Different annular detectors are used to collect the transmitted electrons of certain collection angle ranges and are schematically shown in Figure 3-4. Forward scattered electrons are used for BF STEM imaging ($\theta_1 < 10^{-25}$ mrad). Due to the reciprocity theorem of scattering theory, BF CTEM imaging and BF STEM should produce the same contrast. Phase contrast images in STEM arise from the interference of plane waves in the convergent beam. Higher collection angle ranges are used for annular dark field (ADF, $25 < \theta_2 < 50$ mrad) STEM imaging (thick and crystalline areas appear bright in ADF).

![Figure 3-4 Schematic drawing of the STEM setup with the primarily used detectors for BF, ADF, HAADF imaging respectively EELS analysis and the corresponding semi-collection angle ranges (modified from [120]).](image-url)
Experimental details and characterization methods

Incoherent, elastically scattered electrons, detected at larger angles ($\theta_3 > 50$ mrad), are used for high angle annular dark field (HAADF) imaging. The intensity in HAADF micrographs can be described by the Rutherford cross section and is roughly proportional to the square of the atomic number $Z$ [143], where heavy elements appear bright and light elements appear dark in the micrographs. In contrast to HRTEM, due to their incoherent nature an intuitive interpretation of HAADF STEM micrographs is possible, which is especially advantageous for the analysis of HAADF high resolution STEM micrographs.

The resolution is determined by the dimension of the electron probe which can be improved by $C_s$ correctors in modern microscopes. The detected signals depend on the used convergence semi-angle $\theta_c$ which can be varied in modern microscopes to obtain defined experimental conditions. In addition, analytical signals can be detected with high spatial resolution in the STEM mode, where EDS and EELS are primarily used, especially due to their complementary nature. X-rays, characteristic for each element, are emitted due to the inelastic electron-specimen interaction as described in chapter 3.3.3. Compared to SEM, the detection of forward scattered electrons in TEM allows the analysis of the energy distribution of transmitted electrons which are dispersed according to their energy losses by a magnetic prism which is the basis for EELS. Compared to EDS, EELS allows a higher analytical spatial resolution, higher sensitivity for light elements and further information about the specimen, in addition to the elemental composition, like e.g. electronic structure, bonding or coordination of the atoms or specimen thickness. More details about EELS can be found in the review articles about analytical TEM by Brydson et al. [144] and about EELS by Egerton [145] as well as in the textbooks by Brydson [128], Egerton [121] and Ahn [129].

Characterization of the as-deposited as well as the annealed Al thin films with focus on the different interfaces and grain boundaries was carried out in depth using TEM. Sample characterization was carried out using a Jeol JEM-2200FS field emission gun instrument operated at 200 kV and a FEI Titan Themis 60-300 X-FEG S/TEM instrument operated at 300 kV, equipped with a probe $C_s$-corrector and a monochromator. The micrographs were recorded on a Gatan CCD camera with an image size of $2 \times 2$ k pixels (Jeol JEM) or a complementary metal-oxide-semiconductor (CMOS) camera with an image size of $4 \times 4$ k pixels (FEI Titan Themis). CTEM characterization was primarily carried out at the Jeol JEM. In this work, BF imaging was used to investigate the grain width of the Al thin film and the structure respectively the thicknesses of the different layers in general. Selected area diffraction (SAD) and HRTEM were used to determine the orientation of Al grains as well as of the sapphire substrate and their orientation relationships.
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STEM characterization was mainly carried out at the probe C$_s$-corrected FEI Titan Themis. HAADF STEM imaging was used to investigate which phases occur, to study the interface structure and to determine the orientation relationships between different layers of specimens in the as-deposited state and after annealing. Annular bright field (ABF) imaging was also used to image light element columns, where the outer half of the probe-forming aperture is collected by an appropriate ADF detector [127, 143]. EDS and EELS experiments were performed in STEM mode using a FEI Super-X windowless EDS system with four synchronized SDD detectors and a post column Gatan GIF Quantum ERS spectrometer [146] (used collection angle 35 mrad) respectively, both attached to the FEI Titan Themis. For STEM measurements a spot size of 1.5 nm (Jeol JEM) and 1.5 Å (FEI Titan Themis) was used, respectively. At the FEI Titan Themis, probe currents of ~70 pA have usually been used for imaging and 400 pA for EDS measurements. Three STEM detectors have usually been taken for imaging with the following collection semi-angle ranges: HAADF 73 – 352 mrad, BF <7 mrad and ABF (8-16 mrad). The convergence semi-angle has usually been 17 or 23.8 mrad.

EELS was used for phase identification as well as for determination of the relative thickness (thickness/inelastic mean free path) of TEM samples. For the electron energy loss near-edge structure (ELNES) measurements of the O-K edge (edge onset at ~532 eV [121, 147]) and the Al-L$_{2/3}$ edge (edge onset at ~73 eV [121, 147]), spectra with a dispersion of 0.1 respectively 0.05 eV/channel were recorded in the dual EELS mode. The full width at half maximum (FWHM) of the zero loss peak was ~0.5 eV using a monochromator for the Al-L$_{2/3}$ edge measurements for the chosen dispersion. The FWHM at 0.01 eV/channel dispersion was ~0.27 eV. STEM-EELS mappings were acquired with subsequent sum of the spectra of individual pixels to obtain high signal to noise ratios for the Al-L$_{2/3}$ edge for the three different Al-containing layers: the substrate, the Al thin film and the surface layer. The presented spectra were obtained by addition of 120 to 540 spectra at an acquisition time of 0.1 s (Al thin film, substrate) respectively 0.5 s (surface layer) acquired while scanning over an area of 36 nm by 10.8 nm (surface layer), 62 nm by 46 nm (substrate) respectively 62 nm by 21 nm (Al thin film). For O-K edge measurements the usage of the monochromator led to an insufficient signal to noise ratio, thus non-monochromated spectra were acquired with a FWHM of the zero loss peak ranging between 0.9 eV and 1.2 eV. High signal to noise ratios were obtained by addition of 5 spectra at an acquisition time of 5.0 s for the O-K edge. For all spectra, the pre-edge background was extrapolated using a power law function and subtracted from the original spectrum [121, 148].
Results of e.g. the thickness of the deposited Al films or the oxide scale are presented by the mean value ± standard deviation of several measurements averaging over different regions. Different programs (ImageJ [130], Gatan Digital Micrograph, FEI TEM Imaging & Analysis, MatLab, Origin, Excel) were used for data analysis.

For analysis of HR(S)TEM micrographs, fast Fourier transforms (FFT) and diffraction patterns, the software packages EjeZ [114, 115] as well as Jems [149] were used. The Al \{111\} lattice fringes were used for micrograph calibration. For the shown atomic column resolved STEM HAADF micrographs, image stacking of up to 120 images using the Smart Align software package [150] was applied to obtain high signal to noise ratios.
4 Microstructural evolution and solid state dewetting of tetracrystalline Al films

In this chapter, the temperature induced changes of the microstructure of epitaxial Al thin films on sapphire and the formation of voids are reported. It is based on a publication in *Acta Materialia* [73]. The solid state dewetting behavior is investigated in an ex-situ study by in-depth characterization using XRD, SEM, FIB and TEM methods.

4.1 Introduction

Thin films are usually not stable in the as-deposited state and will dewet or agglomerate when annealed to sufficiently high temperatures. The thermodynamic driving force is the reduction of the total energy of all surfaces and interfaces in the system. The formation of islands is the result after completion of the transformation process [13, 30]. In microelectronic or optoelectronic systems containing thin films dewetting is an undesired degradation process but it can be also a useful technique for targeted nanopatterning [13, 38]. Patterning strategies using dewetting were recently reviewed by Ruffino et al. [24]. Templated solid state dewetting was used to control the formation of complex patterns for various systems, e.g. shown for single crystalline Ni thin films on single crystalline MgO substrates [16]. The control of shape and size can be used for the fabrication of ordered arrays as shown for Pd and Ni thin films on MgO [20]. Especially the combination of solid state dewetting with nanofabrication methods [25] like template masking, electron beam lithography or photolithography is promising. Ruffino et al. used templated deposition techniques with subsequent solid state dewetting to produce self-organized patterned arrays for Au and Ag particles on SiO2 substrates [151].

The mechanisms of dewetting in solid state are still not fully understood, especially for single crystalline thin films [13, 76]. Surface diffusion has always been seen as the dominating diffusion mechanism for solid state dewetting [13, 76]. Recent studies of Kovalenko et al. [38], Amram et al. [40] and Kosinova et al. [39, 101] addressed the influence of interface respectively grain boundary diffusion.

In this study, we investigated the solid state dewetting behavior of a defined model system. Tetracrystalline epitaxial Al thin films on single crystalline (0001) α-Al2O3 (sapphire) substrates were annealed at temperatures below the melting point (Tm(Al): 660°C) under protective atmosphere. Surface diffusion processes were constraint by the presence of the
native oxide layer, thus volume, grain boundary and interface diffusion should dominate [40]. The surface layer leads to a sandwich-like three phase system (Figure 4-1) different to solid state dewetting studies of Ni [57], Au [92], Fe [38] or Au-Fe [72] thin films on ceramic substrates where only two phases are present.

Solid state oxidation experiments of polycrystalline Al thin films on sapphire (0001) revealed the formation of hollow cavities covered by a thin aluminum oxide layer in the vicinity of hillocks and the growth of oxide features at the Al/sapphire interface into the metal film [46, 47]. Finally, liquid dewetting experiments of Al thin films on the basal plane of sapphire in an ultra-high vacuum furnace by Levi et al. [152] showed the shape of single Al droplets after reaching the equilibrium state. A strong droplet/film-substrate interaction was reported, determining the morphology of the droplets and leading to a partly dissolution of the sapphire substrate and diffusing of the dissolved components along the Al|substrate interface [152].

Dehm et al. performed solid state thermal cycling experiments of bicrystalline Al thin films on sapphire (only twin variants of OR I) between 240 and 450°C which showed the growth of one twin variant on expenses of the other [55]. In a further study Dehm et al. reported the presence of a second heteroepitaxial relationship (OR II) in sputtered Al thin films on sapphire in addition to OR I after annealing treatment within the deposition system [54]. The presence of grains with a 30° rotated orientation relationship OR II with a higher full width at half maximum (FWHM) of the {111} pole figure compared to the ones of OR I was also reported by Medlin et al. [53]. Medlin et al. used a purely geometrical explanation for the formation of OR II and pointed out that a closely spaced (~14 Å) periodic array of near-coincidence sites is the reason for the stability of OR II. Both, OR I and OR II, exhibit twin variants each leading to a tetracrystalline microstructure.

In the present work the solid state dewetting mechanism of tetracrystalline films is investigated where surface diffusion is prevented due to an oxide scale. Special focus is laid on the starting points of the dewetting process, as they are still obscure. In addition, the microstructural evolution of the differently oriented grain population is studied and quantitatively analyzed using EBSD, XRD and in-situ annealing XRD. The micro- and nanostructure is characterized in depth using SEM, FIB and TEM techniques. For the details about thin film deposition and microstructure analysis the reader is referred to chapter 3.
4.2 Results

4.2.1 As-deposited film

θ/2θ XRD data of the Al thin film showed only \{111\} and \{222\} Al diffraction peaks in addition to (0006) and (00012) diffraction peaks of the sapphire substrate (Figure 4-2). \{111\} Al pole figures revealed the in-plane orientation of the epitaxial thin films (Figure 4-3a). Two orientation relationships (OR I and OR II, marked in Figure 4-3a) between Al and Al₂O₃ exist containing two twin-related growth variants. As described in chapter 2.2.2, the OR will be referred to as:

\[
OR\ I\ a/b\ \{111\} \pm (\overline{1}\overline{1}\overline{0})_{Al} \parallel (0001)\ \{10\overline{1}\overline{0}\}_{Al_2O_3} \quad (Equation\ 4-1)
\]

\[
OR\ II\ a/b\ \{111\} \pm (2\overline{1}\overline{1})_{Al} \parallel (0001)\ \{10\overline{1}\overline{0}\}_{Al_2O_3} \quad (Equation\ 4-2)
\]

The “±” indicates the two symmetrically equivalent twin variants \(a\) and \(b\) which differ by a 180° rotation around the \(\langle 111 \rangle\) surface normal. The formation of OR I and OR II is in accordance to literature [53, 54].

The lattice mismatches, \(f_{OR\ I}\) and \(f_{OR\ II}\), between the heteroepitaxial Al film and the sapphire substrate amount to [55, 105, 107]:

\[
f_{OR\ I} = \frac{d_{30\overline{3}0} - d_{22\overline{0}}}{d_{30\overline{3}0}} = -0.042 \quad (Equation\ 4-3)
\]

\[
f_{OR\ II} = \frac{d_{30\overline{3}0} - d_{2\overline{1}\overline{1}}}{d_{30\overline{3}0}} = -0.203 \quad (Equation\ 4-4)
\]

Figure 4-2 θ-2θ scan of the as-deposited Al (blue indices) thin film on sapphire (red indices)
With an Al \{220\}, Al \{2\bar{1}1\} and α-Al2O3 \{30\bar{3}0\} lattice plane spacing of $d_{220} = 1.431$ Å, $d_{2\bar{1}1} = 1.653$ Å and $d_{3\bar{0}3\bar{0}} = 1.374$ Å, respectively. The higher lattice misfit of OR II leads to larger misfit strain as for OR II. The OR II Al grains are rotated around the ideal $\langle 111 \rangle$ direction by $\pm 4^\circ$ as indicated by the pole figures derived by XRD and EBSD.

The diffraction peaks lie on arcs of a circle for OR II with an angle deviation of $\pm 9^\circ$ (Figure 4-3a). The arc and the peak splitting for OR II are more pronounced within the XRD data as compared to EBSD data due to better grain statistics. In contrast, sharp diffraction peaks of both OR I twin variants, which have a smaller lattice misfit, are observed.

Figure 4-3 a) Distribution of CSL boundaries and comparison of $\{111\}$ pole figures of the as-deposited film by XRD and generated from EBSD data (grain weighted) with OR I a/b and OR II a/b marked. b) High resolution orientation map in transverse direction (TD, 15 kV) indicating the grain orientation by overlaid cubes (white area not indexed), labels 1 to 6 indicate certain CSL boundaries (see text for details). OR I is shown in purple, OR II in green, each representing both twin variants. Σ3 \{2\bar{1}1\} twin boundaries are illustrated in white, Σ7 GBs in red, Σ13b GBs in yellow and further CSL boundaries of higher order in blue. c) Orientation map in TD acquired at 20 kV acceleration voltage. (Insert: inverse pole figure used for color coding all of the Al orientation maps in this thesis).
EBSD studies of the as-deposited film revealed the OR distribution and grain size in more detail (Figure 4-3b, c). The out-of-plane representation confirms the \{111\}_{\text{Al}} \parallel (0001)_{\text{Al}_2\text{O}_3} orientation relationship. The OR I twin variants (ratio ~1:1) form an interpenetrating network (see Figure 4-3c) with an area fraction of 79%. Thus, in the following the median grain width is used to describe the grain size distribution of OR I. The median grain width is 0.49 µm (0.26 – 0.89 µm). The OR I twin network is interrupted by OR II grains, which are in some cases twinned. The OR II grains (color coded in dark and light green) show a similar median diameter after deposition of 0.58 µm (0.28 – 1.21 µm), but with a much lower area fraction of 21%. Both OR are lognormally distributed, but OR I is narrower with a maximum grain size of ~4 µm, while for OR II grains with a diameter up to ~9 µm occur. The EBSD data were used to determine the grain boundary (GB) type. Due to the \{111\} growth of Al, the microstructure is dominated by CSL boundaries, random low angle or high angle grain boundaries play only a minor role and are not considered further.

