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The role of internal stress on the growth and breakdown of barrier and porous anodic oxide films

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Contents

List of symbols	5
Scientific output	9
1 Outline of the work	13
1.1 Background	13
1.2 Objectives and contributions	14
1.3 Organization of the text	15
2 State of the art	17
2.1 Applications of anodic oxide films	17
2.1.1 Large-scale applications: aluminum anodizing . . .	18
2.1.2 Nanotechnology applications	19
2.1.3 Electrolytic capacitors	20
2.1.4 Model system for corrosion processes	21
2.2 Growth kinetics of dense oxide films	22
2.2.1 Initial oxide growth	22
2.2.2 High-field ionic conduction	23
2.2.3 Transport numbers	32
2.2.4 Incorporation of electrolyte species	35
2.2.5 Internal stress	37
2.2.6 Anodizing of alloys	44
2.3 Porous anodic oxide films	48
2.3.1 Growth kinetics of porous oxide films	49
2.3.2 Dependence of the morphology on the conditions .	55
2.3.3 Pore nucleation	63
2.3.4 Pore growth	67
2.4 Breakdown of dense anodic oxide films	74
2.4.1 Breakdown phenomenology	74
2.4.2 Phenomena related to the breakdown	77
2.4.3 Dependence of the breakdown on the conditions . .	82
2.4.4 Models for the breakdown of anodic oxide films . .	88
2.5 Summary	93

3	Experimental methods	95
3.1	Sample preparation procedure	95
3.2	<i>In situ</i> curvature monitoring during anodizing	101
3.3	<i>Ex situ</i> characterization methods	104
3.3.1	Scanning electron microscopy	104
3.3.2	Transmission electron microscopy	105
3.3.3	Atomic force microscopy	106
3.3.4	Chemical analysis of the solutions	106
3.4	Conclusion	107
4	Measuring the internal stress during anodizing	109
4.1	Stoney equation	109
4.2	Modified Stoney equation for anodizing	111
4.3	Measuring the curvature	115
4.3.1	The multiple beam optical sensor	117
4.3.2	Curvature determination in air	118
4.3.3	Curvature determination in liquids	126
4.3.4	Resolution limiting factors in liquids	132
4.4	Conclusion	136
5	Internal stress and porous anodic oxides	139
5.1	Experimental details	140
5.2	The role of the internal stress on pore initiation	141
5.2.1	<i>In situ</i> detection of porosity initiation	141
5.2.2	Stability analysis of the barrier oxide film	149
5.3	The role of internal stress on pore growth	158
5.4	Conclusions	168
6	Internal stress and the breakdown of anodic zirconia	171
6.1	A new definition of breakdown	172
6.2	Experimental details	174
6.3	Influence of the breakdown on the voltage evolution	175
6.3.1	Experimental results	175
6.3.2	Ionic conduction parameters	182
6.3.3	Simulation of the voltage evolution	184
6.4	Influence of breakdown on the microstructure	185
6.5	The role of the internal stress on the breakdown	189
6.6	Conclusions	199
7	Conclusions and perspectives	201
	Bibliography	207
	Acknowledgments	237
	Abstract	247

List of symbols

Roman symbols

a	Hopping distance (high-field model)	nm
$ A_0A_1 $	Clamp-to-beam distance (MOS)	cm
AR	Anodizing ratio	nm V ⁻¹
d	Spacing between the reflected beams on the CCD (MOS)	mm
d_p	Spacing between the incident laser beams (MOS)	mm
d_c	Cell diameter	nm
d_p	Pore diameter	nm
d_g	Grain size	nm
E	Electric field in the oxide	V nm ⁻¹
$\Delta_f G^0$	Standard free energy of formation	kJ mol ⁻¹
h_{ox}	Thickness of the oxide layer	nm
h_b	Thickness of the barrier oxide layer	nm
h_p	Thickness of the porous oxide layer	nm
h_M	Thickness of the metallic layer	nm
h_s	Thickness of the substrate	μm
j	Macroscopic current density	mA cm ⁻²
j_e	Electronic current density	mA cm ⁻²
j_i	Ionic current density	mA cm ⁻²
j_0	High-field conduction parameter	mA cm ⁻²
L	Sample-to-detector distance (MOS)	m
l_l	Glass cell-to-sample distance (MOS)	cm

List of symbols

M_M	Metal molecular weight	g mol^{-1}
M_{ox}	Oxide molecular weight	g mol^{-1}
n_{liq}	Refraction index of the liquid	
p	Porosity	
q	Charge consumed per unit area	C cm^{-2}
T	Temperature	K
t	Time	s
U	Electrode potential	V
ΔU	Potential drop through the oxide	V
V_I	Type-I breakdown voltage	V
V_{II}	Type-II breakdown voltage	V
W	Hopping activation energy	$\text{J K}^{-1} \text{mol}^{-1}$
Y_s	Biaxial modulus of the substrate	GPa
z	Valence of charge carriers	

Greek symbols

α	Angle of incidence of the laser beams on the sample (MOS)	
α	Asymmetry factor for the hopping barrier (high-field model)	
β	High-field conduction parameter	nm V^{-1}
$\dot{\epsilon}$	Strain rate	s^{-1}
ϵ_r	Oxide relative permittivity	
η	Oxide viscosity	Pa s
η_a	Anodizing efficiency	
η_i	Ionic efficiency	
γ	Surface energy	J m^{-2}
κ	Sample curvature	km^{-1}
$\Delta\kappa$	Curvature change ¹	km^{-1}
λ_1, λ_2	Correlation breaks wavelengths	nm
λ_c	Critical perturbation wavelength	nm
ν	Hopping attempt frequency (high-field model)	s^{-1}
ν_f	Poisson ratio of the film f	
ρ	Density of charge carriers (high-field model)	C m^{-3}

ρ_M	Metal density	g cm^{-3}
ρ_{ox}	Oxide density	g cm^{-3}
ρ_e	Electrolyte resistivity	
$\langle \sigma \rangle_f$	Mean stress in the film f ²	MPa
σ_f	Incremental stress in the film f	MPa
σ^{ES}	Electrostatic stress	MPa

Physical constants

e	Elementary charge	$1.602 \times 10^{-19} \text{ C}$
F	Faraday constant	$96\,485 \text{ C mol}^{-1}$
R	Ideal gas constant	$8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
ε_0	Vacuum permittivity	$8.854 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$

¹The reference curvature is the average curvature prior to anodizing

² $f = ox$: oxide film, $f = M$ ($M = \text{Al}$ or $M = \text{Zr}$): metallic film

Scientific output

Publications in international journals

1. **Q. Van Overmeere**, F. Blaffart and J. Proost, “*What controls the pore spacing in porous anodic oxides?*”, Electrochemistry Communications (I.F. 4.413) 12, 1174–1176 (2010)
2. **Q. Van Overmeere** and J. Proost, “*Stress-induced breakdown during galvanostatic anodising of zirconium*”, Electrochimica Acta (I.F. 3.333) 55, 4653–4660 (2010)
3. **Q. Van Overmeere**, J.-F. Vanhumbecck and J. Proost, “*On the use of a multiple beam optical sensor for in situ curvature monitoring in liquids*”, Review of Scientific Instruments (I.F. 1.677) 81, 045106 (2010)
4. **Q. Van Overmeere**, J.-F. Vanhumbecck and J. Proost, “*Effect of current density on the internal stress evolution during galvanostatic Ti thin film anodising*”, Journal of the Electrochemical Society (I.F. 2.702) 157, C166–C173 (2010)
5. D. Mercier, **Q. Van Overmeere**, R. Santoro and J. Proost, “*In-situ optical emission spectrometry during galvanostatic aluminum anodising*”, Electrochimica Acta (I.F. 3.333) 56, 1329–1336 (2010)
6. J. Proost, Q. de Radigues, **Q. Van Overmeere** and R. Santoro, “*An undergraduate student laboratory on electrochemical engineering*”, Education for Chemical Engineers, accepted (2010)
7. **Q. Van Overmeere**, B. Nysten and J. Proost, “*In-situ detection of porosity initiation during aluminum thin film anodising*”, Applied Physics Letters (I.F. 4.096) 94, 074103 (2009)

8. J. Proost, J.-F. Vanhumbeeck and **Q. Van Overmeere**, “*Instability of anodically formed TiO_2 layers (revisited)*”, *Electrochimica Acta* (I.F. 3.333) 55, 350–357 (2009)
9. J. Proost, J.-F. Vanhumbeeck and **Q. Van Overmeere**, “*In-situ monitoring of the internal stress evolution during thin film anodising*”, *Electrochemical Society Transactions* 11, 35–42 (2008)

International conference contributions

1. **Q. Van Overmeere**, D. Mercier and J. Proost, *Experimental determination of the viscosity of anodic alumina*, to be presented at the 219th Meeting of the Electrochemical Society, Montreal (May 2011)
2. D. Mercier, **Q. Van Overmeere**, R. Santoro and J. Proost, *In situ optical emission spectrometry during the initiation and growth of porous anodic alumina*, to be presented at the 219th Meeting of the Electrochemical Society, Montreal (May 2011)
3. J. Proost, D. Mercier and **Q. Van Overmeere**, “*The growth of anodic oxide films: looking with new eyes into old questions*”, Keynote lecture at the 61st Annual Meeting of the International Society of Electrochemistry, Nice (2010)
4. **Q. Van Overmeere**, F. Blaffart and J. Proost, “*Does internal stress affect pore initiation in anodic oxides ?*”, 7th International Conference on Porous Semiconductors Science and Technology, Valencia (2010)
5. **Q. Van Overmeere**, D. Mercier and J. Proost, “*Stress-assisted growth of porous anodic aluminum oxide*”, 216th Meeting of the Electrochemical Society, Vienna (2009)
6. **Q. Van Overmeere**, B. Nysten and J. Proost, “*In-situ detection of porosity initiation during aluminum thin film anodising using high-resolution curvature measurements*”, International Conference on Materials for Advanced Technologies, Singapore (2009)
7. **Q. Van Overmeere**, J.-F. Vanhumbeeck and J. Proost, “*In-situ detection of mechanical instabilities and failure during the growth*

of thin anodic oxide films", International Conference on Materials for Advanced Technologies, Singapore (2009)