More than 74% of all CSL boundaries are Σ3 twin boundaries (Figure 4-3b and c, white color). Exemplary Σ3 boundaries ① (58.5°) and ② (57.2°) with angles close to the theoretical value of 60° are marked in Figure 4-3b. The dominance of OR I twin boundaries can clearly been seen in the grain boundary distribution chart of the CSL type boundaries (Figure 4-3a). A value of 30° misorientation between OR I and OR II grains is expected from the angle between \langle1\bar{1}0\rangle_{\text{Al}} (OR I) and \langle2\bar{1}\bar{1}\rangle_{\text{Al}} (OR II). The observed grain boundaries between OR I and OR II are dominated by Σ7 (38.2°), Σ13b (27.8°) and Σ21a (21.8°) sigma boundaries and exemplary marked in Figure 4-3b (③ 28.9°, Σ13b; ④ 22.2°, Σ21a; ⑥ 38.5°, Σ7). Higher order CSL boundaries play only a minor role (Σ19b (46.8°), Σ31a (17.9°), Σ39a (32.2°) and Σ43a (15.2°)). OR II/OR II grain boundaries have a much lower fraction of Σ3 boundaries compared to OR I/OR I. Higher order CSL boundaries are found instead (Σ31a, Σ37c (50.6°) and Σ43a (15.2°)) beside a low fraction of Σ7, Σ19b and Σ21a. One example of a Σ37c is shown in Figure 4-3b (⑤ 50.9°, Σ37c).
TEM investigations of cross-sectional samples (Figure 4-4) show a uniform thickness of the film in the range of 242±2 nm. The error has been estimated from averaging over several areas. The majority of the grain boundaries are perpendicular to the basal plane of the sapphire substrate and columnar grains can be observed within the Al film. No voids are observed for the dense Al thin film in the as-deposited state. The dominance of \( \Sigma 3 \) twin boundaries and \( OR\ I \) is confirmed by selected area diffraction and by HRTEM experiments (Figure 4-4c). A thin surface layer is covering the film (Figure 4-4a/c). EDS analysis confirms the existence of a native oxide layer with a thickness in the range of 2.8 ±0.4 nm (Figure 4-5). No lattice fringes are observed indicating an amorphous nature (Figure 4-4c).

The formation of a thin oxide layer on top of the oxophilic Al is the cause for the passivating behavior of aluminum. It may be formed directly after film deposition within the MBE system due to residuals gases like \( \text{H}_2\text{O} \) or \( \text{O}_2 \) or after release of the sample out of the UHV system due to contact with atmospheric oxygen. During the fabrication of the TEM lamella Ga diffusion to the Al/Al grain boundaries and formation of well-known AlGa alloys may occur which embrittles the grain boundaries \([153, 154]\). This artifact may lead to the bright contrast at the grain boundary in Figure 4-4c as well as the film-substrate interface in Figure 4-4b. EDS measurements confirm Ga enrichment at the Al/sapphire substrate interface, at the...
Al/surface oxide interface as well as at Al grain boundaries (see Figure 4-5). The bright contrast at the Al/Al<sub>2</sub>O<sub>3</sub> interface may also be caused by an interface reconstruction [30].

*Figure 4-5 Cross-sectional STEM BF micrograph and corresponding O-, Al and Ga-EDS mappings showing Ga enrichment at the Al/sapphire substrate and at the Al/surface oxide interface as well as at Al grain boundaries.*
4.2.2 Microstructural evolution with annealing time by solid state dewetting

Al thin films were annealed at 600°C for different annealing times (1 – 45 h) under Ar atmosphere to investigate solid state dewetting phenomena. In top view SEM micrographs dark appearing features with distinct facets are already observed after 1 h annealing. An exemplary micrograph obtained for the 24 h annealed sample is presented in Figure 4-6.

![Figure 4-6](image)

*Figure 4-6 Orientation maps in TD showing the evolution of the in-plane orientation of the {111} Al film after annealing for different dwell times (OR I in purple, OR II in green, twin boundaries in white). In addition formation as well as growth of drum-like voids are visible which are represented in bright blue (sapphire signal). Bottom right: SEM micrograph of a dark appearing feature embedded within a uniform aluminum layer exhibiting distinct facets (only sections of full data set presented each). Please note that the images are not taken at identical positions.*

FIB cross sections of such features revealed that a thin membrane layer is still existing above a void where the original Al film has been retracted (see Figure 4-7). In some cases the signal of the void appeared bright as a consequence of a fracture of the surface layer covering the void and charging of the insulating sapphire substrate below (Supplementary figure 4-1). The faceted voids are indexed by EBSD as sapphire (see blue areas in orientation maps for
different annealing times in Figure 4-6). The faceted voids grow with annealing time (see Figure 4-6). Top view high resolution SEM micrographs recorded at low magnification were used to get statistical information about the void growth.

The analysis revealed a bimodal void size distribution as shown in Figure 4-8a for a 6 h annealed sample (665 analyzed voids). Voids with small radii of 0.6±0.2 µm dominate, but also a few bigger voids with radii up to 4.5 µm can be found after 1 h annealing. With increasing annealing time, the area fraction of voids increases from 1.4% after 1 h (max. radius 4.45 µm), 2.2% after 6 h (max. radius 6.15 µm), 3.5% after 24 h (max. radius 6.48 µm) and finally 9.5% after 45 h (max. radius 10.8 µm). The quantitative analysis has been performed for areas in the range of ~250 × 190 to 570 × 430 µm² (see Supplementary figure 4-2 to Supplementary figure 4-5). For each dataset, a bimodal void size distribution is found (see Supplementary figure 4-6) and summarized in Table 4-1.

Table 4-1 Change of void radius with annealing time (evaluated by Gaussian fit to two main classes of size distribution histogram, error bars represented by standard deviation)

<table>
<thead>
<tr>
<th>t [h]</th>
<th>( r_{1,\text{void}} \pm \sigma ) [µm]</th>
<th>( r_{2,\text{void}} \pm \sigma ) [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6±0.2</td>
<td>1.9±1.9</td>
</tr>
<tr>
<td>6</td>
<td>0.7±0.3</td>
<td>3.2±0.9</td>
</tr>
<tr>
<td>24</td>
<td>0.7±0.2</td>
<td>4.2±0.9</td>
</tr>
<tr>
<td>45</td>
<td>0.4±0.2</td>
<td>4.5±1.5</td>
</tr>
</tbody>
</table>

Figure 4-7 a) SEM micrograph showing a void before FIB cross sectioning at the region marked by the orange dashed line (1 h annealed sample). To protect the surface during FIB milling, Pt was deposited by electron beam and subsequent ion beam assisted Pt growth. b) Side-view SEM micrograph after FIB cross section revealing a void covered by a thin membrane (rarely visible in SEM). The Pt is not deposited within the void indicating a continuous surface membrane covering the whole void and the adjacent Al thin film. Milling (redeposition) respectively Pt deposition (overspray) artefacts caused a collapse of the membrane in the foreground of the micrograph.
The small voids are in the range of 0.4 – 0.7 µm independent of the annealing time, while the bigger voids grow from 1.9 µm (1 h) to 4.5 µm (45 h, Figure 4-8b). The occurrence of these two void size classes can be described by parallel formation of new voids and the growth of existing voids. A power law fit shows that the equivalent void radius $r_{2,\text{void}}$ scales with annealing time $t$ as $r_{2,\text{void}} \sim t^{0.23}$ (Figure 4-8b). In accordance to the results of e.g. Saiz et al. [155] we found ridge formation adjacent to the voids. The void formation and ridge growth will be addressed in more detail in chapter 5.

Parallel to the void growth, a change of the (111) Al texture and Al grain growth occurred. The trends of the microstructural evolution of the metallic film are shown in Figure 4-6 and Figure 4-9. For longer annealing times the area fraction of OR II increased at the expense of OR I as shown in Figure 4-9a. The amount of OR I decreased from ~79% to ~13% after 45h annealing.

The major change of the microstructure occurred within the first hour (drop to 33%). The median grain width for OR I increased from 0.49 µm (0.26 – 0.89 µm, as-deposited) up to 2.4 µm (1.35 – 4.17 µm, 45 h), but the twin ratio stayed approximately ~1:1 (Figure 4-9a and c). For OR II also grain growth occurred, but one of the twin variants was dominating (twin ratio after 45 h: 3.80:1). The OR II average median grain diameter increase was more pronounced. After 1 h annealing, the average grain diameter increased from 0.58 µm (0.28 – 1.21 µm) to 4.55 µm (1.48 – 14.03 µm). Until 45 h annealing, the grain size stayed constant as for OR I (average grain diameter: 4.93 µm (1.92 – 12.61 µm)), as shown by a simple power law fit analysis. At the same time, the grain boundary length per area was decreasing as expected. CSL number fractions normalized to the sum of all CSL boundaries (dashed line in
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Figure 4-9b) can be derived from the grain boundary lengths per area shown in Figure 4-9b. In detail, CSL boundaries were still dominating independent from annealing time whereby the number fraction of Σ3 CSL boundaries within the Al film was decreasing with annealing time (~74%, as-deposited ⇒ ~50%, 1 h). At the same time, the number fraction of especially Σ7 (~6% ⇒ ~10%), Σ13b (~6% ⇒ ~18%) and Σ21a (~5% ⇒ ~8%) was increasing noticeably. With proceeding annealing time the number fractions were increasing slowly, whereby Σ13b (~22% after 45 h) as well as Σ7 (~13%) were the dominating CSL boundaries after Σ3 (~40%, Figure 4-9b). In total, each CSL boundary length per area was decreasing during grain growth, the reduction of Σ3 boundaries compared to the others was more pronounced.

Figure 4-9 Evolution of area fraction of OR I within the Al film as well as OR II/OR I twin ratios with annealing time (a), CSL boundary length per area (b, sigma values of CSL boundaries shown), and median grain size of OR I and OR II grains (c,d).
4.2.3 Texture evolution results by in-situ annealing XRD pole figures

\{111\} pole figures were measured at 600°C in nitrogen atmosphere to investigate in-situ the texture evolution of the as-deposited thin film over time. Before and after the in-situ experiments \{111\} pole figures were measured using a point detector for quantitative analysis of the volume fraction of OR I and OR II. The pole figures are shown in Figure 4-10. Void formation was confirmed by SEM micrographs. Before annealing the Al thin film consisted of 80±3\% OR I and 20±3\% OR II (OR I a/b ratio: 1.2±0.5, OR II a/b ratio: 1.5±0.3) which is consistent with the EBSD results. The series of in-situ pole figures are shown in the bottom line of Figure 4-10. Artefacts of the experimental setup due to the area detector prevent a quantitative analysis (see intensity loss in marked sector in Figure 4-10), but the same trend of the texture evolution as found with EBSD can be seen. The major change in texture can be observed in the first in-situ pole figure after ~90 min (see intensity ratios in marked representative sector in Figure 4-10). OR II dominates whereby one twin variant OR II a is more strongly represented which is in agreement with the ex-situ EBSD results after 1h annealing (Figure 4-9a).

![Figure 4-10 Series of in-situ \{111\} pole figures before, during and after annealing at 600°C showing the texture evolution with annealing time. Artefacts of the area detector are marked. The artefacts originate in the background correction which was applied to reduce stray radiation mainly caused by the graphite dome of the in situ annealing device. OR I a/b and OR II a/b are marked in the upper right pole figures.](image-url)
The $OR\ I\ a/b$ twin ratio is close to 1.2 which also fits to the ex-situ annealing results where the ratio stayed below ~1.27 (Figure 4-9a). The in-situ $\{111\}$ pole figures acquired during further annealing show no notable changes in the intensity ratios of the marked sector. The quantitative analysis of the point detector $\{111\}$ pole figures respectively EBSD measurements (in brackets) after annealing (holding time 6 h at 600°C) shows a decrease of the volume fraction of $OR\ I$ to 21±2% (EBSD: 23%) and an increase of $OR\ II$ to 79±2% (EBSD: 77%). No changes in the twin ratio of $OR\ I$ can be found and the value remains at 1.2±0.2 (EBSD: 1.0). For $OR\ II$, one twin variant is dominating with 2.5±0.7 (EBSD: 3.0). The results are in agreement with the ex-situ annealing experiments in Ar atmosphere (Figure 4-9a).

4.3 Discussion

4.3.1 Microstructural and texture evolution

Annealing induced texture evolution towards $OR\ II$ and grain growth was observed for the highly $OR\ I$ textured Al thin film in the as-deposited state. The remaining $OR\ I$ areas are still in a mazed bicrystal structure as for the initial state which was also reported by Dehm et al. [55] for Al films on sapphire containing only $OR\ I$ as well as by Amram et al. [40] for as-deposited Ni thin films on sapphire. Competing grain growth/texture development is known to occur in polycrystalline films compared to single crystalline films [75]. The dominance of $OR\ II$ after annealing was not expected when only considering the lattice misfit of the metallic thin film and the rigid sapphire substrate. Ab initio calculations of the Cu (111)/α-Al2O3 (0001) interfaces for $OR\ I$ and $OR\ II$ revealed only very small differences for the total energy indicating that both orientation relationships compete [156]. Curiotto et al. supported this by determining the interface energies for the Cu/sapphire system using a Winterbottom construction of copper particles formed by dewetting [112]. The geometrical analysis by Medlin et al. [53] has already indicated near-coincidence sites for $OR\ II$ in addition to the well-established $OR\ I$ for fcc metals on sapphire which might lead to a low interface energy. An interface reconstruction as reported by Meltzman et al. for Ni thin films on sapphire [157] as well as the substrate preparation procedure for Cu thin films [158] leading to different terminations at the interface might also explain why $OR\ II$ oriented grains form. However, a full theoretical analysis is required to determine the energetics of $OR\ II$ for Al thin films in detail considering also the increased temperature.

In addition to a low interface energy, minimization of surface, grain boundary and strain energies have a strong influence for thin film systems and can promote grain growth and
texture evolution as pointed out by Thompson [48]. In the present case OR I and OR II have the same surface energies, and the Young's modulus is identical for both orientations leaving only the lattice mismatch and the corresponding interface energy as well as the grain boundary energy minimization as thermodynamic driving forces. Thompson reported that lattice matching between film and substrate is helpful, but not required for grain growth of a single orientation [49]. Since no misfit dislocations are observed and the interface may be reconstructed [157, 158], we speculate that grain boundary energies are of great importance. The preferential growth of OR II might also be controlled by kinetics. Compared to Σ3 boundaries in OR I, OR II containing ⟨111⟩ tilt boundaries have a higher grain boundary energy [159] and a higher mobility [160, 161]. The growth towards OR II grains might be a fast way for energy reduction of the whole system by reducing unfavorable high angle grain boundaries. In addition, the twin variant OR II a is overgrowing the other twin variant as observed in a previous study by Dehm et al. for OR I containing Al thin films on sapphire [55]. The driving force is the reduction in total grain boundary area (in particular Σ3 twin boundaries for the films of Dehm et al.) and is heading to a single crystalline state [55]. Barmak et al. [159] reported deep energy cusps for the relative grain boundary energies as function of misorientation angles of 28° and 38° as well as a shallow energy cusp at 21° which was determined experimentally for μm thick Al films on oxidized silicon. These observations explain the presences of Σ7 (38.2°) and Σ13b (27.8°) boundaries which dominate the OR I/OR II grain boundaries in addition to the Σ3 (60°) twin boundaries within OR II. The presence of these boundaries also explains the broadening of the OR II peaks in the ⟨111⟩ pole figure. In addition, the number fraction of Σ39a (32.2°), which represent almost the theoretical OR I/OR II misorientation of 30°, is increased for annealed samples. A comparison of the number fraction of OR I/OR II boundaries and the corresponding orientation map with highlighted Σ3, Σ7, Σ13b and Σ21a boundaries is shown in Figure 4-11.

OR II a is favored as shown by EBSD and XRD which indicates a lower total energy for the dominating twin variant finally leading to a microstructure containing only OR II a. As discussed above, a detailed theoretical analysis of the Al thin film/sapphire system is needed to understand the energetics of the whole system and dominance of OR II, and the twin variant OR II a in particular, considering all interfaces: film|substrate as well as film|surface (oxide layer) and grain as well as phase boundaries (film|voids) within the film.
Stagnation of grain growth in thin films was attributed to the pinning of grain boundaries due to the formation of grooves by Frost et al. [162]. The voids which form in the present study might act as pinning points and disturb ideal crystal growth (Figure 4-11a and b). The major grain growth seems to occur within the first hour during annealing as shown by EBSD, after the voids form (Figure 4-11a and b).
that the grain diameter remains constant. In-situ XRD annealing experiments confirmed the texture evolution. Void formation and texture evolution are observed independent of the usage of nitrogen or argon as protective gas during annealing. The lack of reducing agents preserves the surface oxide and prevents classic dewetting by surface diffusion due to the surface oxide and the related sandwich-like structure. In addition, residuals gases like water or oxygen can stabilize the surface oxide.

4.3.2 Void formation and void evolution

Solid state dewetting progresses in several stages starting with grooving from the free top surface and hole formation or by void nucleation at the film-substrate interface and growth towards the surface [30]. In polycrystalline films, grooving most likely is initiated at high energy grain boundaries [13]. Dewetting also takes place via nucleation of voids at the film-substrate interface, but the details of the mechanism are not clear and further studies are needed as pointed out by Kaplan et al. [30]. Furthermore, defects in the film like e.g. scratches might weaken the local film stability. After formation of a hole of critical size by grooving, capillary energies cause the retraction of the edge and hole growth [13]. In the sapphire substrate-Al thin film-surface oxide system of this study, void formation starts at the high energy grain boundaries between OR I and OR II grains or between two OR II grains (e.g. Figure 4-11b) whereby initiation at triple junctions can neither be supported nor excluded. High energy grain boundaries were also indicated as initial spots for dewetting in the study of Au thin films on Si (100)/SiOx/SiNx by Müller et al. [51]. Quantitative analysis of the EBSD measurements of all annealed samples (average ± standard deviation of all analyzed samples) revealed that 94±2% of the voids are adjacent to Al OR II grains whereby the majority 82±2% is in addition adjacent to Al OR I grains and 12±2% of the voids are completely surrounded by Al OR II grains. Only a small amount of the voids is surrounded by only Al OR I grains (6±2%) whereby one has to consider that the lateral EBSD resolution is limited and might overlook adjacent smaller Al OR II grains. It is indicated that dewetting starts by void formation at a triple phase boundary of two Al grains at the α-Al2O3/Al substrate interface similar to the findings of Shaffir et al. for thin Au films on YSZ [92, 93]. The driving force is the reduction of the Gibbs free energy by minimizing grain boundary as well as the Al/sapphire interface area. Void formation was also reported in a subsequent study by Shaffir et al. on Au films on YSZ [93] as well as for Pt films on YSZ [96, 97] and Ni films on SiO2 substrate [99]. It cannot be excluded that void formation starts by grooving from top at the triple phase boundary at the Al/surface oxide interface.
Void growth is supposed to occur by the capillary driven retraction of the film below the surface oxide layer and leads to a curved rim in direction from substrate to surface. Shadow-like contrast can be observed in SEM micrographs surrounding the voids indicating a redistribution of the Al of the former void volume (see Figure 4-6 and Figure 4-12). The local thickening at the metal-substrate interface of the groove region was also reported by Amram et al. [40]. They explained the groove shape, differing from the predicted one by the classical Mullins model [90], by mass transport via grain boundary diffusion of Ni towards the metal/substrate interface and followed by local accretion of metal atoms by interface diffusion of Ni at the metal-oxide interface [40]. They pointed out that metal-ceramic interface diffusion should be added as fast diffusion path to the established hierarchy [161] of diffusion paths in crystalline solids (bulk diffusion < dislocation core diffusion [163] < grain boundary (GB) diffusion [164] < diffusion along the solid surfaces) [40]. Thompson as well as Kovalenko et al. also pointed out the importance of grain boundary diffusion for polycrystalline films [13, 38]. The findings in this study confirm the importance of GB diffusion and strongly indicate fast interface diffusion for the mass transport of Al due to the lack of alternative diffusion paths. Surface diffusion would dominate, but it is prevented due to the covering oxide layer and negligible volume diffusion due to the moderate temperature \( D_s \sim 5.0 \cdot 10^{-9} \text{ cm}^2\text{s}^{-1} \) at 600°C [165, 166]. The identified high energy grain boundaries as initial regions for void formation support this model because anisotropic diffusion behavior is expected for grain boundary diffusion with lower diffusion coefficients at ordered CSL (low \( \Sigma \)) boundaries like \( \Sigma 3 \) [161].

Figure 4-12 Adjacent to the voids, formation of a rim is indicated by the shadow-like contrast in SEM micrographs.

Edge retraction during solid state dewetting is often described by a power law where the retraction distance \( x_0 \) scales as \( x_0 \sim t^n \) with time \( t \) and \( n \sim 0.4 \) [89, 167, 168]. In this study we report that the void radius \( r_{2,\text{void}} \) scales with \( r_{2,\text{void}} \sim t^{0.23} \). We assume that the prevention of
surface diffusion due to the oxide layer slows down the speed of void growth respectively edge retraction. The type of interface respectively grain boundary as well as the film thickness might influence the power law exponent. Zucker et al. predicted a strong influence of the involved diffusivities and of the film thickness for edge retraction using a 2D model [167]. The results of this study indicate a discontinuous growth of the voids. The retracting Al thin film is most likely pinned by obstacles and void growth is stopped. Each void (newly formed voids and already existing voids) might overcome the obstacle and starts growing again. Beside the growth of existing voids, new voids are created continuously during the annealing which is in agreement with findings by Shaffir et al. [92, 93] leading to a bimodal void size distribution. The high relative frequency of small voids for each annealed sample support the assumption that voids are continuously formed. Müller et al. reported a bimodal distribution for pores respectively voids after annealing of Au and AuPt thin films on passivated Si substrates [91]. In accordance with Jiran et al., they concluded that voids can form after different incubation times depending on their environment, e.g. type of adjacent grain boundary or triple junction [68]. The pores nucleate at the interface to the substrate and grow along grain boundaries towards the surface whereby the speed might depend on the grain boundary type [91]. Shaffir et al. concluded that the high energy of the Au/substrate interface as well as the grain boundary elimination initiates void formation and subsequent pinhole growth [93]. For our model system, small pores might be also present at the Al/substrate interface, but not detected due to the top view investigations.

In SEM micrographs, additional microstructural features such as bright appearing extrusions and particles are also observed to a minor degree compared to the dominating voids. No clear correlation between the additional features and voids is observed. Some of the bright features might also be contaminants from the furnace. Hillock like structures are observed for the longest annealing time (45h, see Supplementary figure 4-5), but still the amount of voids dominates. Shaffir et al. reported void as well as hillock formation for Au thin films, whereby they stated that both phenomena can occur independently [93].

The presence of faceted rims at the edges of holes (thin films without surface layer) after solid state dewetting, exposing the pure substrate, was reported for different systems, e.g. for Pt thin films on sapphire by Atiya et al. [169], for Au thin films on Si(100)/SiO2/SiNx by Müller et al. [51] and for thin Fe-Au bilayers on sapphire by Amram et al. [170]. A detailed investigation of the cross-sectional microstructure adjacent to the void and the faceted void shape is beyond the scope of this chapter. Further results will be addressed in chapter 5.
4.4 Conclusion

The microstructural evolution as well as the solid state dewetting behavior of Al thin films covered with a native oxide layer were investigated. Epitaxial thin films with defined orientation relationships were grown by molecular beam epitaxy on (0001) single crystalline sapphire substrates to simplify the complexity of the initial film microstructure. The as-deposited Al films form two orientation relationships (OR I/OR II) both containing two twin related variants: OR I \(a/b\ \{111\}\ \pm \langle 1\bar{1}0\rangle_{Al} \parallel (0001) \langle 1\bar{2}0\rangle_{Al_2O_3}\) and OR II \(a/b\ \{111\}\ \pm \langle 2\bar{1}1\rangle_{Al} \parallel (0001) \langle 10\bar{1}0\rangle_{Al_2O_3}\). Annealing below the melting point of Al at 600°C under Ar or N\(_2\) protective gas atmosphere initiated changes of the initial microstructure.

First, texture evolution and growth towards an OR II dominated microstructure occurred. Further grain growth after 1 h annealing was prevented by pinning of grains at voids. Second, the retraction of the Al film below a native oxide layer led to the formation of faceted voids covered with a remaining alumina membrane. Quantitative analysis of EBSD measurements indicated that the initial points of the void formation are grain boundaries involving OR II grains. The major diffusion mechanisms of the solid state dewetting phenomena were identified as grain boundary and interface diffusion. The void growth behavior can be described by a power law with an exponent lower than the one reported for surface diffusion dominated dewetting behavior of non-passivated thin films.

4.5 Supplementary data

In the following supplementary plan-view SEM micrographs for all annealing times are given (Supplementary figure 4-1 to Supplementary figure 4-5). The dark circle appearing in the center of some of the micrographs is an artefact due to usage of the in-lens detector at low magnification. The micrographs were used for further quantitative void size analysis as described in chapter 3.3.3 [73]. The void size results are shown in Figure 4-8 and Supplementary figure 4-6. They are summarized in Table 4-1 in chapter 4.2.2
Supplementary figure 4-1 SEM micrograph showing a fractured surface membrane of the drum-like void and subsequent charging by the bare insulating sapphire substrate (45 h annealed sample).

Supplementary figure 4-2 High resolution SEM micrograph showing the voids formed due to annealing (1 h annealed sample, before binarisation of micrograph).
Supplementary figure 4-3 High resolution SEM micrograph used for void size distribution analysis (6 h annealed sample, before binarisation).

Supplementary figure 4-4 High resolution SEM micrograph for void size distribution analysis (24 h annealed sample, before binarisation).
Supplementary figure 4-5 High resolution SEM micrograph for void size distribution analysis. Note the different scalebar (45 h annealed sample, before binarisation).

Supplementary figure 4-6 Void size distribution data for all analyzed annealing times. The Gaussian fits are shown for new formed small voids as well as for growing voids.
5 Annealing induced void formation in tetracrystalline Al thin films

This chapter describes the temperature induced void formation and the underlying diffusion mechanisms. It is based on a publication in *Acta Materialia* [116]. The void|film interfaces and the corresponding triple phase boundaries with the sapphire substrate respectively the surface layer are investigated by site-specific cross-sectional TEM analysis including characterization by spherical aberration corrected atomic column resolved STEM and EELS.

5.1 Introduction

Thin films are usually thermodynamically unstable in the as-deposited state due to their surface to volume aspect ratio [13, 167]. Heating can lead to fragmentation of a thin film and the formation of islands, which is termed dewetting or solid state dewetting for temperatures below the melting point [13]. The process is driven by the minimization of the total energy of the system [13, 30, 36]. Dewetting can be beneficial for targeted nanopatterning and nanowire growth [13, 24, 38], especially in combination with templating techniques and has been demonstrated for various systems [16, 37, 151]. Leroy et al. reviewed recently how to control and tune solid state dewetting [35].

Miniaturization in microelectronics leads to decreasing film thicknesses in thin film devices, for which solid state dewetting is an undesired degradation process [13, 36, 37]. Thus, understanding the underlying mechanisms of solid state dewetting is important to suppress dewetting and prevent failure of thin film devices [13]. The process is usually described to be governed by surface self-diffusion of thin film material well below the melting temperature [37, 88, 171]. Hence, the addition of a capping layer is one way to suppress dewetting by surface self-diffusion [13]. The native oxide of metal thin films can prevent surface diffusion too, e.g. for Si or Al, which are well-known for their passivating amorphous oxides [172]. Recent works by Kovalenko et al. [38], Amram et al. [40] and Kosinova et al [39, 101] reported the importance of grain boundary as well as interface diffusion for solid state dewetting processes.

Dewetting can start by grooving from top of the film surface or by pore formation at the substrate|film interface [13, 30]. Nucleation of pores can lead to void growth towards the film surface until the complete break-up of the film is achieved [91-93]. Void growth was reported for passivated Al thin films on Si, where grain boundary diffusion was assumed as the
dominating diffusion path. Thermal stresses due to cooling/heating during device operation were identified as driving forces [42-44]. Temperature induced void formation was observed in-situ by optical microscopy for Al thin films by Sugano et al. [45]. Details of the mechanism are not yet fully understood, but grain boundaries seem to be important.

The formation of faceted voids in a tetracrystalline Al thin film covered with a native oxide capping layer by solid state dewetting was investigated primarily in plan-view in chapter 4 [73]. The tetracrystalline film, grown by molecular beam epitaxy, consisted of two growth variants which are both twinned. The dominating growth variant forms a heteroepitaxial orientation relationship (OR) with the single crystalline (0001) sapphire (α-Al₂O₃) substrate in accordance to literature [53, 55] which are termed OR I a/b in this thesis [73]: OR I a/b{111} ± <110>₄₆ || (0001) <1010>₄₆ <1010>α-Al₂O₃ (± indicates the symmetrically equivalent twin variants $a$ and $b$ differing by a 180° rotation around the <111> surface normal). An additional OR was found: OR II a/b{111} ± <211>₄₆ || (0001) <1010>₄₆ <1010>α-Al₂O₃. Beside void formation, annealing led to a texture evolution towards an OR II a/b dominated microstructure. High energy grain boundaries were identified by EBSD analysis of plan-view samples as the initial points of dewetting (see chapter 4.3.2) [73].

The appearance of the temperature induced, faceted voids led to the question which phenomena occur at the triple junctions, i.e. Al thin film|void|sapphire substrate and Al thin film|void|surface layer. The structural changes of the native oxide layer during the void formation process are also unexplored on the nanometer scale. Dutta et al. reported the presence of $\gamma$-Al₂O₃ after annealing of Al thin films using glancing X-ray diffraction on a global scale as local electron diffraction experiments were not successful [47]. The open questions will be addressed in the present work applying high resolution STEM methods including EELS.

## 5.2 Results

### 5.2.1 Annealing induced void formation

The microstructural features induced during annealing are exemplary shown for the 6 h at 600°C annealed sample in Figure 5-1. The voids, formed during annealing of the tetracrystalline Al thin films on sapphire, are faceted and a few µm in diameter (Figure 5-1a). EBSD analysis of the annealed samples confirmed that the Al grains keep the heteroepitaxial orientation relationships OR I a/b and OR II a/b with sapphire. The in-plane orientation map in Figure 5-1b shows the Al grain orientations in the vicinity of a faceted void, OR I and
OR II grains are both adjacent to the void which is the dominating case (82±2% of the voids are in contact with OR I and OR II grains) as described in chapter 4.3.2 [73]. In addition, voids surrounded by Al grains with only OR I (6±2%) or OR II (12±2%) are also found (as shown in the overview in-plane orientation map in Figure 5-2).