8. **Q. Van Overmeere** and J. Proost, "*In-situ monitoring of mechanical and electrical breakdown during Zr thin film anodising*", 5th Kurt Schwabe Symposium on Corrosion, Semiconductors and Solar Cells, Erlangen (2009)
9. D. Mercier, **Q. Van Overmeere**, R. Santoro and J. Proost, "*In-situ gravimetric studies of aluminium anodising*", 5th Kurt Schwabe Symposium on Corrosion, Semiconductors and Solar Cells, Erlangen (2009)
10. **Q. Van Overmeere**, J.-F. Vanhumbeeck and J. Proost, "*In-situ investigation of the relationship between electrical and mechanical properties during the growth of anodic oxide films*", 59th Meeting of the International Society of Electrochemistry, Sevilla (2008)
11. J. Proost, J.-F. Vanhumbeeck and **Q. Van Overmeere**, "*Instability of anodically formed TiO₂ layers (revisited)*", 4th Gerischer Symposium on Electrochemistry with Spatial and Temporal Resolution, Berlin (2008)
12. **Q. Van Overmeere**, J.-F. Vanhumbeeck and J. Proost, "*In-situ monitoring of the growth stress evolution during galvanostatic anodising of aluminium thin films*", 213th Meeting of the Electrochemical Society, Phoenix (2008)
13. J. Proost, J.-F. Vanhumbeeck and **Q. Van Overmeere**, "*On the origin of local voltage maxima during galvanostatic Ti anodising*", 213th Meeting of the Electrochemical Society, Phoenix (2008)
14. J. Proost, J.-F. Vanhumbeeck and **Q. Van Overmeere**, "*In-situ monitoring of the internal stress evolution during thin film anodising*", Invited presentation at the 212th Meeting of the Electrochemical Society, Washington DC (2007)
15. **Q. Van Overmeere**, J.-F. Vanhumbeeck, L. Langer and J. Proost, "*In-situ detection of growth instabilities during aluminum anodizing by high-resolution curvature measurements*", 58th Meeting of the International Society of Electrochemistry, Banff (2007)

Chapter 1

Outline of the work

1.1 Background

Anodic oxidation, or anodizing, can be defined as the electrochemically-controlled growth of an oxide film on a metal. Anodizing is quite simple to perform. Indeed, all one needs is a source of electric current (power source), a conducting liquid (electrolyte), a counter-electrode (cathode), and of course, the metal to be anodized: the anode. Owing to its simplicity, anodizing has extensively been used for nearly a century, in a wide range of applications. Such applications include providing corrosion-protection and an aesthetic finish to aluminum surfaces, manufacturing nanoporous templates for nanomaterial fabrication, or producing the dielectric medium in electrolytic capacitors.

For these applications, processes which terminate the growth of a dense anodic oxide film, are of key importance. These processes are, however, not fully understood. A first instance of such processes is pore growth in anodic oxide films. It allows the self-organized growth of nanometer-scaled pores over very large surfaces. An understanding of pore development in anodic oxides would allow producing porous films with a controlled morphology, tailored for specific applications. In the long-term, a fundamental understanding of pore growth would also potentially allow producing self-organized growth of nanometer-scaled pores in other materials.

A second process which terminates the growth of dense anodic oxide films is breakdown. The breakdown of anodic oxide films, generally

1. Outline of the work

defined as a detrimental localized modification of the oxide properties, is an undesirable phenomenon. The breakdown practically limits the thickness up to which anodic oxide films can be grown. An understanding of breakdown would therefore allow growing thicker flawless anodic oxide films. Increasing the thickness of anodic oxide films would, for instance, increase the amount of energy per unit volume that can be stored in electrolytic capacitors.

1.2 Objectives and contributions

Internal stresses in anodic oxide films have often been proposed to be a key factor controlling pore initiation and growth, and the breakdown of anodic oxide films. However, no quantitative direct correlation between the internal stress and either the development of pores or the breakdown of anodic oxide films has ever been established. Therefore, the objectives of this work were to:

1. develop a technique to accurately measure the internal stress *in situ* during the growth of anodic oxide films ;
2. determine the role of the internal stress on the initiation and growth of porosity in anodic oxide films ;
3. determine the role of the internal stress on the breakdown of anodic oxide films.

Stresses in anodic oxide films were measured using a multiple beam optical sensor. This technique has already been used by numerous investigators to monitor the internal stress during the growth of thin films in vacuum. It consists in measuring the stress-induced curvature of the substrate on which the film is deposited by monitoring the mean differential spacing of an array of laser spots reflecting off the sample surface. The validity of the equations used to extract the internal stress from the mean differential spacing was thus verified in order to apply the multiple beam optical sensor to anodizing.

To investigate on the role of stress on porosity initiation and growth, or breakdown of anodic oxide films, the following strategy was used. The anodizing conditions were systematically varied to produce anodic oxide films with internal stress of different magnitude. By characterizing the

different growth stages of these films, such as the growth of a dense oxide film, the initiation and growth of porosity, or the moment of breakdown and the resulting morphology, the role of the internal stress could be elucidated.

With respect to the aforementioned three objectives, the major contributions of this thesis are fourfold:

- Provide, for the first time, an analysis of the validity of the equations for internal stress monitoring in liquids, using a multiple beam optical sensor.
- Identify, for the first time, the fundamental physical mechanisms responsible for the transition from a dense to a porous anodic oxide, and for the selection of the distance separating the pores in anodic oxide films. The pores were found to result from a surface instability, induced by electrostatic energy. Internal stress measurements during aluminum anodizing indicated that strain energy is unlikely to be responsible for the instability, in contrast to what had been suggested several times in the literature.
- Provide additional experimental evidence for pore growth by viscous flow of oxide in anodic alumina and estimate, for the first time, the viscosity of anodic alumina at room temperature in the presence of large ionic currents and its dependence on the anodizing conditions.
- Identify, for the first time with quantitative experimental evidence, the internal stress as a key factor for one of the two types of breakdown that have been documented to occur during the growth of anodic zirconia films, and relate this type of breakdown to a phase transformation in the anodic oxide film.
- Provide new, reliable and reproducible data on the dependence of the internal stress in anodic oxides on experimental conditions.

1.3 Organization of the text

The manuscript has been divided into seven chapters. After introducing the context, objectives and accomplishments of this work in the present

1. Outline of the work

chapter, the current state of knowledge on the growth of anodic oxide films is summarized in the second chapter. The generic growth mechanisms of dense anodic oxide films are presented, together with the particular mechanisms for porous anodic oxide film growth and for anodic oxide film breakdown¹. In chapter three, the details of our experimental setup for monitoring the internal stress *in situ* during anodizing are provided, together with details on the *ex situ* characterization techniques used in this work. Our results are then presented in the fourth, fifth, and sixth chapters. In the fourth chapter, we develop the theoretical framework to reliably use our internal stress monitoring setup during thin film anodizing. The fifth chapter presents our results for *in situ* stress measurements during the growth of porous anodic alumina. The sixth chapter presents our results for *in situ* stress measurements during the breakdown of anodic zirconia. Chapter seven provides a general conclusion of the thesis, and directions for future research.

¹The reader already familiar with anodizing may want to skip chapter 2.

Chapter 2

State of the art

In this chapter, we perform a review of some of the current viewpoints regarding the growth mechanisms of anodic oxide films relevant for our work.

Section 2.1 presents the applications in which anodic oxide films are used, and how an understanding of pore growth and breakdown in anodic oxide films would help to solve the technological challenges faced in these applications.

The general growth mechanisms of anodic oxide films, more specifically the growth of the so-called barrier anodic film are then presented in section 2.2. This type of film first grows before the anodic film becomes porous or breaks down. It is therefore important to understand how they grow.

Section 2.3 presents the current knowledge on the formation mechanisms of porous anodic films, emphasizing porous anodic films on aluminum, since these films have been the most studied so far.

Finally, section 2.4 presents the state of the art on the breakdown mechanisms of anodic oxide films.

2.1 Applications of anodic oxide films

In this section, the importance of anodic oxide films in technological applications is emphasized, and current challenges are linked to the need for our work.

2.1.1 Large-scale applications: aluminum anodizing

The most anodized, or electrochemically oxidized, materials are without a doubt aluminum and aluminum alloys. Aluminum alloys feature a high ratio between mechanical properties and density compared to other metals, hence are extensively used in aeronautical applications. While pure aluminum is known to be corrosion-resistant due to the native oxide film present on its surface, the corrosion resistance may significantly decrease when it is exposed to aggressive environments, or when an aluminum alloy is used. In the latter case, surface “defects” such as second-phase particles may increase the corrosion rate compared to pure aluminum.

Fortunately, the corrosion rate can be decreased by thickening the native oxide layer by anodizing the part to be used. The first reports of anodizing processes of aluminum alloys date from the 1920’s. It was noticed that a particular electrochemical treatment improved the corrosion resistance of Al-Cu alloys to be used in airplanes. Today, aluminum anodizing is also used for various applications such as for light reflectors, architecture panels, electrical appliances fronts, sporting goods, . . . (cfr. Figure 2.1). Anodized aluminum products represent a market of about 100 000 tonne/year. For these applications, porous anodizing is typically used: it allows growing thicker layers (thickness $\approx 20\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$) than barrier layer anodizing (thickness $\approx 0.5\text{ }\mu\text{m}$ — limited by breakdown). Furthermore, as will be described in section 2.3, porous anodizing allows the voltage of the electrochemical cell to be smaller, compared to barrier layer anodizing, thus reducing electrical consumption and safety concerns when anodizing is performed at the industrial scale. Furthermore, porous anodized aluminum is easily colored, by incorporating inorganic salts or organic dyes into the pores. For instance, this kind of process has allowed Apple to decline its famous iPod in various casing colors.