The faceted shape of the void is also observed in orientation maps, whereby the facets are less well resolved due to the sample tilt. The plan-view SEM micrograph in Figure 5-1c shows a hexagonal shaped void with clearly defined facets, whereby short and long facets are alternating. A remaining Al feature of the retracting film is visible at one of the long facets. No rim, surrounding the void, is observed for this exemplary void which will be discussed later.
The voids can be described as inversions of Al single crystal Wulff shapes. The adjacent remaining Al film exhibits the facets originating from the anisotropy of the Al surface energy. The lowest surface energies for Al are calculated for \{111\}, \{100\} and \{110\} surfaces [50]. However, the calculated surface energies in literature differ a lot depending on the methodology, thus the experimentally determined averaged Al surface energy value of Kumikov et al. (1130 mJ/m²) [173, 174] was used as input value for the Wulff shape construction using the WulffMaker Mathematica code developed by Zucker et al. [84]. The Wulff shape is plotted in Figure 5-1d in [111] direction and with \([\bar{1}10]\) in vertical direction as for the Al thin film marked by the white rectangle in Figure 5-1c. The corresponding TEM investigation is described later. Three long sides of inclined \{110\} facets (yellow in Figure 5-1d) and three short sides of inclined \{100\} facets (red) lead to the facet length alternation of the plan-view (111) facet (blue). The side facets intersect with the (111) top facet with the three directions \([\bar{1}10]\), \([01\bar{1}]\) and \([10\bar{1}]\) as indicated by the bright blue lines, arrows and captions in Figure 5-1d.

Figure 5-2 Overview EBSD orientation map showing the in-plane orientation of the Al thin film and the presence of faceted voids (6 h annealing at 600°C, for color code see Figure 5-1, voids \(\neq\) area not containing indexed Al grains in black).
5.2.2 Cross-sectional TEM investigations of void regions

Two different types of void shapes are found in SEM plan-view micrographs. Hexagonal voids surrounded by a homogenously thick Al film (Figure 5-1c) and irregular voids surrounded by a rim are observed (Figure 5-3), the latter will be addressed later in this section. Cross sections of these regions were prepared by FIB to analyze the Al thin film|void interface as well as the triple junctions at the sapphire substrate and at the surface layer in detail.

Figure 5-3 Exemplary plan-view SEM micrographs containing voids with an isotropic rim (a, 1 h annealing at 600 °C) and with an anisotropic rim around the void (b, 6 h annealing at 600 °C), respectively.

The HAADF STEM overview micrograph in Figure 5-4a shows the cross section of the Al thin film|void|substrate region marked with the white square in Figure 5-1c (a low magnification HAADF STEM micrograph of the complete TEM lamella is shown in Figure 5-5a). The corresponding Al- and O-EDS mapping confirm the retraction of the Al thin film (Figure 5-4b and c). The thickness of the Al layer is uniform over the lateral size of the TEM lamella in accordance to the plan-view SEM micrograph (Figure 5-1c), where no rim formation at the Al|void interface was observed. Compared to the as-deposited film, the thickness increased from 242±2 nm to 286±2 nm. The Al thin film and the void are both covered by a continuous surface oxide membrane leading to a drum-like cavity. Pt for surface protection during the FIB process growths on top of the surface oxide membrane instead of filling it as in a hole-like case.
Annealing induced void formation - Results

Figure 5-4  a) STEM HAADF micrograph of the region marked by a rectangle in Figure 5-1c of a film annealed for 6 h at 600°C. The Al facets at the Al|void interface are indexed using the corresponding high resolution micrographs d), e) and f). b,c) Al- respectively O-EDS mappings of the region showing a continuous surface oxide layer covering the dense Al thin film as well as the void. An additional thicker Al oxide layer is found at the Al side wall at the Al|void interface and below the surface membrane. d) Spherical aberration corrected STEM HAADF micrograph of the OR I oriented film|substrate interface of a region close to the void taken in [110] Al zone axis respectively [10\(\overline{1}\)0] Al\(_2\)O\(_3\) zone axis. e,f) STEM BF micrographs showing atomically sharp facets at the triple junction of Al|void|sapphire respectively Al|void|surface layer.

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The Al thin film|sapphire substrate interface close to the void is shown in Figure 5-4d and reveals OR I with the close-packed planes and directions parallel to each other. HAADF STEM micrographs of both triple junctions are shown in Figure 5-4e and f. The distinct Al facets at the Al|void interface are assigned as (001) at the triple junction surface oxide|Al|void respectively (111) at the triple junction substrate|Al|void and possess atomically sharp interfaces. The Wulff shape in the corresponding viewing direction confirms the identified facets. The (111) facet is more pronounced compared to the (001) facet, which turns into a rounded shape. The Al|void interface located on the opposite side of the void in Figure 5-4 was also analyzed (not shown, for an overview micrograph of the complete lamella see Figure 5-5a). The Al thin film possess the same orientation relationship, whereby a well-defined (111) facet is now found on the upper part of the interface. The (001) facet on the lower part is also observed, but only for the small region close to the Al|sapphire interface and turns into a rounded shape (corresponding to the upper part of Figure 5-4a). The edges at the triple junction at the surface as well as at the substrate interface are also rounded (Figure 5-4e and f) which can be described as surface roughening transition.

Figure 5-5 a) Overview HAADF micrograph of the complete TEM lamella presented in Figure 5-4 revealing preferential \(\alpha\)-Al\(_2\)O\(_3\) thinning at the void region (various micrographs stitched using the Fiji plugin by Preibisch et al. [175]). b) ABF micrograph of the Al|void interface (represented by the HAADF micrograph in Figure 5-4a) revealing a continuous crystalline surface layer covering both, the Al film as well as the void and a thin Al oxide layer at the side wall. Redeposition due to the FIB process is marked.
Annealing induced void formation - Results

Al- and O-EDS mappings reveal an additional aluminum oxide layer with 5±1 nm thickness at the Al side wall between the Al thin film and the void (compare Figure 5-5b). No lattice fringes are observed in high resolution STEM (Figure 5-4e, f) or TEM (not shown) micrographs indicating an amorphous state. A FIB artifact leading to amorphization [136] of a crystalline oxide is unlikely due to the adjacent atomic column resolved Al lattice, but cannot be excluded. On top of the side wall oxide, a non-uniform layer, containing Al, O and Ga as determined by EDS, is observed. It is probably caused by redeposition during the FIB milling process (Figure 5-4a, b, c).

Figure 5-6 Cross-sectional STEM HAADF micrograph as well as Ga-, Al- and O-EDS mappings of a 1 h annealed sample showing the three different layers: α-Al_2O_3 sapphire substrate, Al thin film and γ-Al_2O_3 surface oxide layer. The surface layer is continuous covering the Al thin film. Both, surface layer and Al film, are homogenous in thickness. Ga enrichment at both Al|Al oxide interfaces, caused by the FIB preparation of the TEM samples, is found.

High contrast in HAADF micrographs of FIB prepared samples at Al interfaces indicates that heavier atoms are located there (see Figure 5-4d). The high contrast might be caused by an interface reconstruction [30] or Ga segregation due to FIB milling [153, 154] as described in chapter 4.2.1 [73]. EDS (see Figure 5-6) and EELS measurements reveal the presence of Ga at the interface in accordance to the HAADF contrast confirming Ga artefacts of the FIB preparation process. Ga artefacts might alter the atomic interface structure which is not further
investigated within this thesis. Independent of that, an interface reconstruction might have occurred, too [30]. Another FIB artefact is the preferential thinning of the sapphire (Figure 5-4c, Figure 5-5a). Defects, such as small dislocation loops, are visible in the Al film in the corresponding BF images which are most likely due to the FIB sample preparation [60, 176]. Investigations of cross-sectional specimens of irregular Al|void regions by HAADF and corresponding Al- and O-EDS mappings confirm that the remaining Al thin film as well as the void are covered by a continuous oxide layer (Figure 5-7a,b). On top of the oxide, a Pt layer is present resulting from the FIB sample preparation process. In contrast to the triple junction described above, a ridge is found at the sapphire|Al|void triple junction. A steep rim of the Al layer at the void interface with a thickness up to ~340 nm formed. The local nature of the rim is confirmed by the thickness decrease ~400 nm away from the void down to ~250 nm which is close to the initial film thickness.

At higher magnification, atomic steps towards the Al|void interface are observed at the Al|surface layer interface (Figure 5-7c). A HAADF high resolution STEM micrograph of the adjacent Al thin film|sapphire substrate interface is shown in Figure 5-7d and the dominating orientation relationship $ORII$ after annealing is identified. From the Wulff shape a $\{110\}$ Al facet is expected, but the Al|void interface does not exhibit distinct facets. In contrast to the Al|void interface, faceting of the $\text{Al}_2\text{O}_3$ ridge is observed (Figure 5-7e) at the sapphire|Al|void triple junction. A distinct assignment of the facets is not possible as the viewing direction of the Al|ridge interface ($< 2\overline{1}1 >_\text{Al} \parallel < 10\overline{1}0 >_{\text{Al}_2\text{O}_3}$) is not edge on. The ridge grows epitaxially on the $\alpha$-$\text{Al}_2\text{O}_3$ sapphire substrate continuing the basal plane of the single crystalline sapphire substrate (see Figure 5-7f).
Figure 5-7 a) STEM HAADF image of a rim-containing region of an Al\void interface (sample annealed at 600°C for 1 h). b) Combined Al- and O-EDS mappings of the region indicating a faceted Al oxide ridge in addition to the Al side wall\void as well as the continuous surface Al oxide layer. c) STEM BF micrograph of the Al\surface layer interface revealing atomistic steps of the Al thin film leading to an increased film thickness towards the void (rim). d) STEM HAADF image of the OR II orientated film\substrate interface of a region close to the void taken in [2\bar{1\bar{1}]} Al zone axis respectively \{10\bar{1}\} Al\sub oxide zone axis. e) HAADF micrograph of the ridge formed at the Al\void\substrate triple junction (collection semi-angle range 38-189 mrad). f) STEM BF micrograph revealing faceted, epitaxial ridge growth continuing the sapphire substrate lattice.
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Like for the ridge-free void, an additional oxide layer with \(~15 – 20\) nm thickness between the Al thin film and the void is observed by EDS and HAADF. EDS reveals the presence of Al, O and a large amount of Ga in the outer part which is most likely redeposition due to FIB sample preparation. The sample is not viewed edge on and thus the homogenous side wall oxide is not observable. However, it can be excluded that the oxide would have completely filled the void. At the sapphire|Al film|Al sidewall oxide triple junction, lattice fringes are observed for the thin oxide between Al and the void as well as for the oxide on top of the Al film (see Figure 5-8). The oxide can be indexed as \(\gamma\)-Al\(_2\)O\(_3\) which will be addressed in the next section 5.2.3.

![Figure 5-8](image)

**Figure 5-8** a) STEM BF micrograph of a region of the Al film and the surface layer after 1 h annealing reveals a crystalline surface oxide layer containing nanograins in different orientations. b) STEM BF micrograph of the Al|sapphire ridge|Al side wall oxide triple junction in Figure 5-4b revealing \(\gamma\)-Al\(_2\)O\(_3\) lattice planes for the interfacial Al oxide layer (1 h annealed sample).

5.2.3 Phase transformation and orientation relationships of the oxide layer

A thin surface oxide layer with a thickness of \(2.8\pm0.4\) nm is covering the as-deposited Al thin film. The surface scale has probably been formed after the removal of the sample from the MBE system and the first contact to atmospheric oxygen. Cross sections of samples with different annealing times were prepared by FIB to investigate the changes of the surface layer with annealing time in detail using various TEM techniques (Figure 5-9).

No lattice fringes are observed for the native oxide in the as-deposited state indicating an amorphous nature. The high resolution TEM micrograph in Figure 5-9a shows the surface oxide on top of a \(\Sigma 3\) twin boundary region between \(OR I a\) and \(OR I b\) which have the highest
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relative frequency. With increasing annealing time, the thickness of the surface oxide scale is increasing from 2.8±0.4 nm (as-deposited), 10.7±1.6 nm (1h annealing), 13.3±1.1 nm (6h annealing) to finally 26.2±3.5 nm (45 h annealing).

With increasing annealing time, the surface oxide becomes less uniform and rougher as indicated by the larger scatter for the 45 h annealed sample (see Figure 5-10). The STEM HAADF micrographs in Figure 5-9b and c reveal lattice fringes within the surface oxide for annealed samples indicating a phase transformation from the amorphous to the crystalline state. Local EELS measurements in STEM mode of the Al-L2,3 and O-K edges of the different regions of the annealed samples are shown in Figure 5-9f and g. Fingerprint correlation of the individual ELNES spectra [148, 177] revealed the presence of three different phases: α-Al2O3, Al and γ-Al2O3. As expected, metallic Al for the thin film and α-Al2O3 for the substrate can be confirmed by the characteristic ELNES features: α-Al2O3 for the substrate exhibits an asymmetric peak at ~99 eV with an additional shoulder at ~95 eV in the Al-L2,3 ELNES (highlighted by the arrow). The Al-L2,3 ELNES of the surface layer shows a symmetric peak at ~99 eV and a pronounced shoulder at ~79 eV similar to EELS data reported in [148, 177] indicating γ-Al2O3. The presence of δ-Al2O3 cannot be excluded since δ-Al2O3 is usually described as a superstructure of γ-Al2O3 and accordingly, the ELNES differences are expected to be small [106, 148]. The O-K ELNES of the sapphire substrate shows one dominant peak at 540 eV and two characteristics peaks at ~558 eV and ~567 eV instead of one peak at ~558 eV as for amorphous, γ- or δ-Al2O3 [148, 177]. The metallic Al layer shows a low amount of oxygen, probably due to a surface oxide of the FIB exposed side surfaces of the TEM lamella.

γ-Al2O3 can be described as a defect cubic spinel structure (space group Fd3m) with a fully occupied oxygen sublattice [172, 178]. Al cations are distributed over the octahedral and tetrahedral sites. A refined structure, where Al ions occupy non-spinel positions, was reported in a single-crystal X-ray diffraction study [179]. The later one was used for indexing of the γ-Al2O3 surface layer. Figure 5-9d and e show the FFTs of the regions marked in the STEM micrographs (in Figure 5-9b and c) as well as the simulated diffraction patterns of the corresponding zone axis. An OR with (111) ± [110]Al || (111) [110]γ-Al2O3 (ORγ Ia) exists between the OR Ia oriented Al and the covering oxide. This is expected to have the lowest lattice mismatch and was found for various regions. Within the γ-Al2O3 twin variants are observed. The HAADF micrograph in Figure 5-9c shows the heteroepitaxial growth of the surface oxide possessing the twin variant ORγ Ib with (111) ± [110]Al || (111) [110]γ-Al2O3.
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Figure 5-9 a) HRTEM micrograph of the surface-near part of a cross-sectional as-deposited sample indicating a continuous amorphous oxide layer covering a $\Sigma 3$ twin boundary in the Al thin film. The twin boundary is observed close to edge on with the Al grains in [110] respectively [1\bar{1}0] zone axis. b) STEM BF micrograph revealing a crystalline surface layer covering the Al thin film after 6 h annealing. c) STEM BF micrograph of atomistic steps at the OR I oriented Al|surface layer interface. Nano-twinning occurs within the surface layer. d,e) The FFTs (top) of the corresponding regions in the high resolution STEM micrographs in b) respectively c) are indexed using the diffraction patterns for $\gamma$-Al$_2$O$_3$ in <110> orientation (bottom, simulated pattern by JEMS [149]). The FFTs represent the two twin variants in accordance to the twin variants of the underlying Al film present in the sample. f,g) Normalized EEL spectra of the Al-L$_{2,3}$ and O-K edge of the surface layer ($\gamma$-Al$_2$O$_3$, blue spectra), the Al film (red spectra) and the sapphire substrate ($\alpha$-Al$_2$O$_3$, black spectra).
A nanometer-wide twin in the $\gamma$-Al$_2$O$_3$ surface layer is visible close to the $\gamma$-Al$_2$O$_3$|Al interface. Due to the projection of a 3D sample, small twins embedded in the oxide layer might lead to additional $\{004\}$ spots of $OR\ I\ b$ in the FFT of the corresponding twin $OR\ I\ a$ in Figure 5-9d (marked by red circles, also in the simulated diffraction pattern in Figure 5-9e). Nanometer-thin crystals are observed for different regions within the $\gamma$-Al$_2$O$_3$ layer (see Figure 5-8a).