There is a need to understand the relationship between the processing parameters and the porous layer morphology, which could then be tuned for specific applications. For instance, when an adhesive is to be applied on the anodized aluminum part, phosphoric acid anodizing is preferred. The reason for this choice is that phosphoric acid anodizing produces larger pores, in which the adhesive penetrates, compared to other electrolytes. However, the fundamental relationship between the processing



Figure 2.1: Architectural applications of porous anodic alumina.

conditions and the resulting morphology are not yet completely understood. Thus, a detailed understanding of these relationships, including the precise role of internal stress, may potentially lead to the synthesis of anodic films tailored for specific applications.

2.1.2 Nanotechnology applications

Up to about 1995, the primary interest in aluminum anodizing resided in the previously described, aesthetic and anticorrosion-purpose properties. There had been few attempts to use porous anodic films in nanotechnology applications. For instance, cobalt or nickel deposition into the pores was proposed to fabricate magnetic recording devices [1]. However, it is not until 1995, and the successful synthesis of an ideally ordered porous anodic alumina layer and its subsequent replication into another material by Masuda [2], that porous anodic alumina templates started to be used extensively. These films, diverse examples of which are shown in Figure 2.2, allow to synthesize 2-dimensional nanostructured materials by a bottom-up approach.¹

For these kinds of applications, the experimental conditions leading to the self-organization of the pores in anodic alumina are well-documented (see for instance the works of H. Masuda and co-workers [2, 3, 5] and U. Gösele and co-workers [6–10]). However, neither the specific processes leading to self-organization nor the dependence of

¹Bottom-up versus top-down approaches: in top-down approaches, the material is synthesized “from the top”, for instance, by lithography. While in bottom-up approaches, universal small-scale forces are taken advantage of to do the job.

2. State of the art

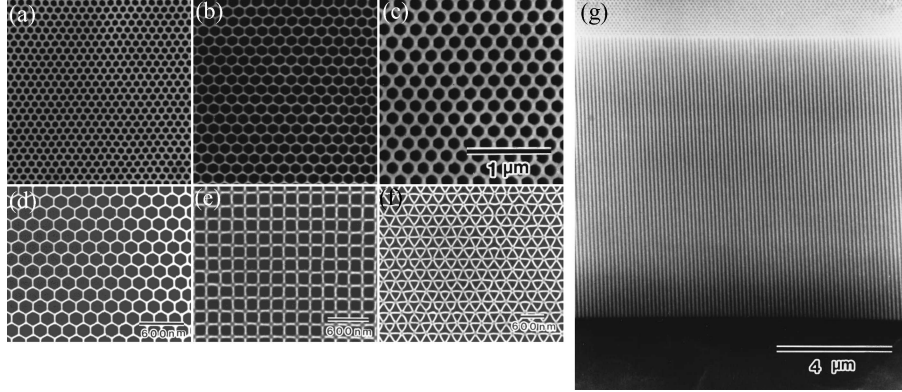


Figure 2.2: Scanning electron micrographs of self-organized nanoporous alumina formed in various conditions. (a–c, g) Reproduced from reference 3 and (d–f) reproduced from reference 4.

the porous layer morphology on the experimental conditions are well-understood. A fundamental understanding of these processes could allow faster fabrication of the templates (it now requires up to several days) or extending these processes to other materials than alumina. Note that regarding the direct synthesis of porous anodic oxides other than alumina, a recent success in that direction has been the synthesis of anodic titania nanotubes [11]. The direct synthesis of a nanostructured functional material would also reduce processing times, as no template fabrication would be required.

2.1.3 Electrolytic capacitors

While the previously described applications used porous anodic oxide films, dense barrier anodic oxide films are also used in technological applications. An example of such an application is electrolytic capacitors. Compared to other types of capacitors, electrolytic capacitors have a higher capacitance to volume ratio. They are used, for instance, in photographic flashes. Electrolytic capacitors consist in an anode and a cathode separated by a spacer. The spacer is an absorbent medium which contains the electrolyte, while the anode and cathode are made of aluminum or tantalum foils. While the cathode is only covered by a thin native oxide film, a thick dense oxide is grown by anodic oxidation

at the anode.

The maximum voltage that the capacitor can withstand is determined by the thickness of the oxide layer at the anode. Above the maximum voltage, breakdown of the oxide film occurs. Increasing the thickness of the anodic oxide film would definitely increase the attainable working voltage of electrolytic capacitors. A fundamental understanding of the breakdown, for which the internal stress in the oxide has been suggested as a key factor, is thus needed.

2.1.4 Model system for corrosion processes

Anodic oxide films are also potentially interesting to study the corrosion processes of zirconium and its alloys. Zirconium alloys are used in the nuclear power industry, mainly for fuel cladding. However, the corrosion of zirconium and its alloys is cyclic, with an oscillating oxide growth rate. The cyclic growth rate is associated with cracks in the oxide film, illustrated in Figure 2.3. These make the lifetime prediction of zirconium parts difficult [12].

Such cyclic processes are only observed for more than 110 days exposure, when the oxide film thickness is about $2\text{ }\mu\text{m}$. Thus, pre-forming a thick zirconium oxide film by anodizing would potentially accelerate corrosion tests. The zirconia thickness attainable by anodic oxidation is currently limited to about $0.7\text{ }\mu\text{m}$ [13]. Understanding the mechanisms of the breakdown, which are responsible for such thickness limitations would allow to grow thicker films.

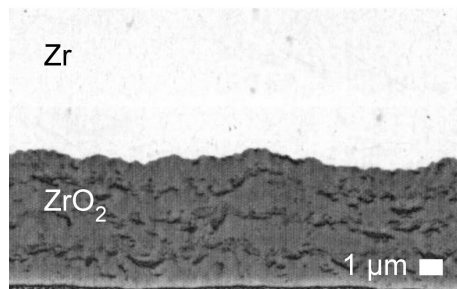


Figure 2.3: Oxide morphology resulting from the cyclic high-temperature corrosion of zirconium. Reproduced from reference 12.

In conclusion, the synthesis of porous anodic films is thus of valuable technological interest, and a deeper understanding of the formation processes of these films would potentially allow improving their synthesis. On the other hand, the breakdown of anodic oxide film is an undesirable effect, which has to be avoided for specific applications. A better understanding of the breakdown would allow producing thicker oxide films.

2.2 Growth kinetics of dense oxide films

In this section, the general growth mechanisms of an anodic oxide film on a metal are presented. These processes apply to the growth of dense anodic films—the so-called barrier films—but also apply to some extent to the growth of porous anodic films and to the breakdown of anodic films, because before these phenomena occur, the anodic film is a barrier film and its growth proceeds by the mechanisms presented below.

2.2.1 Initial oxide growth

In order to be anodized, or electrochemically oxidized, a metal or a semiconductor has to meet several criteria. Firstly, when the metal or semiconductor is used as the anode of an electrochemical cell in a given electrolyte, ionization of the compound must occur, with the produced ions reacting with anions from the electrolyte to form a solid film, generally an oxide. Secondly, the formed film must be relatively insoluble in the electrolyte. Thirdly, the formed film should be an ionic conductor, as its further growth proceeds by transport of cations and anions through the film. Several metals fulfill these conditions in a variety of electrolytes, the most anodized ones being aluminum (Al), zirconium (Zr), tantalum (Ta), niobium (Nb), hafnium (Hf), titanium (Ti), and tungsten (W).

These metals present a strong reactivity towards oxygen, and upon contact with air, they tend to form a native oxide film a few nanometers-thick. This enhanced reactivity can be seen from the quite large standard free energy $\Delta_f G^0$ of formation of these oxides (see Table 2.1).

In aqueous solutions, a native oxide film usually forms before anodizing starts. This can be seen on the potential-pH (U -pH) diagrams of these metals. Figure 2.4 shows the potential-pH diagram of Al, Ti

Table 2.1: Standard free energy of formation of the oxide of various valve metals, showing that the formation of a native oxide film is thermodynamically favored. Data from HSC [14].

metal	oxide	$\Delta_f G^0$ / kJ mol ⁻¹
Al	Al ₂ O ₃	-1582
Zr	ZrO ₂	-1042
Ta	Ta ₂ O ₅	-1911
Nb	Nb ₂ O ₅	-1766
Hf	HfO ₂	-1059
Ti	TiO ₂	-889
W	WO ₃	-764

and Zr, which have been anodized in our research group. Valve metals are characterized by an oxide-stable region covering a wide range of potential and pH values. Even though the diagrams of Al and Zr suggest that these metals and their oxides dissolve at low pH, the dissolution kinetics are quite slow. Furthermore, when metallic ions are produced at the electrode, the formation of oxide is thermodynamically favored, even at low pH. Thus, even if the aqueous electrolyte tends to dissolve the native oxide film, or if attempts are made to reduce the oxide by cathodic polarization, a native oxide film forms continuously [15]. Because the ionic conduction properties of thin native oxide films are the same than those of thicker anodic oxide films [16], initial oxide growth by anodic polarization proceeds by the same conduction mechanisms than when a thicker anodic oxide film is already present. These mechanisms are presented in the following section.

2.2.2 High-field ionic conduction

When a valve metal anode is polarized, either by supplying a current to the electrochemical cell, or by imposing a constant electrode potential, an anodic oxide film forms. Early work on Al and Ta anodizing established an empirical exponential dependence of the ionic current density j_i on the electric field E within the oxide:

$$j_i = j_0 \exp(\beta E) \quad (2.1)$$

2. State of the art

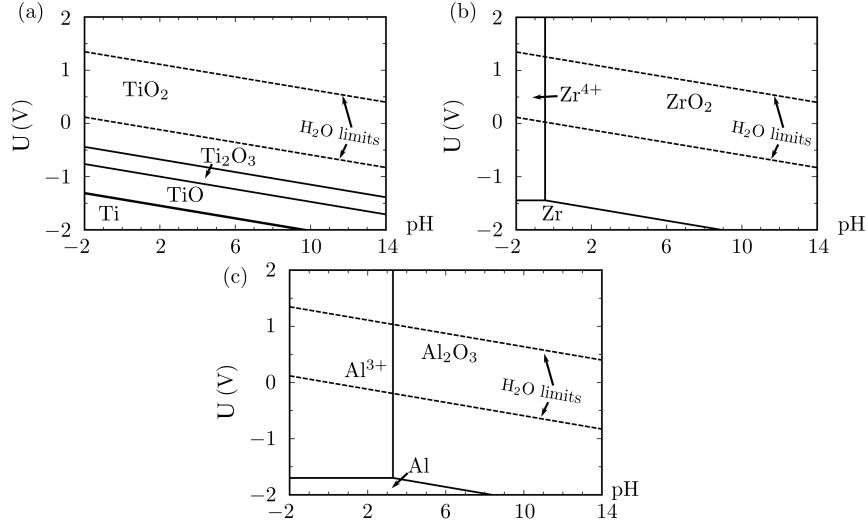


Figure 2.4: Potential (U)-pH diagrams of Al, Zr and Ti in water, calculated with HSC Chemistry [14].

where j_0 and β are metal and temperature-dependent constants [17]. This relationship has subsequently been reported in numerous studies. However, no general agreement on the fundamental processes behind Equation (2.1) has been reached. Several models succeeded in predicting the experimental dependence between E and j_i , while differing in several key aspects.

For instance, Cabrera and Mott postulated that the rate-limiting step of oxide growth was the escape of metallic ions [18], while in the early point defect model of Macdonald and co-workers, the metal/oxide interface is in equilibrium [19]. Transient experiments seem to indicate that for anodic oxide films, the rate-determining step is actually the movement of ions within the oxide [20]. Intuitively, the relative importance of interfacial processes in determining the kinetics of oxide film growth should indeed be small for thick films, such as anodic oxide films, at least when no significant dissolution of the film, or parasitic interfacial reaction occur. Based on a rate-determining movement of ions within the oxide film, the high-field model relates the parameters j_0 and β in Equation (2.1) to the oxide microstructure.

The high-field model is based on a hopping mechanism. Charge

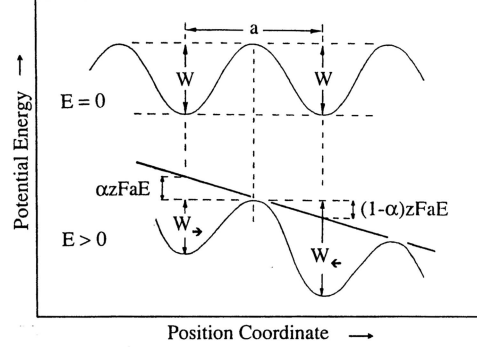


Figure 2.5: Activation energy for charge carrier hopping. Reproduced from reference 20.

carriers “jump” from their current position to a nearby one. The hopping activation energy is field-dependent, as illustrated on Figure 2.5. An implicit assumption is that the oxide is homogeneous, i.e. is defect free and of uniform composition. When the electric field in the oxide is high, which is the case during the growth of anodic oxide films, the ionic current density is equal to:

$$j_i = \nu \rho a \exp\left(-\frac{W}{RT}\right) \exp\left(\frac{\alpha a z F E}{RT}\right) \quad (2.2)$$

where ν is the hopping attempt frequency, ρ is the density of charge carriers, a is the hopping interdistance, W is the zero-field hopping activation energy, α is a parameter describing the asymmetry of the activation barrier when the field is not zero, z is the valence of the charge carrier, and F is Faraday’s constant [20]. By equating Eq. (2.1) and Eq. (2.2), we obtain:

$$j_0 = \nu \rho a \exp\left(-\frac{W}{RT}\right) \quad (2.3)$$

$$\beta = \frac{\alpha a z F}{RT} \quad (2.4)$$

The parameter a is related to some extent to the inter-atomic distance in the oxide. This can be seen by comparing typical electric fields in anodic oxides with the oxygen ionic density in crystals of the same oxide, see

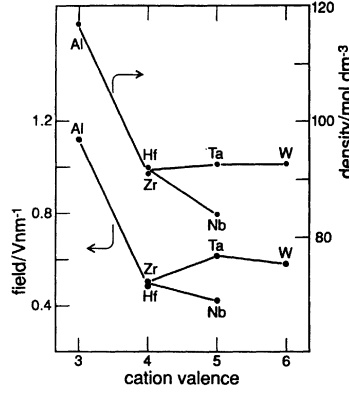


Figure 2.6: Mean electric field in growing anodic films on valve metals in various electrolytes at 1 mA cm^{-2} , and molar oxygen ion density in oxide crystals. Reproduced from reference 23.

Figure 2.6. From Equation (2.2), when the oxygen ion density increases (thus a decreases), E increases, everything else being constant. Such a dependence of the electric field on the packing density of the oxide has also been observed for different grain orientations of anodic zirconium oxide [21].

The electric field in the oxide is related to the measured (or applied) electrode potential U . The measurable potential drop between the metal and the electrolyte is equal to the sum of the potential drop in the oxide ΔU and at the metal/oxide ($\Phi_{m/f}$) and oxide/electrolyte ($\Phi_{f/s}$) interfaces. Since the rate-determining step for oxide growth is the movement of ions within the oxide, the interfaces can be considered to be in equilibrium and the potential drop at the interfaces should not depend much on the current density, which is confirmed to be the case [22]. The potential drop is generally of the order of millivolts, and is at most -1500 mV for Ta anodizing. This is quite small compared to the several volts of potential drop through the oxide, and the contribution of the interfaces are therefore usually neglected. Thus, the electric field in the oxide is here taken equal to:

$$E \equiv \frac{\Delta U}{h_{ox}} \approx \frac{U}{h_{ox}} \quad (2.5)$$

where h_{ox} is the oxide thickness. The potential profile in an anodic oxide

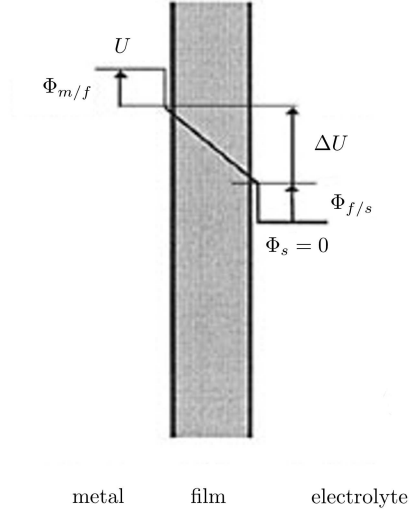


Figure 2.7: Potential profile in the metal/anodic oxide/electrolyte system. $\Phi_{m/f}$ and $\Phi_{f/s}$ are the potential drop at the metal/film and film/electrolyte interface, respectively. Φ_s is the potential in the electrolyte solution. Reproduced from reference 24.

film is schematically represented in Figure 2.7. Due to the relatively high potential drop through the oxide, several investigators monitor the cell voltage (2 electrodes setup) rather than the electrode potential (3 electrodes setup). In that case, the cell voltage V is related to the electrode potential U by:

$$V = U + \Delta V_{\Omega} + V_c \approx U \quad (2.6)$$

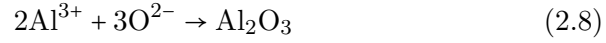
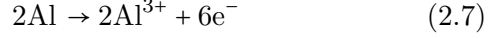
where ΔV_{Ω} and V_c are the potential drop associated with ohmic resistance, such as the electrolyte resistivity, and V_c is the potential drop associated with the cathode. Again, these two terms are usually much smaller than U and are usually neglected.

To further link the ionic current density in the oxide j_i with the macroscopic applied (or measured) current density j , let us consider the elementary reactions occurring during the growth of anodic oxide films

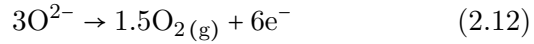
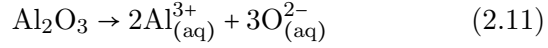
2. State of the art

on valve metals, illustrating the case of Al anodizing:

- At the metal/oxide interface:



- At the oxide/electrolyte interface:



These reactions are illustrated schematically in Figure 2.8. It should be noted that the reactions that involve a transfer of species from one phase to the other are associated with the creation or annihilation of free volume in the corresponding phases. Vacancies or interstitials are, however, not considered here. Only reactions (2.7) and (2.12) produce electrons, hence are linked to the macroscopic current density. For reaction (2.12) to occur, the oxide must be an electronic conductor. We define the ionic efficiency η_i as the ratio of the current density involved in reaction (2.7) over the macroscopic current density:

$$\eta_i = \frac{j_i}{j} \quad (2.13)$$

Usually, $\eta_i = 1$ until breakdown of the oxide occurs. The sum of ionic and electronic current densities are equal to the applied current density:

$$j = j_i + j_e \quad (2.14)$$

Besides the ionic efficiency, we also define the anodizing efficiency η_a as the ratio of the net current density used for oxide growth (reactions (2.8) and (2.9) minus reaction (2.11)) over the ionic current density:

$$\eta_a = \frac{j_{ox}}{j_i} \quad (2.15)$$

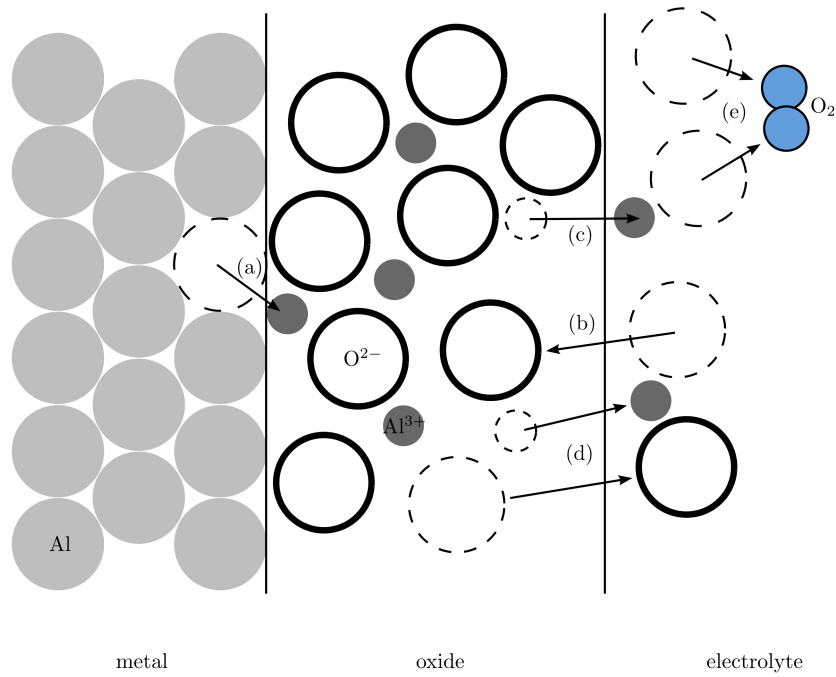


Figure 2.8: Schematic illustration of the elementary reactions (2.7)–(2.12) potentially occurring in growing anodic alumina films. (a) Oxide formation at the metal/oxide interface (2.7) and (2.8). (b) Oxide formation at the oxide/electrolyte interface (2.9). (c) Direct cation ejection in the electrolyte (2.10). (d) Oxide dissolution (2.11). (e) Oxygen evolution (2.12).