Analysis of several regions indicate the presence of a second orientation relationship $OR\ II$ with $(111) \pm \{2\bar{1}\bar{1}\}_A l \parallel (111) \{\bar{1}10\}_{\gamma-Al_2O_3}$ similar to $OR\ II$ for Al and $\alpha$-Al$_2$O$_3$. The lattice mismatches, $f_{OR\ I}$ and $f_{OR\ II}$, between the heteroepitaxial $\gamma$-Al$_2$O$_3$ surface layer and the Al thin film amount to:

$$f_{OR\ I} = \frac{d_{\gamma-440} - d_{Al220}}{d_{Al220}} = -0.020 \quad (Equation\ 5-1)$$

$$f_{OR\ II} = \frac{d_{\gamma-422} - d_{Al220}}{d_{Al220}} = 0.132 \quad (Equation\ 5-2)$$

with an Al $\{220\}$, $\gamma$-Al$_2$O$_3$ $\{440\}$ and $\gamma$-Al$_2$O$_3$ $\{442\}$ lattice plane spacing of $d_{Al220} = 1.431\ \text{Å}$, $d_{Al440} = 1.403\ \text{Å}$ and $d_{\gamma-442} = 1.620\ \text{Å}$, respectively [105, 179]. The presence of a high mismatch $OR$ is discussed later. To summarize, EELS and high resolution STEM images have shown that the surface layer has transformed from the amorphous state to $\gamma$-Al$_2$O$_3$ which is in accordance with literature [172, 180-182].

Figure 5-10 Cross-sectional STEM HAADF micrograph and the corresponding O-EDS mapping of a 45 h annealed sample show an increase in surface oxide thickness. The surface layer is continuously covering the Al thin film whereby variations in thickness are observed.
5.3 Discussion

5.3.1 Faceted void formation

The driving force of the void formation is the reduction of the total Gibbs free energy of the system [13] by reduction of the grain boundary and the Al\|substrate interface area. High energy grain boundaries involving \textit{OR II} grains were identified as initial locations for the solid state dewetting process. Void formation occurs by retraction of the Al thin film below a continuous surface oxide layer in accordance with literature reports for polycrystalline Al thin films on Si [44] as well as on sapphire [46, 47]. The surface oxide is described as flexible [44, 183] enough to allow void formation without rupture.

Faceting after solid state dewetting was observed for various thin film systems whereby faceting occurs for holes, for particles close to the equilibrium shape after long annealing times and at the thin film\|hole interface [13, 32, 51, 72, 76, 169, 184]. Dutta et al. reported faceted void formation after solid state annealing of polycrystalline Al thin films on (0001) sapphire [47]. The influence and the importance of specific crystallographic orientations of the substrate respectively of the grains of the film on the dewetting mechanism were discussed in recent literature [31, 39, 51, 73, 101, 169] and are confirmed in the present study involving a defined thin film containing only four \textit{ORs}. Some voids are rotated against each other by \(~30^\circ\) which is in accordance to the rotation between \textit{OR I} and \textit{OR II} grains.

Solid state dewetting experiments by Amram et al. of Au-Fe thin films on (0001) sapphire [170] revealed the presence of faceted, hexagonal holes after annealing. Their site-specific cross-sectional TEM investigations revealed alternating \{111\} and \{100\} planes which determine the shape of the hole in the Au-Fe alloy film, similar as observed in this study. The round shape can be explained by facet roughening transitions as proposed by Burton et al. [185] due to the influence of entropy at high temperatures close to, but below the melting temperature. Above the roughening temperature facets undergo a roughening transition and become curved [186]. It is assumed that the retraction front, i.e. the Al\|void interface, has a more rounded shape due to the higher impact of entropy at high temperatures and defined facets form during cooling, whereby \{111\} facets form faster. These observations are in accordance with literature reporting the lowest surface energy for \{111\} facets [50, 187].

The shape of the void is determined by the mobility of the facets and can be described by the Wulff construction (Figure 5-1d). The aspect ratios are reflected by an inverted Wulff shape containing the lowest energy facets which have the slowest motion. However, the aspect ratios of the short and long facets are not fully described by the idealized model as we use
only an averaged experimental value for the surface energy (1130 mJ/m²) as an input value for the Wulff construction. Small variations of the surface energies can lead to modifications in the length of the different facets intersecting the \{111\} top facet. A hexagonal shape is obtained constructing a Wulff shape whereby the anisotropy of the surface energies \(\gamma_{(111)}\) (1199 mJ/m²), \(\gamma_{(110)}\) (1271 mJ/m²) and \(\gamma_{(100)}\) (1347 mJ/m²) was considered and values from first principles calculations were used [188] (see Figure 5-11). However, the calculated surface energies in literature differ a lot depending on the methodology used. \(\gamma_{(111)}\) has always the lowest, but e.g. is reported in the range from 783 – 1199 mJ/m² [50, 187, 188] which changes the calculated facets in the Wulff construction strongly. Müller et al. described faceted edges in Au thin films after dewetting and also stated the importance of anisotropic surface energies [51]. Growth of hexagons with alternating short and long facets were also reported in literature for island growth of different systems, e.g. Pd islands on a bicrystalline Al₂O₃ thin film [189] or Fe on single crystalline sapphire [190].

Many of the observed voids in this study exhibit irregular or mixed faceted shapes indicating the presences of various non-equilibrium facets. We speculate that the void growth is disturbed by obstacles, i.e. steps in the substrate, grain boundaries or contamination, which is discussed in the next section. Ye et al. observed the presence of non-equilibrium facets of higher order in SEM cross sections after dewetting and hole growth in Ni (100) and Ni (110) thin films on MgO (100) and MgO (110) substrates [37]. Thus, the observed structures of ex-situ annealed thin films in this thesis are not in equilibrium and a frozen snapshot of the solid state dewetting process.

\[\text{Figure 5-11} \text{ The equilibrium crystal shape of a faceted Al crystal calculated with WulffMaker is shown in [111] orientation. Anisotropic surface energies from first principles calculations were used as WulffMaker input (see text for details) in contrast to Figure 5-1d where only one, experimentally determined value was used for all surface energies. The same facets are observed, but variations in facet length occur.}\]
5.3.2 Al|void regions in cross section

Two different types of Al|void regions were observed in cross sections, (i) ridge-free Al|α-Al₂O₃ interfaces and (ii) those containing a rim and often a ridge. An oxide layer between the retracted Al thin film and void is observed for both types. Due to the surface layer on top of the Al film, surface diffusion is suppressed and grain boundary as well as interface diffusion were identified as important diffusion mechanisms [40, 73]. The origin of O and the O diffusion processes needed for the formation of the ridge as well as of both oxide layers will be addressed later, the Al diffusion will be discussed directly.

Rim formation is often observed for solid state dewetting of thin films without passivating oxide or capping layer [39, 40, 51, 101, 102]. It is driven by capillary energies due to the curvature of the edge at hole|film interfaces [13]. Rim formation is usually accompanied with a valley formation behind the rim. When the bottom of a valley reaches the underlying substrate, the film can break-up and single islands might form [13, 35]. Solid state dewetting without formation of an elevated rim was reported for a few thin film studies in contrast to the commonly observed rim formation [31, 38, 40]. Kovalenko et al. reported an increasing surface roughness as well as increasing average thickness with annealing time for Fe thin films instead of rim formation [38]. In this study, no valley formation was observed, neither for the ridge-free nor the ridge-containing Al|void regions.

Al diffusion is expected to occur along the Al|oxide interfaces. We speculate that the Al|surface layer interface is the preferred Al diffusion path as the initial amorphous as well as the vacancy-rich γ-Al₂O₃ [179] are both less dense compared to α-Al₂O₃ [191]. It is assumed that Al from the growing void region is transported to the surrounding resulting in an increased film thickness. For both Al|void|sapphire triple junction types, an increased Al film thickness is observed by SEM and TEM (see cross-sectional micrographs in Figure 5-4 and Figure 5-7). The Al film thickness is uniformly increased for the ridge-free type, whereas a very local increase and rim formation is observed for a ridge-containing type.

We speculate that the void formation is a discontinuous process and Al redistribution to the surrounding is highly anisotropic (see Figure 5-3). The void, or in more specific terms distinct sides of the void, are pinned at obstacles, e.g. triple lines or steps in the substrate and the motion of the Al|void interface is stopped (see Figure 5-12a). After initial void formation, the Al|void interface might act as additional, fast surface diffusion (dashed, blue arrows) path allowing circumferential diffusion at the Al side walls as well as leading to a continuing Al flux towards the Al|void|surface triple junction. Al from unpinned sites of the void accumulates at the triple line and a rim develops similar as for surface layer-free thin films.
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during dewetting [13]. Rim formation is usually driven by the reduction of the curvature of the retracting film edge [13]. We speculate that due to the surface layer, the process only occurs in the case of pinning of the retracting Al film side wall. Due to ongoing interface diffusion (continuous, blue arrows) of Al away from the void, a curved rim with steps forms (see Figure 5-12b and Figure 5-7a). We assume that this process only occurs after sufficient pinning time.

The formation of a rim is also observed by Dutta et al. using cross-sectional micrographs of annealed polycrystalline Al thin films on (0001) sapphire [47]. However, the 2D scheme is an idealized model and detailed simulations are needed to investigate the mechanism in more detail. Rim formation at Al|void regions is observed for voids with well-defined facets (see Figure 5-3a) as well as for voids with irregular shapes (see Figure 5-3b). Anisotropic rim formation seems to be correlated with irregular void shapes as observed in plan-view SEM micrographs.

In addition to rim formation, sufficient pinning time may induce the formation of a sapphire ridge. The investigations in this study reveal the presence of epitaxial $\alpha$-Al$_2$O$_3$ ridges at some of the Al|void|sapphire triple junctions, despite the low temperature of 600°C. Upon pinning, a ridge forms to compensate the unbalanced vertical component of the capillary force present at the triple phase boundary Al|void|sapphire substrate [30]. Ridge formation at triple junctions was reported in literature for various metal|Al$_2$O$_3$ systems [79, 155, 192-194]. Most of these studies were performed at high temperatures, e.g. sessile drop [194] or liquid
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dewetting experiments [193] where mass transport is sufficiently rapid [30]. It was also observed in the solid state dewetting experiments of Dutta et al. [46]. They reported epitaxial ridge formation after annealing of polycrystalline Al thin films on sapphire at 650°C. In a subsequent study they found that the sapphire ridges formed at the periphery of faceted oxide features within Al thin films after annealing [47]. We assume that the requirement for ridge formation is sufficient time, which can be achieved due to pinning of the retracting Al film at an obstacle (e.g. surface step as in Figure 5-12). The ridge prevents further retraction and may lift an existing Al rim on top. For the same annealing time, different ridge heights were observed, even for the same void at different locations. Curiotto et al. discussed the presence of ridge-free as well as ridge-containing triple phase boundaries after dewetting (both, liquid and solid) of Cu on sapphire [112, 193]. Insufficient time for the receding films was reported to prevent the formation of ridges despite the unbalanced vertical forces. If pinning is overcome, the retraction of the film continues. Post annealing SEM analysis revealed the presence of ridge remains appearing as bright features (see Figure 5-13). The plan-view SEM micrograph also shows the non-uniform formation of rims surrounding the void.

Figure 5-13 Plan-view SEM micrograph after 24 h annealing at 600°C reveals the remains of a ridge formed during pinning and visible after subsequent film retraction.

An oxidized Al side wall next to the void was observed, which has a constant thickness for the rim-free Al|void regions. On top of this, a layer caused by redeposition and containing Al, O and Ga is visible. The moment when oxidation took place is not clear. It could be within the furnace (during annealing or cooling), after annealing or during the FIB sample preparation. Due to the specific facets for the rim-free sample, we speculate that the front of the retracting Al film is metallic during receding. Only during cooling, the amorphous oxide
covering the Al sidewall with a thickness in the range of the native oxide is formed. For the pinned triple phase boundaries, the presence of lattice fringes in high resolution STEM micrographs indicates that the sidewall oxide forms during annealing in the furnace after sufficient pinning time (Figure 5-8b). The origin of the oxygen will be discussed in the next section.

Thus, in conclusion rim-free triple junctions form, when the film is continuously receding and Al is uniformly redistributed to the surrounding. Pinning breaks the continuous retraction and leads to irregular faceted void shapes as well as the formation of rims and ridges. Their sizes depend on the pinning time of the retracting Al film. Al rim and sapphire ridge formation are separate processes, only linked by the stopped motion of the Al|void interface, but seem to occur parallel. However, further experiments are needed to identify the microstructural features responsible for the different Al|void regions.

5.3.3 Surface oxide layer transformation

Dutta et al. reported the presence of $\gamma$-Al$_2$O$_3$ after annealing of Al thin films at varying temperatures between 350°C and 650°C using glancing X-ray diffraction on a global scale [47]. Local phase identification by electron diffraction was not successful. We showed by complementary EELS/ELNES and high resolution STEM analysis on the nanometer-scale that the surface layer of the Al thin film as well as the thin membrane above the void crystallizes from the amorphous state to $\gamma$-Al$_2$O$_3$.

The oxidation mechanism and oxide scale growth are complex and not yet fully understood [104, 195]. The surface layer thickness increases with annealing time which can only occur with sufficient oxygen supply and oxygen diffusion. The presence of residual water vapor or oxygen in the Ar protective gas of the furnace might act as oxygen source. Sapphire as oxygen source is unlikely, but cannot be fully excluded. The partial pressure gradient leads to a chemical potential towards the Al thin film which can account for the oxygen inward diffusion and outward Al diffusion. The surface layer continuously covered the Al thin film as well as the voids in ex-situ investigations after the annealing except rare, negligible ruptures.

Polycrystalline Al$_2$O$_3$ showed strongly temperature depending oxygen permeability under steep oxygen partial pressure gradients using grain boundary pathways for interdiffusion [196, 197]. Inward diffusion of oxygen through the surface oxide was also reported for the growth of $\gamma$-Al$_2$O$_3$ crystallites below an amorphous oxide layer on Al substrates by Jeurgens
et al. [172]. They reported the formation of a $\gamma$-Al$_2$O$_3$ layer up to 80 nm after annealing (500°C, ~5.5 h, $p_{O_2} = 1.33 \cdot 10^{-4}$ Pa). Nabatame et al. and Nakamura et al. reported oxygen diffusion coefficients in amorphous and $\gamma$-Al$_2$O$_3$ layers using $^{18}$O as a tracer [198, 199]. The calculated diffusion length for oxygen into amorphous alumina varies depending on the temperature due to the different diffusion coefficients ($D_{587°} = 4.5 \cdot 10^{-21}$ m²/s at 587°C [199], $D_{627°} = 1.3 \cdot 10^{-20}$ m²/s at 627°C [199], $7.0 \cdot 10^{-20}$ m²/s at 700°C [198]).