2. State of the art

Table 2.2: Anodizing ratios (AR) reported in reference 20.

anodic oxide	reported (AR) / nm V^{-1}
Al_2O_3	0.8 to 2.0
Ta_2O_5	1.5 to 2.4
TiO_2	1.4 to 3.4
ZrO_2	1.7 to 3.0

It should be noted that the direct ejection of cations in the electrolyte is implicitly included in η_a . Indeed, if direct cation ejection occurs, the current density used for reactions (2.8) and (2.9) will be lower than the ionic current density (reaction (2.7)). It will be seen in section 2.3 that during the growth of porous anodic oxide films, $\eta_a < 1$, even during the initial barrier layer growth stage.

The oxide thickness can be calculated by measuring the cell voltage V and the electric current. Combining Equation (2.1), (2.5), and (2.6) yields:

$$h_{ox} = \frac{V}{E} = V (AR) = \frac{V}{\ln(\eta_i j / j_0)} \beta \quad (2.16)$$

where (AR) is called the anodizing ratio. If for a particular set of anodizing conditions (metal and electrolyte), j_0 and β are known, the electric field can be calculated as a function of the current density. In fact, due to the logarithmic relationship between the electric field and the ionic current density, the (AR) is usually constant over a large range of current densities. Typical values of anodizing ratios are given in Table 2.2 for selected valve metals.

Not only the voltage indicates the thickness of the oxide layer, the charge consumed per unit area $q = jt$ also allows to calculate the oxide thickness, using Faraday's law:

$$h_{ox} = h_{ox}|_{t=0} + \eta_i \eta_a \frac{M_{ox} q}{\rho_{ox} z F} \quad (2.17)$$

or equivalently:

$$\frac{dh_{ox}}{dt} = \eta_i \eta_a j \frac{M_{ox}}{\rho_{ox} z F} \quad (2.18)$$

where z is the number of electrons to produce a stoichiometric unit of oxide, t is the anodizing time and M_{ox} and ρ_{ox} are, respectively, the

2.2. Growth kinetics of dense oxide films

molecular weight and density of the oxide. In a similar way, Faraday's law allows calculating the thickness of the metal h_M :

$$h_M = h_M|_{t=0} - \eta_i \frac{M_M q}{\rho_M z_M F} \quad (2.19)$$

or equivalently:

$$\frac{dh_M}{dt} = -\eta_i j \frac{M_M}{\rho_M z_M F} \quad (2.20)$$

where z_M , ρ_M and M_M are, respectively, the number of electrons per oxidized atom, the metal density and molecular weight.

Deriving Equation (2.16) with respect to time and equating with Equation (2.17) leads to the following expression for the derivative of the voltage evolution:

$$\frac{dV}{dt} = \eta_i \eta_a j \frac{M_{ox}}{\rho_{ox} z F} \frac{1}{(AR)} = \eta_i \eta_a j \frac{M_{ox}}{\rho_{ox} z F} \frac{1}{\beta} \ln \left(\frac{\eta_i j}{j_0} \right) \quad (2.21)$$

Thus, if the anodizing ratio is relatively independent of the current density and time invariant, the cell voltage increases linearly with time, and the rate of cell voltage change increases linearly with the current density.

Finally, let us note that the concept of a defect-free oxide of homogeneous composition is imprecise. Indeed, the transport of ions occurs probably through defects such as vacancies or interstitials, which are not considered in the high-field model. Furthermore, while anodic Al_2O_3 , Ta_2O_5 and Nb_2O_5 are usually amorphous, ZrO_2 and HfO_2 are generally crystalline [25–27]. In the crystalline anodic oxides, ionic transport presumably occurs through the oxide grain boundaries [28]. It is also known that incorporation of anions from the electrolyte occurs to some extent. The presence of defects, anion incorporation and the formation of oxide at both interfaces, together with the possible dependence on the field of the microstructural parameters in Equation (2.2) have been put forward to explain observed deviations from Equation (2.1) [29,30]. Section 2.2.3 discusses the formation of oxide at both interfaces, resulting from coupled anion and cation migration, while section 2.2.4 discusses the incorporation of electrolyte species.

2.2.3 Transport numbers

As previously mentioned, anodic oxide formation occurs generally at both the metal/oxide and oxide/electrolyte interfaces (reactions (2.8) and (2.9)). The cationic and anionic transport numbers t_c and $t_a = 1 - t_c$ quantify the relative fractions of transported ions through the oxide, and the ratio of oxide formed at these interfaces. Various measurements have been carried out to determine these transport numbers. The basic idea behind these measurements is to use a “marker”, a compound whose position in the anodic oxide film indicates to which extent oxide was formed at each interface. An ideal marker should fulfill several conditions [31]:

1. be uncharged, so that it does not migrate under the influence of the electric field in the oxide ;
2. be large in size, so that it does not migrate in the oxide lattice ;
3. be present in trace amount, so that it does not modify the oxide properties ;
4. be detectable in order to quantify its depth in the oxide ;
5. furthermore, the process of implantation of the marker should not alter subsequent anodic oxide film growth [32].

These conditions are fulfilled when an inert gas is implanted in a pre-formed thin oxide film and subsequently anodized. Implantation directly into the metal seems to result in an altered anodizing behavior [32], probably due to the creation of implantation defects in the metal. Usual choices are ^{125}Xe [31], Xe [33–35] and ^{222}Rn [36–38]. The use of radioactive tracers allows to measure the thickness at which they are buried by monitoring the energy of emitted α or β particles. Other techniques to measure the buried thickness are Rutherford Backscattering Spectrometry (RBS), and direct observation of Xe by cross-sectional Transmission Electron Microscopy (TEM).

A synthesis of the dependence of cation transport numbers on current density for selected valve metals at room temperature is shown in Figure 2.9. The cation transport number is seen to increase slightly with current density. For Al_2O_3 , ZrO_2 , TiO_2 and Ta_2O_5 , the mean transport numbers are respectively of 0.48, 0.10, 0.37 and 0.26. The low cation

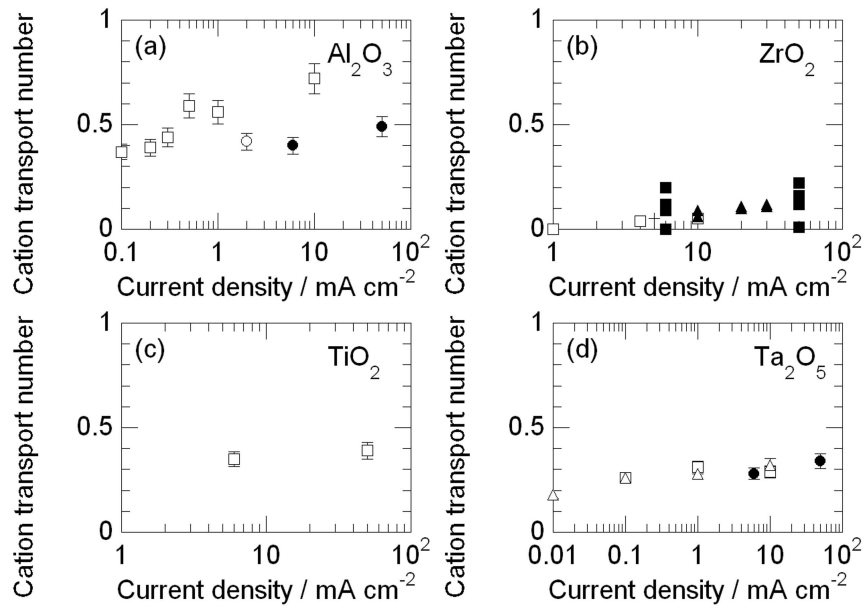


Figure 2.9: Dependence of cation transport number on current density in barrier anodic oxide films grown at 100% ionic and anodizing efficiency (a) anodic alumina, (b) anodic zirconia, (c) anodic titania and (d) anodic tantalum. Data obtained from [31] (□), [36] (●), [37] (■), [38] (▲), [33] (○), [34] (△) and [35] (+)

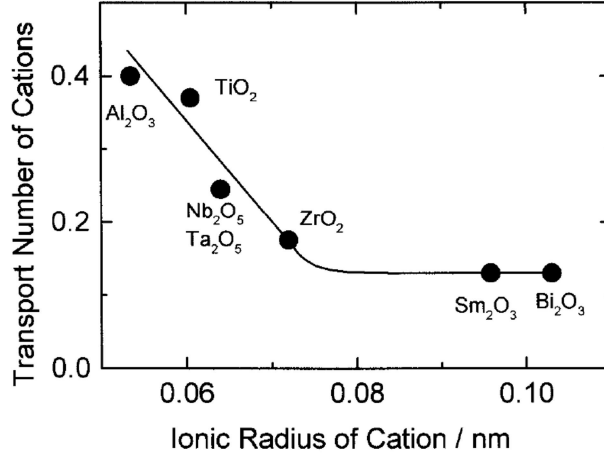


Figure 2.10: Dependence of cation transport number in anodic oxide on the cation ionic radius for various valve metals. Reproduced from reference 39.

transport number of ZrO_2 has been related to the crystallinity of anodic zirconia. Similarly low cation transport numbers are found for HfO_2 , which is also a crystalline anodic oxide [27]. Other anodic oxides are generally amorphous.