Table 5-1 Comparison of calculated diffusion length for amorphous alumina and the measured oxide thicknesses

<table>
<thead>
<tr>
<th>Annealing time $t$ [h]</th>
<th>Diffusion length [nm] ($D_{587°}$ used [199])</th>
<th>Diffusion length [nm] ($D_{627°}$ used [199])</th>
<th>Thickness of the oxide layer [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0</td>
<td>6.8</td>
<td>10.7±1.6</td>
</tr>
<tr>
<td>6</td>
<td>9.9</td>
<td>16.8</td>
<td>13.3±1.1</td>
</tr>
<tr>
<td>45</td>
<td>27.0</td>
<td>45.9</td>
<td>26.2±3.5</td>
</tr>
</tbody>
</table>

For amorphous alumina, the calculated diffusion lengths are in the range of the measured oxide thickness, except for the 1 h annealed sample, which is too low (Table 5-1). This is different when considering $\gamma$-Al$_2$O$_3$, where reported diffusion coefficients are two or three orders of magnitudes lower than for amorphous oxide [198]. The calculated diffusion length for this case is below ~2 nm using the reported volume diffusion values ($1.8 \cdot 10^{-23}$ m²/s at 700°C [198]). Thus penetration of the $\gamma$-Al$_2$O$_3$ surface membrane by volume diffusion seems to be unlikely. However, Nabatame et al. commented that grain boundary coefficients are about four orders of magnitude higher compared to volume diffusion [198]. For $\alpha$-Al$_2$O$_3$ enhanced grain boundary diffusion as short-circuit path is also reported by Heuer et al. who studied oxide scale growth [104, 197]. As the crystalline $\gamma$-Al$_2$O$_3$ surface oxide layer on top of the Al film and the void has several grain boundaries we assume that grain boundary diffusion is taking place (Figure 5-5b).

Dutta et al. reported a surface oxide thickness of 20±3 nm after 24 h annealing of Al films at 550°C (40±5 nm at 650°C) [47]. They discussed that oxygen transport occurs via apparent fast interfacial diffusion. The homogenous thickness of the surface oxide layer in the samples indicates a fast distribution of oxygen at the Al|surface layer interface. We speculate that interfacial oxygen diffusion (continuous, green arrows in Figure 5-12) is the dominating diffusion mechanism relevant for the growth of all three oxide features (surface layer, ridge, interfacial oxide at Al|void interface). Subsequent volume diffusion of oxygen through the Al thin film is unlikely due to the low solubility of oxygen in Al [46, 47, 81]. Al/O ion respectively Al/O vacancy diffusion at the film|surface oxide interfaces as well as at the
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substrate|film and at Al grain boundaries is more likely to occur [104, 180]. It is assumed that the interface between film and void acts as fast oxygen surface diffusion path (dashed, green arrow in in Figure 5-12b) towards the film|substrate interface for ridge growth. Further experiments would be needed to determine the diffusion path.

High resolution STEM reveals a cube-on-cube orientation relationship of two fcc materials for the γ-Al2O3 surface oxide on Al possessing OR I a/b in accordance with literature [172, 180-182]. The presence of OR II between γ-Al2O3 and Al is also observed (see Figure 5-8a). High lattice mismatch heteroepitaxial orientation relationships are reported for different thin film systems involving metal|oxide interfaces [73, 158, 181]. OR II is unexpected considering the coincidence site lattice model, a purely geometric approach generating an idealized model describing strain. Oh et al. [158] explained the stability of OR II for Cu thin films on sapphire by metal-oxygen bonds. Theoretical calculations by Hashibon and Elsässer for the Cu|Al2O3 system revealed only slight differences in the interface energy for OR I and OR II [156]. Reichel et al. stated that ultra-thin oxide overgrowths on Al can be stabilized by a low surface energy and a high number of metal-oxygen bonds [181] which may be also the case in this study.

High resolution STEM analysis also confirmed a phase transformation to γ-Al2O3 of the oxide layer covering the Al side wall at the Al|sapphire ridge|void triple junction (Figure 5-8b). We speculate that after formation of an amorphous oxide at the Al|void interface, a subsequent phase transformation to γ-Al2O3 also occurs at the triple junction. By etching of annealed Al thin films Dutta et al. [47] exposed hollow, three-dimensional oxide features which were completely surrounded by a sapphire ridge [46]. A pinned void with γ-Al2O3 covering the remaining Al side wall might be a primary stage of such a hollow oxide feature. Nevertheless, it cannot be excluded that the formation of oxide features within the void or Al thin film is an additional process caused by the inward diffusion of oxygen. Faceted hollow oxide features with much smaller dimensions (max. ~2 µm in diameter) grown in the void under the surface membrane were observed by SEM and TEM in FIB prepared cross sections. A detailed analysis is beyond the scope of this study.
5.4 Conclusion

The formation of faceted voids induced by solid state dewetting of tetracrystalline Al thin films covered with a native oxide layer was investigated. Voids formed by the retraction of the Al thin film underneath the continuous surface oxide induced by annealing at 600°C under Ar protective gas atmosphere.

Two different Al|void shapes were observed. In some cases, Al was redistributed isotropically to the surrounding leading to a homogenous thickness increase of the Al film and hexagonal voids with alternating short and long side facets. The ideal void shape is described by an inverse Wulff shape of Al. A faceted Al|void interface with \{111\} and \{100\} facets formed whereby surface roughening is found for the \{100\}/\{111\} facet junction as revealed by a rounded shape. Pinning of distinct sides of the retracting Al film led to a discontinuous and anisotropic retraction of the thin film and irregular void shapes. A rim formed by accumulation of Al at the Al|surface|void triple junction. Additionally, an epitaxial sapphire ridge formed as consequence of the capillary energy force component acting perpendicular to the film|substrate interface.

In both cases, the thickness of the surface oxide layer was increasing with time, whereby the layer was continuous and covered both, the Al thin film as well as the void. The details of the oxygen diffusion are not clear, but residual oxygen in the Ar atmosphere was identified as likely oxygen source. The initial amorphous surface oxide layer in the as-deposited films underwent a phase transformation to $\gamma$-Al$_2$O$_3$ after annealing. High resolution STEM and ELNES analysis of the nm-range thin oxide layer confirms $\gamma$-Al$_2$O$_3$ on a local scale. A cube-on-cube orientation relationship between Al thin film and surface oxide was observed whereby two OR containing twin variants were found.
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6  Dewetting mechanisms and kinetics of bicrystalline Al thin films

In this chapter, the dynamics of dewetting of Al thin films on sapphire are reported. It is currently in preparation for publication [117]. Instead of tetracrystattaline Al thin films, bicrystalline ones containing only $\Sigma 3$ boundaries were used to reduce grain boundary and texture effects. In-situ annealing experiments in a dedicated ESEM enable the direct observation of solid state dewetting mechanisms below a passivating capping layer.

6.1  Introduction

Interpretation of kinetics on post mortem samples is challenging due to a complex interplay between the competing or interfering mechanisms taking place during the experiment which cannot be frozen instantaneously [31, 36]. In-situ techniques allow the direct observation of time-dependent phenomena, e.g. grain growth, oxidation or phase transformation and reveal details of the dynamics and the involved mechanisms due to the advantage of temporal resolution [31, 59, 200]. In the present chapter in-situ environmental scanning electron microscopy was used to investigate the dynamics of the solid state dewetting behavior of mazed bicrystalline Al thin films under well-defined atmosphere and temperatures.

Solid state dewetting is usually controlled by surface diffusion and capping layers can be added on thin films in order to suppress dewetting [13]. However, despite these capping layers, void formation is known as a degradation phenomenon for Al thin films on oxidized Si, which are used as conductor lines [42]. Thermally induced stresses were identified as driving forces for dewetting with grain boundary diffusion as major diffusion path [43, 44]. The ex-situ annealing induced void formation in 250 nm tetracrystatlike Al thin films was described in chapter 5. Voids were observed to form within the Al thin film underneath the continuous oxide layer via grain boundary and interface diffusion due to the suppression of surface diffusion [73, 116]. Irregular void shapes indicated a discontinuous void growth mechanism. Temperature induced void formation of Al thin films covered with a capping layer was observed in literature for Al on passivated Si [44, 111] and Al on Al$_2$O$_3$ [46, 47, 73, 116]. All mentioned studies analyzed the solid state annealing behavior indirectly after ex-situ annealing without direct observation of the involved processes. Sugano et al. observed temperature induced void formation in Al thin films in-situ by optical microscopy and reported void formation during heating without major changes during cooling [45].
In this chapter, direct observations of the dynamics of the solid state dewetting behavior of bicrystalline, nominal 50 nm Al thin films on sapphire (α-Al₂O₃) in oxidizing atmosphere using an ESEM are reported. In contrast to the ex-situ annealed Al thin films (chapter 4 and 5), mazed bicrystalline thin films containing only OR I a/b were used in the in-situ study. The mazed bicrystalline Al thin films served as a defined model system to reduce the influence of interfering texture evolution or grain boundary effects as observed for oligocrystalline or polycrystalline thin films [35, 73]. The mechanisms of annealing induced void formation, void growth and faceting as well as fingering instabilities and their evolution with time were directly observed in-situ and provided quantitative data on the void growth behavior. Dewetting under reducing atmosphere was also investigated to resolve the impact of the surface oxide on the thin film evolution.
6.2 Results

6.2.1 In-situ void formation

The initial, dense, homogenous Al film possessed defects like scratches and surface contamination in the form of aggregates. They were visible at a few locations and were used as markers during the in-situ experiments. The in-situ SEM micrograph sequence in Figure 6-1 (left) shows the discontinuous evolution of a void with annealing time (~40 min). The void is initiated close to a defect (scratch) in the dense Al film and forms a well-defined hexagonal shape with alternating short and long facets.

![Figure 6-1](image)

*Figure 6-1 Left: Void evolution with annealing time observed in-situ in the ESEM (~40 min, O2, ~500°C. A part of the micrographs is missing due to sample drift. The full region of interest can be seen in Figure 6-2). Right: Superposition of the perimeter after selected annealing times and variations of the void centroid with annealing time.*

The void grows and its shape deviates from the hexagon due to pinning of the triple line at various locations, e.g. defects. Pinning can eventually be overcome, and Al film retraction continues. As a consequence of pinning and variations in growth speed, faceted voids develop asymmetric shapes. The evolution of the shape is shown in Figure 6-1 (right) as overlays of the void perimeter for different annealing times (background SEM micrograph for \( t_0 + 904 \text{ s} \)). The changing boundary conditions and resulting variation of the growth direction can be
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visualized by a change of the centroid of the void with annealing time shown as overlay in Figure 6-1. The centroid moves by ~1.7 µm for this void (max. diameter ~5.0 µm), while the void grows in a direction away from the pinning obstacles, which is in this case the scratch on the top left side.

The void perimeter increases linearly with time for the major growth regime which indicates a constant diffusion rate of Al. Subsequently, the velocity of the retracting facets decreases as the hole grows. For example, in the case of void 1 in Figure 6-1, the velocity of the moving facets is in the range of ~50 – 100 nm/min for the main growth regime. The corresponding equivalent void radius $r_{\text{void}}$ can be described by a power law function of the annealing time $t$: $r_{\text{void}} \sim t^\alpha$. The power law fit applies for the main growth regime, while at the beginning the growth can occur faster. In the initial stages, facet velocities up to ~300 nm/min were obser-
Figure 6-3 a) Initial microstructure of the region of interest for the long-term in-situ annealing experiments (~15.3 h, O₂, ~500°C). b) Equivalent void radius evolution with annealing time for the voids 4 to 6 (Note: for void 4 the time of the initial void formation was set as t₀, for void 5 and 6, the absolute time was used because the initial void formation was not observed). c) Temperature induced microstructural changes after ~15.3 h annealing (see text for details). The evolution of different features with time is indicated by the white rectangles.
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Devoid depending on the pinning sites (e.g. Void 1 in Figure 6-2a). Different power law exponents are observed for different voids tracked in the same dataset: $r_{\text{void } 1} \sim t^{0.36}$, $r_{\text{void } 2} \sim t^{0.26}$ and $r_{\text{void } 3} \sim t^{0.11}$ and they stay constant for short-term experiments. The power law fits are shown in Figure 6-2c. In the long-term experiment, the growth of individual voids slows down (void 4: $r_{\text{void } 4, \text{ beginning}} \sim t^{0.55}$, $r_{\text{void } 4, \text{ major phase}} \sim t^{0.10}$ and void 5: $r_{\text{void } 5, \text{ beginning}} \sim t^{0.36}$, $r_{\text{void } 5, \text{ major phase}} \sim t^{0.13}$) or even stops (void 6, $r_{\text{void } 6, \text{ growth phase}} \sim t^{0.21}$). This can be seen in the change of the slope in the log-log-plot in Figure 6-3b. In summary, the power law exponent $x$ of the individual voids varies from 0.10 and 0.55 depending on the pinning of the retracting film at obstacles.

New voids form after variable incubation times. This is clearly visible in the long-term experiment comparing the first and the last micrographs after $\sim 15.3$ h shown in Figure 6-3a and c. The region of interest shown in Figure 6-3a was chosen, once the target temperature was reached. Some voids are already present indicating void formation during heat up. The complexity of the dewetting progress increases with increasing annealing time as observed for the 15.3 h annealed sample presented in Figure 6-3. Additional features evolve as a result of the variation of the boundary conditions due to pinning as shown in Figure 6-4. Faceting instabilities or micro faceting, fingering instabilities, and pinch-off processes are observed at different edges of the same void.

Pinning and depinning of a retracting Al front during the dewetting process is shown for void 4 in the SEM image sequence (only selected frames) and the perimeter evolution of the void is displayed in Figure 6-5. The curvature of the remaining Al film feature increases. The curvature is described by the angle $\phi$ between both feature facets which decreases from $\sim 120^\circ$ down to $\sim 41^\circ$ when the pinning condition is overcome and the Al film retraction continues. A second pinning event occurred at the lower Al|void interface, but is overcome despite a comparably high angle $\phi$ of $\sim 109^\circ$. Faceting instabilities occur, but as annealing time increases straight facets reform as observed for the right part of the void shown in Figure 6-5.
Figure 6-4 Plan-view SEM micrograph after annealing revealing faceting instabilities as well as a fingering instability (~40 min, O2, ~500°C).

Figure 6-5 Left: Sequence of SEM micrographs of void 4 in Figure 6-3 revealing pinning and subsequent overcome of the pinning conditions for distinct region of the retracting Al film. Faceting instabilities are observed for different annealing times. Right: The superposition of the void perimeter is shown for selected annealing times for the main growth phase.
Regions of the long-term annealing experiments and their evolution with time are shown in Figure 6-6 and Figure 6-7. Figure 6-6 shows a kink-flow like diffusion mechanism along void facets. Figure 6-4 shows the “height” of the micro-kinks which is generally around ~100 nm. The average micro kink velocity along the facet is ~10 nm/min. The intermediate stages reveal a structure with faceting instabilities or micro facets.

Figure 6-6 The solid state dewetting mechanism of a large void via a kink-flow process along the Al sidewall facet is shown in the sequence of SEM micrographs of the marked region of void 5 in Figure 6-3.