Regarding the strong dependence of transport numbers on oxide composition, Habazaki *et al.* have found a correlation between the cation transport number in anodic oxides and the ionic radius of the metallic cation [39]. This dependence is illustrated in Figure 2.10, where it can be seen that the higher the ionic radius, the lower the cation transport number. Above a critical ionic radius, the cation transport number does not decrease anymore. This result is intuitively consistent with an ion hopping mechanism such as proposed in the high field-model. The dependence of transport number on current density has been rationalized by the systematically higher valence of the cation, thus increasing the cationic current more rapidly than the anionic current as the field increases, everything else in Equation (2.2) being constant [29].

2.2.4 Incorporation of electrolyte species

As mentioned earlier, the view of anodic oxides as pure stoichiometric oxides is inaccurate. As we have shown above, the oxide is formed at both the metal/oxide and the oxide/electrolyte interfaces. It can be anticipated that these two layers have different characteristics. One of these is that a significant amount of species from the electrolyte are incorporated in the oxide layer which forms at the oxide/electrolyte interface.

Anion incorporation is an important process during valve metal anodizing. It accounts for the different properties of anodic oxides compared to pure oxides. It also accounts for the fact that films formed in different electrolytes may have different properties. For instance, anodic zirconia grown in sulphate solutions may transform from the cubic to the monoclinic crystalline phase, while anodic zirconia grown in borate solutions is cubic [40]. Moreover, the incorporation of electrolyte species in the growing anodic oxide film has been suggested to be responsible for breakdown of growing anodic oxide films [41]. This will be discussed in more details in section 2.4.

Evidence for the incorporation of electrolyte species principally originates from nuclear analysis [42], secondary ion mass spectrometry [43], energy dispersive X-ray analysis of oxide cross-sections in a transmission electron microscope [44], and glow-discharge optical emission spectroscopy [45]. The distribution of anions within an anodic oxide film has also been determined for anodic alumina by chemical sectioning, which consists in dissolving the formed anodic oxide film homogeneously, and to quantify the amount of dissolved anions [46]. A typical profile, determined by chemical sectioning, of incorporated phosphate in an anodic alumina film formed in an aqueous phosphate electrolyte is shown in Figure 2.11. Near the interface with the electrolyte, the concentration of phosphate is the highest, which is probably related to adsorption rather than absorption processes. The outer, phosphate-contaminated oxide layer is clearly visible, and the concentration of phosphate in this layer is constant. Determination of the relative thickness of the contaminated oxide layer has also been performed for various types of anodic oxides by partially crystallizing a thin cross section of an anodic film under the beam of a transmission electron microscope. Due to the lower crystallization rate of the anion-contaminated layer relative to the non-contaminated anodic oxide layer, the thickness of the anion-

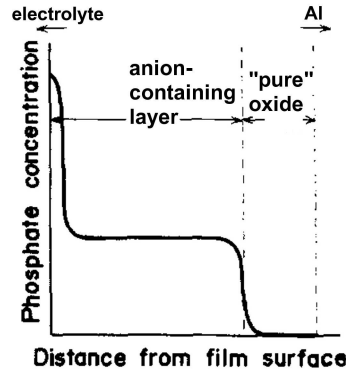


Figure 2.11: Schematic distribution of phosphate in an anodic alumina film formed in a phosphate-containing electrolyte. Reproduced from reference 49.

contaminated layer can be measured [47,48].

Depending on the metal anodized and the electrolyte, the thickness of the contaminated layer can be smaller, equal to or greater than the thickness of the oxide layer that forms by migration of metal cations, at the oxide/electrolyte interface. In those cases, the electrolyte species are said to be migrating outward, immobile, or migrating inward, respectively. Instances of each case for anodic alumina are tungstate, borate and phosphate species for outward migration, immobility, and inward migration respectively, as shown schematically in Figure 2.12.

The direction of migration of the incorporated electrolyte species has been suggested to be determined by whether or not the electric field was strong enough to break the bond between the incorporated element and oxygen [50]. For instance, tungstate (WO_3) species are incorporated and the field strips oxygen from tungsten, hence W^{6+} species migrate outward ; in borate-containing electrolytes, B_2O_3 is incorporated but the field is not strong enough to break the bonds ; finally in phosphate-containing electrolytes, PO_4^{3-} anions are unaffected by the electric field and migrate inwards, at a rate slower than that of O^{2-} anions. Regarding the magnitude of the migration rate, a correlation seems to exist between the size of the species, and their relative mobility, compared to that of O^{2-} , as illustrated on Figure 2.13 for anodic oxide films on aluminum.

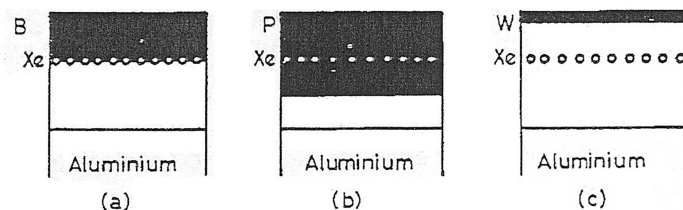


Figure 2.12: Schematic diagram of sections of barrier oxide films formed on aluminum in (a) borate; (b) phosphate; (c) tungstate electrolytes. The location of xenon markers is also shown. Reproduced from reference 50.

However, other factors seem to have an influence on the migration rate of different species, as similar relative rates are observed for SO_4^{2-} , PO_4^{3-} , and Cl^- anions, although their ionic radius is quite different [51].

Regarding the amount of incorporated species in anodic oxide films, typical values are between 1 and 10 % (by either weight or atomic ratios) for typical anodizing conditions in relatively dilute aqueous electrolytes. For instance, typical average compositions of contaminated anodic alumina layers are $\text{Al}_2\text{O}_3 \cdot 0.02(\text{WO}_3)$, $\text{Al}_2\text{O}_3 \cdot 0.03(\text{B}_2\text{O}_3)$, and $\text{Al}_2\text{O}_3 \cdot 0.07(\text{AlPO}_4)$ for films formed in tungstate, borate and phosphate-containing electrolytes.

Finally, a certain amount of protons may also be incorporated in anodic oxide films because OH^- can also be incorporated at the oxide/electrolyte interface. Indeed, the amount of OH^- ions incorporated in anodic alumina was found to increase with the pH of the electrolyte, while the hydrogen concentration is larger in the oxide layer formed by cation migration, at the oxide/electrolyte interface [46, 52]. Typical hydrogen concentrations in the film are quite low, only being about 1 at.% [53].

2.2.5 Internal stress

Early measurements of the internal stress in anodic oxide films were made by Vermilyea [54], for a wide range of valve metals anodized at 2 mA cm^{-2} in borate solutions, and by Bradhurst and Leach for anodic

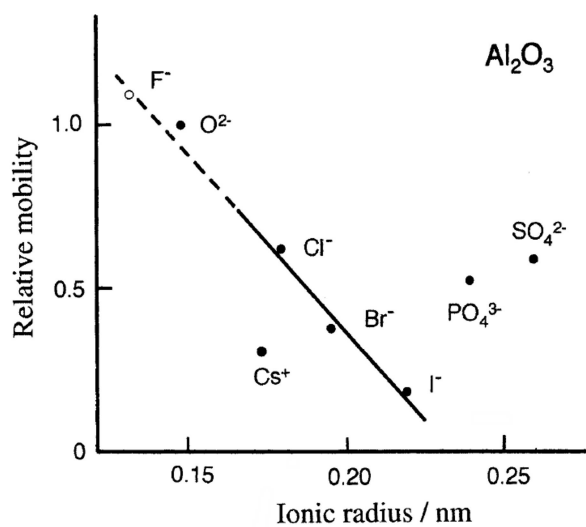


Figure 2.13: Rate of migration of various anionic species relative to that of O^{2-} anions, in growing anodic oxide films on aluminum. Reproduced from reference 51.

oxide films on aluminum [55]. Vermilyea performed stress measurements using a bending-beam technique and made several generic observations:

- the stress is nearly always tensile at small film thickness;
- when the electric field is turned off, the stress in the oxide becomes more tensile;
- the higher the formation rate, the more compressive the stress during the film growth, but
- the higher the formation rate, the more tensile the stress once the electric field has been switched off;
- when gas is produced on the anode surface, the stress is more compressive;
- the stress is relatively independent of the electrolyte unless concentrated electrolytes are used, such as 85 % H_3PO_4 , or 95 % H_2SO_4 ;
- the stress depends on the surface preparation, prior to oxide growth.

Some of these generic observations have been confirmed by other investigators. However, the quantitative consistency between the different studies is difficult to establish because not all studies report on stress values. Table 2.3 compiles some stress values for various anodic oxides reported by different research groups. With the exception of Wüthrich who measured stress by means of a membrane-deflection technique [56], all other investigators used a bending-beam technique whose principle of operation is similar to the one used in this work. The following trends have been reported.

Bradhurst and Leach measured tensile stress in anodic alumina growing in ammonium borate solution [55, 57]. They also observed a deflection of the aluminum beams in the tensile direction upon switching the field off. They compared the open-circuit residual stress in anodic alumina grown 15 nm to 300 nm-thick at different current densities and observed that the lower the current density, the more compressive the stress with a transition from compressive to tensile stress occurring at about 1 mA cm^{-2} . They correlated the stress dependence on current density with the documented evolution of transport numbers [31]. A tensile stress was also measured during titanium anodizing at 10 mA cm^{-2}

2. State of the art

Table 2.3: Compiled ranges of internal stress values reported by different research groups for anodic oxides anodized in various conditions.