Different phenomena are observed in the SEM micrograph sequence in Figure 6-7. As the Al film adjacent to a pinning point retracts, a fingering instability builds up and lasts for ~300 min. The adjacent Al film possess distinct facets with increasing time while faceting instabilities occur due to the kink-flow mechanism as observed in Figure 6-6. Within a recorded image frame (acquisition time ~2 min), the finger pinches off and forms an isolated thin line. The base of the former finger is unstable and is subsequently removed. The removal of the base and the reformation of a defined facet occurs relatively fast (<100 min) compared to the depinning of the fingering instability in Figure 6-5 (~500 min). The resulting facet becomes more straight. The dewetting process continues via the kink-flow mechanism along the newly formed facet resulting in faceting instabilities.
In-situ annealing at ~550°C in reducing atmosphere (67% H₂/33% N₂, ~50 Pa) led to a different solid state dewetting behaviour compared to annealing in oxidizing atmosphere. After dwell times in the range of minutes after reaching the desired temperature, the dense film ruptures, giving rise to the formation of isolated, μm-sized features. The process is relatively fast at 550°C (takes less than 35 s). Figure 6-8 shows the resulting, complex microstructure which is beyond the scope of this thesis. These experiments confirm the correlation of the void formation and diffusion-limited dewetting in conditions where a continuous surface oxide film is stable.
Comparison of the microstructure before and after annealing

Figure 6-9a shows the columnar grain structure containing grains with an average grain width in the range from 50 – 200 nm for the as-deposited thin film. The \{111\} Al pole figure in Figure 6-9b, obtained by XRD, revealed a ~1:1 ratio between the two twinned in-plane orientations in accordance to literature [55]. A uniform Al film thickness of 57.2±0.7 nm was determined for the as-deposited sample. The Al- and O-EDS mappings in Figure 6-9c show that the Al thin film is covered by an amorphous and continuous native Al₂O₃ oxide layer of 3.6±0.4 nm in thickness. The twin-related heteroepitaxial orientation relationship \textit{OR I a/b} between Al and the single crystalline α-Al₂O₃ can be seen Figure 6-9d.

The atomic column resolved STEM micrograph shows a triple junction of a \Sigma 3 \{2\overline{1}1\} Al twin boundary and the substrate. The high interface contrast is due to Ga enrichment at the Al|Al₂O₃ interfaces which happened during the FIB TEM sample preparation. The presence of Ga is confirmed by EDS (data not shown) and is in accordance to literature [73, 153, 154] and the results in the chapters 4.2.1 and 5.2.2.
Selected in-situ annealed samples were analyzed post mortem. For TEM analysis, regions of the short-term (~40 min) in-situ annealed sample containing voids as well as fingering instabilities were prepared by FIB. Figure 6-10 displays the region of interest chosen for TEM analysis in plan-view. Different features are shown in cross section in Figure 6-11a.

Figure 6-10 Plan-view SEM micrograph of the selected region of interest for site-specific TEM analysis shown in Figure 6-11.
Both, the Al film and the void, are covered by a surface oxide layer 5.5±0.4nm thick. The voids underneath a continuous surface oxide membrane appear dark in the SEM micrographs. When the surface membrane is collapsed (mainly after the in-situ experiment), the voids appear bright in plan-view SEM micrograph due to charging effects of the Al$_2$O$_3$ substrate. In that case, the surface layer is in contact with the substrate as for the marked region in Figure 6-11a.

![Figure 6-11](image)

**Figure 6-11** Annealing induced microstructural changes revealed by post mortem analysis (~40 min at ~500°C). a) Cross-sectional SEM micrograph of the final TEM lamellae of the region marked by a dashed line in Figure 6-10). Voids, a fingering instability and a region with a collapsed surface membrane are observed. Cross-sectional STEM HAADF micrographs showing b) the Al|void interface region with a surface membrane, continuously covering both, the Al thin film as well as the void and c) the marked fingering instability. d) Combined Al- and O-EDS mapping of the fingering instability region. The finger consists of pure Al, the Al oxide membrane is intact for this region. e) STEM micrograph of a region adjacent to the Al|void interface confirming OR I. The twin variants can not be distinguished in the present Al [211] zone axis ([2110] Al$_2$O$_3$ zone axis, overlay of red Al and white O atoms).

Figure 6-11b shows the Al|void interface region without rim or ridge formation at the triple junctions. Corresponding Al-, O- and Ga-EDS mappings of the Al|void interface region are shown in Supplementary figure 6-1. Minor change in Al film thickness was observed
compared to the as-deposited film. Small variations from one to another region occurred, e.g. 54.1±0.8nm and 56.6±0.5nm. The total thickness (metal film plus oxide) remains almost constant indicating that Al redistributes over large areas [116]. The STEM micrograph in Figure 6-11c reveals that the sectioned fingering instability is tapered towards the periphery (centre thickness ~55 nm, outer thickness 51 nm). The corresponding combined Al-O-EDS mappings, shown in Figure 6-11d, confirm that the fingering instability consists of pure Al and that the adjacent voids are also covered by a continuous oxide membrane.

Post mortem EBSD analysis of short-term as well as of long-term in-situ annealed samples reveal no change in texture. In-plane orientation maps are shown in Supplementary figure 6-2. After annealing, the Al twin growth variants OR I a/b are still arranged in a mazed structure, typical for fcc metallic thin films on single crystalline (0001) α-Al₂O₃ [40, 55, 201-203]. Atomic column resolved STEM micrographs adjacent to the Al|void interface confirm OR a/b (Figure 6-11e). Neither pores nor voids are observed in the HRSTEM micrographs. An atomically sharp Al|substrate interface is observed and as for the FIB prepared TEM sample of the as-deposited thin film, the high contrast at the interface is caused by a Ga artefact. The O-, Al- and Ga-EDS mappings shown in Supplementary figure 6-1 confirm this. The elongated white features in the sapphire correspond to Al and O columns as indicated by the projected crystal structure overlay. Despite dominating HAADF conditions, the O columns between the elongated features are indicated by the low contrast.

Along annealing the grain size increases to 1.7±1.4 µm (short-term, ~40 min) and 1.9±1.5 µm (long-term, ~15.3 h) which is a factor of ~10 compared to the grain size in the as-deposited thin films. Within the same time, the OR I a/b twin ratio barely changes (short-term ~1.28:1 and long-term ~1.04:1). Plane trace analysis of the Al film surrounding the void confirms that the directions along the facets are <110> directions. In contrast to the plan-view observation, no defined Al sidefacets at the Al|void interfaces were found in cross-sectional TEM samples.

6.3 Discussion

6.3.1 In-situ observed dynamics

During the in-situ annealing experiments in reducing atmosphere, the covering oxide membrane was partially removed. The lack of oxygen prevented healing of the cracks [81, 204]. In that case, surface diffusion is possible [13] and the growth of a complex microstructure with µm-sized particles next to the exposed substrate occurred as shown in Figure 6-8. Void formation was only observed in-situ in oxidizing atmosphere during solid
state dewetting of Al films on sapphire. This indicates that the Al interfacial diffusion underneath the surface oxide is responsible for the diffusion-limited, sluggish void formation and void growth. We speculate that the removed Al is redistributed to the surrounding via diffusion along the film|substrate and film|surface oxide interface \[116\]. The involved diffusion processes are described in more detail in chapter 5.3.2. The surface oxide is stabilized, e.g. in O\(_2\) atmosphere in the ESEM in this in-situ study or by O\(_2\) or H\(_2\)O as residual or process gases during ex-situ annealing \[47, 73, 116\]. The surface oxide increases in thickness and it is still continuously covering the film respectively the void in accordance to ex-situ annealing results of 250 nm Al films containing four ORs described in chapter 4 and 5 \[73, 116\].

The in-situ study of 50 nm passivated mazed bicrystalline Al films allowed the direct identification of the (weak) points, where the voids initiated, e.g. at surface scratches and defects at the film surface. However, voids were also observed to a minor degree within regions where no surface defect was detectable in the SEM. Void formation could also start at substrate imperfections at the interface to the films, which could be e.g. contaminants or surface steps being present prior Al film deposition. The EBSD analysis in the ex-situ study indicated that initial void formation might also occur at high energy grain boundaries (chapter 4.3.2) \[73\]. As the \(\Sigma 3\ \{2\overline{1}1\}\) twin boundaries are the only grain boundaries in the mazed bicrystalline films, dewetting might also start at triple junctions. Dewetting is also reported for mazed bicrystal thin films without capping layer, e.g. Ni on sapphire \[40\] and Au-Fe on sapphire \[170\]. Processes at the substrate interface cannot be resolved by the applied imaging conditions in the ESEM. Müller and Spolenak reported that pores initially form at the film|substrate interface, grow preferentially along grain boundaries in Au thin films and evolve to voids \[91\]. In-situ SEM and post mortem STEM investigations (Figure 6-11) in the present work neither support this statement nor grain boundary grooving from top, but pore formation cannot be excluded.

The in-situ observed void size evolution is represented by the change of the equivalent radius with annealing time \(t\) in Figure 6-2c for the short-term experiment. It can be described by one power law \(r_{\text{void}} \sim t^x\), where \(r_{\text{void}}\) is the equivalent void radius and the exponent \(x\) varies in the range from 0.10 to 0.55 for different voids. While the growth behavior for the short-term (~40 min) experiments can be described by one power law function, the results of the long-time (~15.3 h) annealing experiment can only be explained by using two power law functions with different exponents. The reason for two different growth regimes of the voids in the long-term experiment is unknown. The void size evolution for ex-situ annealed
tetracrystalline 250 nm Al thin films was described with the power law $r_{\text{growing void}} \sim t^{0.23}$ (see chapter 4.2.2) [73]. The differing exponent of the ex-situ study can be explained by statistics as well as by other parameters such as film thickness, texture or grain size (evolution).

This in-situ study confirms a discontinuous void growth mechanism due to pinning. Void facet pinning and its sudden release was observed as shown in Figure 6-5. The degree of complexity to describe the dewetting phenomena is increasing with annealing time due to varying boundary conditions affecting the void growth and also leading to additional microstructural features, e.g. fingering instabilities, which affect the initial hexagonal void shape. This can explain the irregular shaped voids observed in ex-situ studies [47, 116]. New voids formed after different incubation times constantly in-situ and were also observed in the ex-situ study in chapter 4.2.2, where a bimodal void size distribution was found [73]. The ongoing formation of new voids was also reported by Shaffir et al. [92, 93] and Müller and Spolenak [91].

With increasing annealing time faceting instabilities were observed. Al is transported along the facets in $<110>$ directions by a kink-flow like mechanism via surface diffusion, finally leading to straight facets again as shown in the SEM sequences in Figure 6-5 and Figure 6-6. Faceting instabilities are described in literature as result of anisotropic edge retraction [37].

Another phenomenon caused by pinning is the formation of fingering instabilities which can pinch-off. Depinning can occur as shown in Figure 6-5, film retraction continues and fingering instabilities regresses. Fingering instabilities during dewetting without capping layer are reported to account for the arrangement of faceted particles after dewetting [51]. They can also completely retract and disappear as observed in-situ by Niekiel et al. [76]. Figure 6-4 shows faceting instabilities as well as a fingering instability for the same void. In the previous ex-situ study [73], faceting instabilities and film retraction adjacent to a pinned position were also observed, while almost no fingering instabilities occurred.

6.3.2 Microstructural evolution

The twin ratio of the initial bicrystalline mazed microstructure remained during annealing, in contrast to the results of Dehm et al. who observed that one variant grew on the expense of the other without void formation during annealing of 350 nm thin films up to 450°C [55]. We speculate that the formation of voids might disturb grain growth and texture evolution as indicated in the ex-situ study in chapter 4.3.1 [73]. Similar grain sizes for short-term and long-term annealed thin films were found in the present study indicating grain growth
stagnation with grain sizes up to ~40 times the film thickness. As described in chapter 4.3.1, grain growth might be pinned by the voids or the driving force might be low due to the low energy of $\Sigma 3 \{21\overline{1}\}$ twin boundaries compared to the one of higher energy CSL boundaries [73, 159] as grain boundary energy and interface energy minimization is the main driving force for grain growth [49].

Plan-view SEM micrographs as shown in Figure 6-12 after ~15.3 h in-situ annealing revealed that the voids occupied ~3.9% of a ~381 by 286 µm large area. The average void diameter (35 voids analyzed) was ~12.2±2.4 µm, the $OR I$ grain width 1.9±1.5 µm and the ratio of both ~6:1. The post mortem analysis only leads to an averaged value as the ratios of individual tracked voids differ, e.g. ~10:1 (void 5, Figure 6-3) and ~3:1 (void 6, Figure 6-3). For 250 nm thin tetracrystalline Al thin films annealed at 600°C ex-situ, the average void diameter to $OR I$ grain width ratio after 24 h annealing was ~3:1 (exposed void area ~3.5%) [73]. The in-situ dewetting occurs faster despite a lower annealing temperature of 500°C leading to faster exposure of the substrate.

Figure 6-12 Plan-view SEM micrograph after annealing, before binarisation and subsequent void size analysis (~15.3 h, $O_2$, ~500°C).

Beside differences in $\{111\}$ texture, we speculate that the ~5 times lower film thickness in this study is the major cause for this different time dependence as decreasing film thickness
is well-known to strongly affect the solid state dewetting behavior by reducing the required temperature [13]. For bicrystalline films, the covering surface membrane of most of the voids collapsed, probably after the in-situ experiment due to the small film thickness as shown in Figure 6-12.

The in-situ setup allowed fast cooling (estimated cooling time down to 200°C ~30 seconds compared to 3 or more minutes for ex-situ annealing) and hence quenching of the microstructure. The directly observed kink-flow mechanism indicates surface diffusion at the Al sidewall, i.e. the Al|void surface. The correlated diffusion processes for void growth were discussed in the cross-sectional study of ex-situ annealed tetracrystalline Al thin films in chapter 5.3.2 in detail [116]. In brief, Al diffusion from the Al|void|sapphire triple junction towards the Al|void|surface oxide and subsequent outward Al diffusion at the Al|surface oxide interface was assumed as major Al diffusion pathways. Still, interfacial diffusion at the Al|sapphire cannot be excluded.

No rim or ridge was observed adjacent to Al|void interface after short-term in-situ annealing in contrast to the ex-situ annealed tetracrystalline samples. Al|void interfaces with and without rim as well as ridge formation were found for the latter samples as described in chapter 5.2.2 [116] and also in [46]. However, ridge formation was indicated by straight features after long-term in-situ annealing, e.g. as observed in Figure 6-13. These features reflect the void perimeter evolution with annealing time as indicated by the colored overlays in Figure 6-1 and Figure 6-5. After ridge formation, depinning might have occurred and the ridges were left behind during further film retraction. That ridges actually form after sufficient

Figure 6-13 Plan-view SEM micrograph after in-situ annealing experiments revealing voids with a collapsed surface membrane (~15.3 h, O₂, ~500°C). Within voids, bright features are observed indicating pinning, ridge formation and subsequent continuation of the Al film retraction leading to leftover ridges. b) The leftover ridges reflect intermediate states of the dewetting process in the magnified section marked in a).
pinning time is well-known in literature [116, 193]. Sapphire ridge growth due to the unbalanced capillary energy force component acting perpendicular to the film|sapphire interface at triple phase boundaries was reported for different metal|Al2O3 interfaces [79, 155, 193, 205].

Figure 6-12 shows other microstructural features such as hillocks observed in SEM, but only to a minor degree considering the area fraction. Void formation and void growth were the major phenomena observed in plan-view SEM imaging in-situ as well as post mortem. However, hillocks can be closely connected to the initiation and growth of voids. Kovalenko et al. reported the formation of hillocks in the vicinity of, but not directly located next to holes, which formed due to dewetting [38]. They explained the hillock formation within the film by material diffusion via grain boundaries and interface diffusion at the film|substrate interface. Shaffir et al. reported hillock and void formation in Au thin films, but stated that both are independent phenomena [93]. However, in the present in-situ study a direct correlation of hillocks and voids was not found.