	Stress (MPa)		
	Vermilyea [54]	Leach <i>et al.</i> [57–59]	Ueno <i>et al.</i> [60]
Al_2O_3	–50...+250	–200...+100	
TiO_2	–20...+150	+50...+200	–600...–400
ZrO_2	–200...+200	–1000...0	
Ta_2O_5	–10...+100		
Nb_2O_5	20...50		
WO_3	+50		

in ammonium borate [59]. Archibald and Leach measured compressive stress during anodizing of zirconium in ammonium borate [58]. The magnitude of the stress decreased when the current density increased from 1 mA cm^{-2} to 20 mA cm^{-2} .

Wüthrich measured stress in anodic alumina formed in borate electrolyte between 0.05 and 1 mA cm^{-2} [56]. Open-circuit stresses were tensile, increasing with increasing current density, while during oxide growth, the measured stress was compressive and the magnitude increased with increasing current density.

Nelson and Oriani measured stress during thin ($U < 4 \text{ V}$) anodic oxide film growth on aluminum and titanium, at current densities in the range 0.01 to 0.80 mA cm^{-2} in sulfuric acid [61]. For aluminum, stress was compressive below 0.5 mA cm^{-2} while it was tensile above that current density. On the other hand, stress in anodic titania was always tensile.

Moon and Pyun measured compressive stress during the early growth stages of dense anodic alumina in acidic and alkaline solutions [62].

Ueno *et al.* measured compressive stress in the range 400 to 600 MPa during the potentiodynamic anodic oxidation of titanium up to 11 V [60].

Finally, Vanhumbeeck and Proost reported compressive stresses in the range of -320 MPa to 4700 MPa during anodic oxide film growth of titania in 1 mol l^{-1} sulfuric acid [63].

Regarding the mechanisms of stress generation in anodic oxide films, a simple correlation between the internal stress and the Pilling-Bedworth

ratio (PBR) has been rejected by all of the above authors. The PBR is defined as the ratio between the oxide volume and the volume previously occupied by the converted metal [64]. According to the PBR-theory, compressive (tensile) stresses would be measured for $\text{PBR} > 1$ ($\text{PBR} < 1$). However, all anodic oxides having a PBR greater than one, no tensile stresses would have been measured according to the theory.

Vermilyea tentatively explained tensile stress by assuming the formation of an hydrated oxide, whose subsequent dehydration by proton migration would generate tensile stress [54]. However, the amount of incorporated hydrogen in the film is quite low, of the order of 1 at.%, making the expected contribution of oxide dehydration to the stress signal quite small.

Subsequent investigators have associated cation migration with tensile stress and anion migration with compressive stress [57, 61]. The rationale behind this kind of model is that cation migration creates free volume at the metal / oxide interface, while anion migration increases the specific volume of the film at the metal / oxide interface. This kind of model is partially supported by the fact that large compressive stress are measured during the growth of anodic zirconia, which is known to grow almost exclusively by anion migration through the film.

However, up to date, no comprehensive model has been able to accurately predict the magnitude, nor the sign of stress in anodic oxide films, and its precise dependence on anodizing conditions for all valve metals.

Electrostatic stress

Internal stresses in thin films are usually classified in two categories. On the one hand, extrinsic stresses originate from external contributions. For instance, thermal stresses are due to the mismatch of the coefficient of thermal expansion of the film and the substrate and a temperature change after the film growth. On the other hand, intrinsic stresses are due to the growth of the film itself. For instance, island coalescence during the growth of metallic thin films by physical deposition processes induces tensile stress in the film [65]. Such a classification is also appropriate for anodic oxide films, since the application of an electric field to the oxide results in a reversible stress component. It should be noted that thermal stresses are generally small in anodic oxides, since the oxide

2. State of the art

is generally grown at room temperature, and the oxide growth does not increase the oxide temperature significantly [66,67].

Electrostatic stress encompasses two contributions. The first one, the Maxwell stress, results from the attraction between charges of opposite sign located at both sides of the oxide film. The second contribution, electrostriction², arises from the additional field dependence of the dielectric constant of the material during its deformation. Using a model originally developed for linear isotropic dielectrics and determining its parameters by measuring the electrostatic stress σ^{ES} as a function of the electric field E in anodic titania, Vanhumbecq and Proost have derived the following relationship for anodic oxide films:

$$\sigma^{ES} = -\frac{\nu_{ox}}{(1-\nu_{ox})} \frac{\varepsilon_0}{2} [\varepsilon_r - (\alpha_1 + \alpha_2)] E^2 \quad (2.22)$$

where ν_{ox} is the Poisson ratio of the oxide, ε_0 is the vacuum permittivity, ε_r is the oxide relative permittivity and $\alpha_1 = -2/5(\varepsilon_r - 1)^2$ and $\alpha_2 = -1/3(\varepsilon_r - 1)(\varepsilon_r + 2) + 2/15(\varepsilon_r - 1)^2$ are electrostriction parameters [68]. Rearranging Equation (2.22) leads to:

$$\sigma^{ES} = -\frac{\nu_{ox}}{(1-\nu_{ox})} \frac{\varepsilon_0}{2} (0.6\varepsilon_r^2 + 0.8\varepsilon_r - 0.4) E^2 \quad (2.23)$$

Electrostatic stresses are thus compressive in nature, which is qualitatively consistent with the observation that the stress becomes more tensile in anodic oxide films upon switching the current off. Table 2.4 summarizes calculated electrostatic stress from Eq. (2.23) using typical values for ν_{ox} , ε_r and E , and reported electrostatic stress from the literature. The table clearly shows the diverging values obtained from different studies. Moreover, there seems to be little agreement between the expected stress and the stress reported by different experimentalists, except for the compressive sign of the effect. The discrepancies could be due to the dependence of the oxide's dielectric constant or of the electric field on the formation conditions.

Stress-driven ionic transport in anodic oxide films

While the contribution of the electric field to the ionic current density is well-described by the high-field model, there is an increasing body of

²Note that some electrochemists tend to use the term “electrostriction” to describe electrostatic stress, which can be confusing.

Table 2.4: Typical measured reversible electrostatic stress of barrier anodic oxide films on valve metals, and calculated electrostatic stress from Eq. (2.23) [68].

	measured σ^{ES} (MPa)	calculated σ^{ES} (MPa)	E (V/nm)	ε_r (-)
Al	-120... - 50 [54] -27 [71]	-42	0.8 [69]	8 [70]
Ta	-60... - 10 [54]	-460	0.6	30 [72]
Ti	-110... - 60 [54] -10... - 20 [60] -141... - 236 [68]	-690	0.5 [73]	55 [68]
W	0 [54]	-950	0.6 [74]	50 [75]
Zr	-50... - 20 [54]	-170	0.5 [35]	23 [35]

evidence — principally coming from studies performed on porous anodic oxide films (see section 2.3.4) — suggesting that stress gradients in the oxide also contribute to ionic transport. Hebert and Houser have developed a model describing the dependence of the ionic fluxes in the oxide on both potential and stress for aluminum oxide [76]. In their model, they distinguish between stress gradient-driven ionic migration and stress gradient-driven creep. The former is described by the dependence of the ionic current density on the gradient of chemical potential $\nabla\mu_i$ [77]:

$$J_i = -C_i u_i^0 \sinh\left(\frac{a}{RT} \nabla\mu_i\right) \quad (2.24)$$

where J_i , C_i , u_i and a are the ionic flux, concentration, pre-exponential velocity and migration jump distance of ion i in the oxide, respectively. The chemical potential μ is related to the hydrostatic stress σ_H and electrical potential ϕ by:

$$\mu_i = \mu_i^0 + z_i F \phi - \Omega_i \sigma_H \quad (2.25)$$

where μ_i^0 , z_i and Ω_i are the standard chemical potential, charge number, and molar volume of the ion i , respectively.

Oxide creep is accounted for by applying momentum balance equation for Newtonian fluids to the oxide. Appropriate boundary conditions allowed Hebert and Houser to model the stress in aluminum oxide [76].

They predicted the average stress in dense anodic aluminum oxide to be compressive when the current density is smaller than 0.5 mA cm^{-2} , while average tensile stress of the order of 50 MPa are predicted above 0.5 mA cm^{-2} . Their predictions are in good agreement with the stress data of Bradhurst and Leach [57].

2.2.6 Anodizing of alloys

In most engineering applications, pure metals are rarely used. For instance, the addition of alloying elements to aluminum allows improving the mechanical properties such as the yield strength for structural applications. Therefore, it is important to understand how the addition of metallic alloying elements to a valve metal modify its anodizing behavior.

Generic features of the anodic oxidation of binary homogeneous solid solution alloys are first presented. These alloys, more specifically, aluminum alloys have been extensively studied. The anodizing behavior of multi-component and multiphase alloys will then be briefly addressed. Most of the work presented here has been performed on sputter-deposited metastable alloys. However, sputter-deposited alloys and bulk alloys are expected to have the same anodizing behavior [78].

The anodizing behavior of alloys depends on the concentration of the alloyed metallic element in the anodized valve metal. Below some concentration, which depends on the valve metal and the alloying element, during the initial anodizing stages, only the valve metal is oxidized. In the meanwhile, the alloying element accumulates in a 1 nm to 2 nm-thick layer, located at the alloy-oxide interface. Once the alloying element concentration in the enriched layer is large enough, oxidation of the element proceeds, and it is incorporated in the film as “clusters” [79]. This two steps scheme is illustrated schematically in Figure 2.14 for a dilute Al-W alloy.

If the concentration of the alloying element is larger than a specific concentration, no enrichment occurs. For Al-W alloys, this concentration is somewhere between 2 and 30 % [80, 81]. For Al-Ta alloys, the concentration is somewhere between 15 and 39 % [82]. Another requirement for accumulation of the alloyed element to occur is that the Gibbs free energy per equivalent for formation of the alloying element oxide is higher than the one of the valve metal oxide [79].