6.4 Conclusion

The solid state dewetting behavior of a passivated mazed bicrystalline Al thin film model system was investigated in-situ in an ESEM. Faceted void formation and growth were observed at ~500°C in 30 Pa O2 atmosphere. In-situ annealing experiments in reducing atmosphere at ~550°C led to rapid solid state dewetting and the formation of particles. Thus, the surface oxide suppresses surface diffusion and slows down dewetting in terms of void formation and growth.

Void growth dynamics is influenced by the pinning events of the triple line. It can be described by a power law \( r_{\text{void}} \sim t^x \) with an exponent \( x \) varying in the range of 0.10 to 0.55. The void growth dynamics is discontinuous with fingering instabilities forming at pinning sites. With time, fingering instabilities heal or pinch-off and form elongated islands as observed in some of the dewetted areas. Both processes require sufficient incubation time. As a consequence of pinning, the void shapes deviate from the ideal hexagonal shape. Furthermore, a kink-flow like diffusion mechanism participates to film retraction. These faceting instabilities are the intermediate step of the final state where straight facets again formed. The \{111\} texture of the Al thin film stayed bicrystalline with a twin ratio ~1:1. Grain size stagnated when the grains have grown by a factor of ~10.
In summary, the in-situ annealing ESEM experiments confirmed the proposed discontinuous void formation mechanism for surface-passivated Al thin films on sapphire \([116]\). Details of the void formation and growth dynamics were revealed. This study shows the potential of in-situ annealing experiments at low pressures with defined gas compositions. The time-dependent observation of solid state dewetting processes can proof conclusions derived from ex-situ experiments.

### 6.5 Supplementary data

*Supplementary figure 6-1* Al-, Ga- and O-EDS mappings of the corresponding HAADF micrograph of the Al|void interface in Figure 6-11b.
Supplementary figure 6-2 EBSD orientation maps revealing the in-plane orientation of the Al thin film containing only OR 1 a/b and the presence of faceted voids (left: ~40 min, O₂, ~500°C, right: ~15.3 h, O₂, ~500°C; OR 1 a/b in purple, voids in bright blue, Σ3 twin boundaries in white, area not containing indexed Al or α-Al₂O₃ grains in black).
Summary and outlook

This thesis focused on the solid state dewetting phenomena, the microstructural evolution and the underlying diffusion mechanisms of passivated, epitaxial Al thin films on single crystalline (0001) oriented sapphire substrates. Thin film deposition by molecular beam epitaxy led to defined model systems, in more detail tetracrystalline respectively bicrystalline Al thin films. The as-deposited films possess highly twinned orientation relationships with the underlying substrate:

\[ \text{OR I } a/b \{111\} \pm <\bar{1}10 >_{Al} \parallel (0001) < 10\bar{1}0 >_{Al2O3} \]

\[ \text{OR II } a/b \{111\} \pm <2\bar{1}\bar{1}>_{Al} \parallel (0001) < 10\bar{1}0 >_{Al2O3}. \]

All as-deposited films were dominated by \text{OR I } a/b with the close-packed planes and directions parallel to each other, which are the only growth variants in the bicrystalline film. A second, minor \text{OR II } a/b is present in the tetracrystalline film leading to a microstructure containing further, higher order CSL boundaries in addition to the most frequent \( \Sigma 3 \) twin boundaries.

The tetracrystalline Al thin films were annealed ex-situ under Ar protective atmosphere below the melting point of Al at 600°C. Post mortem analysis of the resulting microstructure in plan-view revealed the occurrence of accompanying and potential interfering solid state phenomena. First, grain growth and texture evolution towards an \text{OR II} dominated microstructure occurred. In-situ annealing XRD experiments confirmed the texture change. Second, the capillary driving forces caused a retraction of the Al thin film underneath the passivating, continuous oxide scale which led to the formation of faceted voids. The interplay of these phenomena was confirmed by the quantitative analysis of the post annealing samples. High energy grain boundaries between \text{OR I} and \text{OR II} were identified as initial points for void formation as the majority of the voids were adjacent to both, \text{OR I} and \text{OR II}, Al grain orientations.

The void analysis revealed a bimodal size distribution which indicates besides growing voids (average radius \(~4.5 \mu m\) after 45 h annealing) constantly ongoing formation of new voids after varying incubation times (average radius \(~0.4 – 0.7 \mu m\) for each annealing time). The voids inhibited further grain growth and texture evolution as a quantitative analysis of the grain orientation and grain size distribution data confirmed. The major change in Al film texture from \(~80\% \text{OR I}\) to \(~70\% \text{OR II}\) occurred within 1 h annealing and changed only slightly with increasing annealing time. The average grain size increased from \(~0.5 \mu m\) to
~2.5 µm (OR I, grain width) respectively ~4.5 µm (OR II, grain diameter) within 1 h annealing and stayed constant within the error bar for longer annealing times.

Site-specific cross-sectional TEM investigations confirmed that the surface oxide was still continuously covering both, the Al thin film and the void, after annealing. In addition, the oxide increased in thickness which was correlated to inward diffusion of residual oxygen in the furnace atmosphere through the surface oxide. ELNES investigations of the surface oxide confirmed a phase transformation of the amorphous oxide in the as-deposited state to \(\gamma\)-\(\text{Al}_2\text{O}_3\) due to the annealing. High resolution STEM revealed a twinned cube-on-cube orientation relationship with the close-packed planes and directions parallel to each other between the \(\gamma\)-\(\text{Al}_2\text{O}_3\) surface oxide and the underlying Al film. From the presence of a continuously covering surface oxide, it was concluded that surface diffusion was suppressed at each processing step and grain boundary as well as interface diffusion were the major diffusion pathways.

The annealing induced voids could be subdivided into hexagonal and irregular shaped ones. The ideal shape was described by an inverse Wulff shape of an Al crystal resulting in alternating short and long facets parallel to the \(< 1\bar{1}0>\) Al directions. Al of the former void volume was redistributed to the surrounding and resulted in a homogenous increase in Al film thickness over several µm. Pinning of selected, retracting Al film fronts at obstacles, and potential overcoming of these obstacles and further retraction, broke the symmetry of the voids. The related anisotropic, discontinuous growth process resulted in the formation of irregular void shapes. Site-specific cross-sectional TEM investigations revealed the formation of Al|void regions containing a rim and often also a ridge. A pile up of Al at the Al|void|surface triple junction led to the formation of a rim and the unbalanced vertical capillary force component at the Al|void|substrate triple junction led to formation of a sapphire ridge, which grows epitaxially on the single crystalline substrates.

The bicrystalline Al thin films were annealed in-situ in an environmental SEM to get insights into the details of the void growth mechanism and its dynamics. Bicrystalline Al thin films were used to reduce the interference of grain boundaries and texture evolution with the void formation. Plan-view as well as cross-sectional analysis prior and after in-situ annealing revealed only minor changes of the \{111\} texture and grain growth to a minor degree compared to the ex-situ annealed tetracrystalline Al films. The void growth process was observed in-situ exclusively in oxidizing atmosphere. The surface oxide slows down dewetting by suppressing the surface diffusion resulting in sluggish void formation and void growth. On the contrary, in-situ annealing in reducing atmosphere led to a spontaneous solid
Summary and outlook

state dewetting behavior, including film rupture and the formation of micron-sized isolated particles. H₂ might partially remove the surface oxide and prevent healing. Consequently, the former suppressed surface diffusion can facilitate dewetting.

The analysis of the void growth dynamics confirmed the discontinuous growth mechanism as indicated from ex-situ annealing experiments. Pinning of the distinct sides of the retraction of the Al film and potential release of the pinned Al film front led to an increased complexity of the solid state dewetting processes and consequently variations from the initial hexagonal void shape. In addition, the formation of faceting instabilities via a kink-flow mechanism and fingering instabilities were directly observed in the ESEM. Fingering instabilities can pinch-off leading to isolated straight features or be removed after sufficient time. The void size change with annealing can be described with a power law $r_{\text{void}} \sim t^x$ as derived from a quantitative analysis of the in-situ as well as the ex-situ data. The power law exponent $x$ was found in the range from 0.10 to 0.55. The variation is caused by the individual growth behavior due to the individual pinning conditions.

In summary, the findings of this work revealed details of the solid state dewetting processes of passivated thin film systems by combining complementary ex-situ and in-situ techniques at different length as well as time scales. The dynamics of solid state dewetting processes were observed directly at high spatial resolution and complement the results derived from post mortem analysis. However, several details of the underlying mechanism are still not fully understood. Further plan-view as well as cross sections studies of in-situ annealed bicrystalline Al thin films are needed to clarify the presence or lack of rim and ridges. The indicated high energy grain boundaries for void initiation could be studied by in-situ annealing of tetracrystalline Al thin films. The nature of obstacles leading to pinning is still unexplored and could be triggered by modification of the substrate before film deposition. Plan-view in-situ TEM experiments would offer a higher spatial resolution of selected triple phase boundaries whereas the need for a surface layer and a substrate would make the realization challenging.

The obtained results about solid state dewetting, derived from ex-situ and in-situ studies of defined thin film systems, should be considered for further refinement of solid state dewetting models, e.g. phase field approaches. In addition to surface diffusion, grain boundary as well as interface diffusion need to be taken into account and implemented in simulations. Understanding of solid state dewetting is beneficial to avoid thin film degradation. On the other hand, the formation of voids with a defined size distribution within a dense metallic film on a transparent substrate like sapphire can be exploited for optical applications,
e.g. plasmonics. Optimization of the main parameters for dewetting, film thickness, annealing temperature, capping layer and film texture, allows tuning of the dewetting behavior for solid state dewetting engineering.
8 References


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9 Appendix

9.1 Chapter contributions

Stefan Hieke wrote all chapters, performed the literature review and edited the figures. The following overview lists briefly the main contributions of the authors of the publications, on which the main chapters 4, 5 and 6 are based on, and collaborators.

Chapter 4: For this chapter, writing of the manuscript, screening the literature, editing of the graphics, data interpretation and discussion was done by Stefan Hieke. The thin film growth was done by Gerhard Bialkowski and Stefan Hieke. Gerhard Bialkowski supported the annealing treatments which were performed by Stefan Hieke. Benjamin Breitbach performed the ex-situ and the in-situ XRD measurements and data processing. Katja Angenendt supported Stefan Hieke with the EBSD measurements and data processing. Stefan Zaefferer helped with the EBSD data interpretation. Rasa Changizi preprocessed a part of the SEM data for quantitative analysis. The SEM, FIB and TEM experiments, data analysis and interpretation was done by Stefan Hieke. Tristan Harzer supported the HRTEM investigations. Christina Scheu and Gerhard Dehm revised the published manuscript, on which the chapter is based on.

Chapter 5: For this chapter, Stefan Hieke wrote the manuscript, performed the literature study, data interpretation and discussion. Gerhard Bialkowski and Stefan Hieke did the thin film growth. The annealing treatments which were performed by Stefan Hieke and supported by Gerhard Bialkowski. SEM, EBSD, FIB and TEM measurements, data processing and analysis was done by Stefan Hieke. Christian Liebscher supported the acquisition of high resolution STEM and EELS data as well as the processing of high resolution STEM image stacks. Diffraction pattern simulation and FFT analysis of STEM micrographs was done and interpreted by Stefan Hieke. Christina Scheu and Gerhard Dehm revised the published manuscript, on which the chapter is based on.

Chapter 6: The writing of the manuscript, the literature review, data interpretation and discussion was done by Stefan Hieke. The thin film growth was done by Ilsemarie Lakemeyer and Stefan Hieke at the Max Planck Institute for Intelligent Systems in Stuttgart. Benjamin Breitbach performed the XRD measurements of the as-deposited film and data processing. The in-situ annealing experiments in the ESEM were carried out by Zhu-Jun Wang and Stefan Hieke at the Fritz Haber Institute of the Max Planck Society in Berlin. ESEM data analysis as well as EBSD, SEM, FIB and TEM investigations of the samples after deposition and post mortem, data processing and interpretation was done by Stefan Hieke. Marc-Georg Willinger,
Appendix

Gunther Richter, Dominique Chatain, Gerhard Dehm and Christina Scheu discussed the data and revised the manuscript, on which the chapter is based on and which is currently prepared for publication.
10 Curriculum Vitae

Personal Information

Name and Surname: Stefan Werner Hieke
Date of Birth: 12.05.1987
Place of Birth: Rosenheim
Nationality: German

University Education

08/2013 – present: PhD thesis at the Max-Planck-Institut für Eisenforschung GmbH (MPIE), Düsseldorf, Germany, research group Nanoanalytics and Interfaces (Prof. Christina Scheu)

10/2010 - 06/2013: Studies of Chemistry at the Ludwig-Maximilians-Universität München, Germany
Degree: Master of Science (M. Sc.), final grade: excellent (1.03)
Major fields of study: Physical and Inorganic Chemistry
Minor field of study: Theoretical Chemistry

10/2007 - 10/2010: Studies of Chemistry and Biochemistry at the Ludwig-Maximilians-Universität München, Germany
Degree: Bachelor of Science (B. Sc.), final grade: good (1.73)
Major fields of study: Chemistry (Physical Chemistry, Inorganic Chemistry, Organic Chemistry)
Minor fields of study: Computer Science, Spectroscopy and Diffraction, Biochemistry

Work Experience

08/2013 – present: Research assistant at the Max-Planck-Institut für Eisenforschung GmbH (MPIE), Düsseldorf, Germany, research group Nanoanalytics and Interfaces (Prof. Christina Scheu)
09/2012 - 06/2013  Master thesis “Electrochemical and Material Characterization of ESC10 Solid Oxide Fuel Cells” at EADS Innovation Works (now Airbus Group Innovations), Research Team Power Generation, TCC Energy & Propulsion (field of research: solid oxide fuel cells), München, Germany

02/2012 – 06/2012  Student research assistant, Ludwig-Maximilians-Universität München, Germany, research group Prof. Christina Scheu

11/2011 – 02/2012  Research internship, Ludwig-Maximilians-Universität München, Germany, research group Prof. Christina Scheu

10/2011 – 02/2012  Tutor, Ludwig-Maximilians-Universität München, Germany, Exercise course accompanying the lecture about fundamental inorganic chemistry

04/2011 – 08/2011  Research internship, Ludwig-Maximilians-Universität München, Germany, research group Prof. Karaghiosoff

06/2010 - 10/2010  Bachelor thesis “DSC analysis of HEDM compositions and new nitrogen-rich energetic materials based on 1H-1,2,4-triazole-1-carboxamidine” at the Ludwig-Maximilians-Universität München, Germany, research group Energetic Materials (Prof. Thomas Klapötte, Inorganic Chemistry)

09/2006 – 05/2007  Civilian service, Nachbarschaftshilfe Rosenheim e.V.

**School Education**

09/1997 - 05/2006  Abitur (general qualification for university entrance), Finsterwalder-Gymnasium Rosenheim (final grade: 1.5)

**Languages**

- German  Native speaker
- English  Business fluent
- French  Basic

**Membership**

- Gesellschaft Deutscher Chemiker e.V. (GDCh)
- Deutsche Gesellschaft für Elektronenmikroskopie (DGE)
- European Microscopy Society (EMS)
11 List of publications and presentations

11.1 Scientific publications

Journals


Conference Proceeding


11.2 Conference Contributions

Oral presentation


**Poster presentation**


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