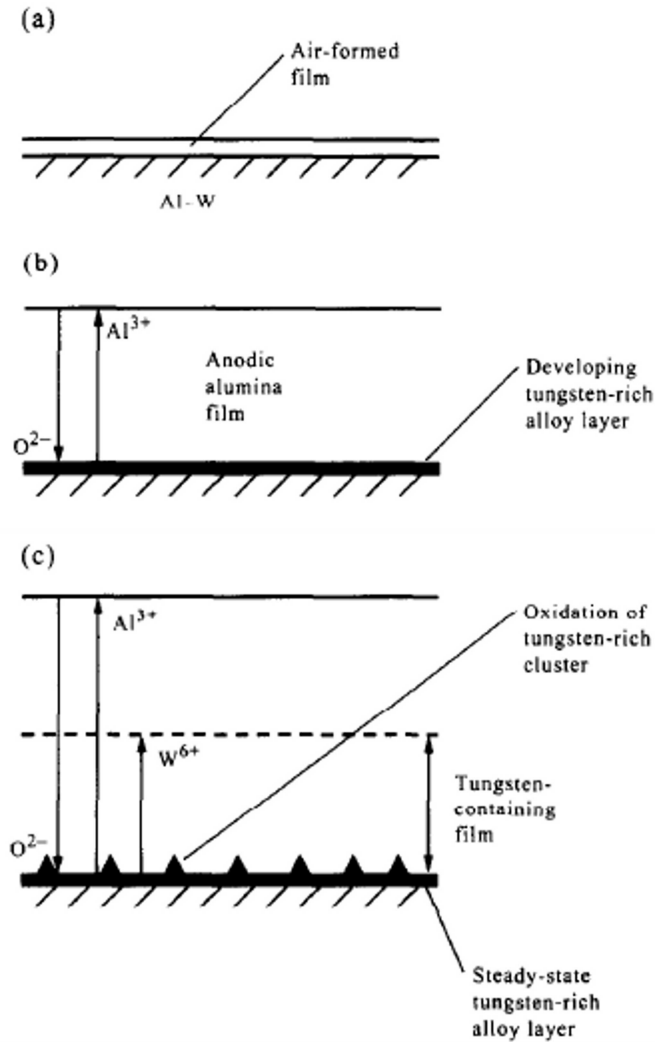


Figure 2.14: Principle of anodic oxide film growth on a dilute Al-W alloy. (a) Prior to anodizing. (b) First stage of growth of anodic alumina and enrichment of tungsten. (c) Tungsten oxidation and incorporation in the anodic oxide film. Reproduced from reference 79.

2. State of the art

Once sufficient enrichment of the alloyed element occurred, or if the conditions are such that no prior enrichment occurs, the alloying element is incorporated in the anodic film with the same average concentration than in the alloy. A duplex structure is usually observed in all cases. If the alloying element first accumulated in the alloy, the multilayer structure results from the initial formation of the relatively pure anodic film and subsequent incorporation of the alloying element in the oxide at the metal / oxide interface. If no enrichment occurred and the alloying element is readily incorporated in the anodic film from the onset of anodizing, the different ionic mobilities of the valve metal and the alloying element under the electric field result in a duplex structure [79].

When the alloying element is also a valve metal, the oxide properties such as the anodizing ratio, Pilling-Bedworth ratio and cation transport numbers depend linearly on the alloy composition, as long as the composition does not modify the structure of the anodic film. This has been shown for Al-Ta [83] and Ti-Zr alloys [84]. When the alloying element is not a valve metal, these properties are different from that of the pure anodic oxide. For instance, an anodizing ratio of 2.3 nm V^{-1} was reported for an anodized Ti-11.5 at.% Mo alloy [85], compared to 1.9 nm V^{-1} for anodized titanium [84, 86].

In some cases, the alloying of a specific element to a valve metal modifies fundamentally its anodizing behavior. For instance, the addition of copper to aluminum results in the production of oxygen gas bubbles within the anodic film [87]. The addition of silicon to titanium delays the amorphous-to-crystalline transition during oxide growth, which is observed at a larger thickness compared to pure titanium anodizing in otherwise similar conditions [88].

The behavior of binary alloys may be extended qualitatively to multi-component alloys by assuming that the possible interaction of different alloying elements will not modify their general behavior. The interaction of alloying elements however modifies the behavior of the individual elements from a quantitative point of view. For instance, the individual alloying elements reach a lower concentration in the enriched layer prior to their incorporation in the oxide compared to the anodizing of the corresponding binary alloys [89].

The behavior of multiphase alloys is more complex. Second phase

2.2. Growth kinetics of dense oxide films

particles may oxidize at a different rate than the matrix, as there is a marked dependence of their oxidation behavior on their composition and the nature of the electrolyte [90].

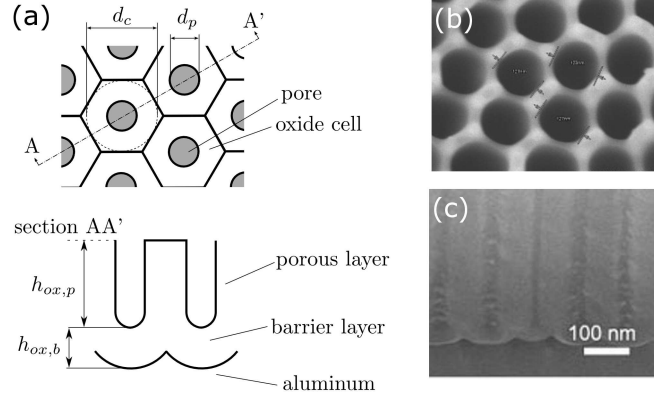


Figure 2.15: (a) Schematic representation of porous anodic oxide films together with scanning electron micrographs of (b) the oxide surface and (c) barrier layer. Reproduced from references 94 (b) and 95 (c).

2.3 Porous anodic oxide films

In this section, the growth mechanisms of porous anodic oxide films are presented. First, the differences between porous and dense barrier anodic oxide films are highlighted. Second, the dependence of the porous oxide morphology on anodizing conditions is described. Third, theories for pore initiation are presented. And fourth, pore growth theories are presented.

The morphology of porous anodic oxide films, which has been disclosed by numerous electron microscopy studies, consists in an oxide film, in which cylindrical pores, perpendicular to the metal/oxide interface, are disposed in an hexagonal arrangement [91–93]. These pores are separated from the metal by a dense oxide barrier layer of curved (or scalloped) appearance. This is illustrated schematically on Figure 2.15, with a scanning electron micrograph of a porous anodic oxide film on aluminum for comparison. As will later be seen, the view of an oxide with an homogeneous pore size and perfect hexagonal ordering is somewhat ideal, but such films can be obtained in very specific anodizing conditions.

The growth of porous anodic oxide films takes place in four stages, which are classically detected by monitoring the cell voltage (current)

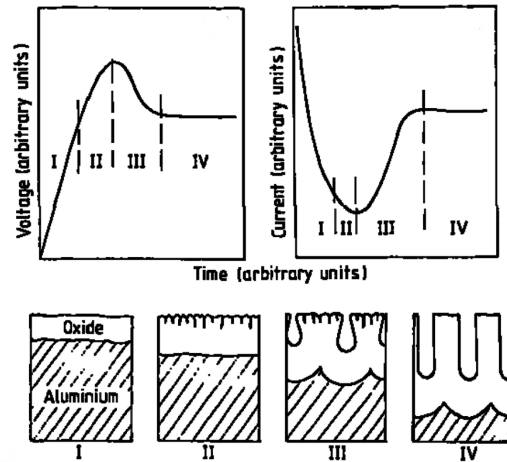


Figure 2.16: Illustration of the four distinct stages of porous anodizing, with the corresponding voltage or current density during, respectively, galvanostatic or potentiostatic growth. Reproduced from reference 96.

during galvanostatic (potentiostatic) anodizing. When the metal starts being anodized, a dense barrier oxide grows (stage I in Fig. 2.16). Incipient pores appear in the barrier oxide film while it is still thickening (stage II). Some of the incipient pores then turn into bigger pores (stage III), and after a certain amount of time, a steady-state pore morphology is reached so that only the porous layer thickness increases while the barrier layer thickness remains constant (stage IV). The corresponding cell voltage, or current density evolution are also shown on Figure 2.16, together with the corresponding characteristic four stages.

2.3.1 Growth kinetics of porous oxide films

The growth mechanism of porous anodic films are very similar to the mechanisms of growth of dense barrier anodic films described in section 2.2. The fundamental difference between the growth of dense barrier anodic films and the growth of the initial barrier oxide during porous anodizing is that the anodizing efficiency is much smaller in the latter case. This is discussed in the following section.

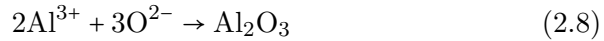
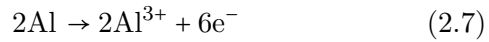
High-field ionic conduction

Fundamentally, the ionic processes involved in the growth of anodic oxide films do not change whether experimental conditions lead to porous or dense barrier films.

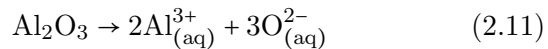
In the case of porous anodic oxide films, however, the geometry of the film is such that the electric field is not homogeneous in the oxide layer. While in the case of dense barrier films, the electric field was calculated as the ratio of the potential drop in the oxide on the oxide thickness, it is not the case for porous films. In the case of porous anodic films, the electric field is calculated as the ratio between the voltage drop in the oxide over the barrier layer thickness, thereby assuming the electric field in the pore walls is zero. Reported electric fields for aluminum anodizing are slightly different for dense barrier anodizing and porous anodizing. For instance, at a current density of 5 mA cm^{-2} , the electric field for porous anodic alumina grown in 0.4 mol l^{-1} phosphoric acid is 0.78 V nm^{-1} while it is 0.84 V nm^{-1} in 0.1 mol l^{-1} ammonium pentaborate [69]. Such a different electric field could also originate from different ionic conduction properties of the anodic film, such as a different migration jump distance (see Eq. (2.2)).

Considering again the reactions occurring at the metal/oxide and the oxide/electrolyte interfaces of an anodic oxide film, the following reactions possibly occur (written for alumina, but they can be extended to other valve metal anodizing):

- at the metal/oxide interface:



- at the oxide/electrolyte interface:



Significant amounts of oxidized aluminum have been measured in the electrolyte after anodizing [97, 98]. Successive anodizing of aluminum

in ^{18}O -enriched and -depleted electrolytes revealed that the reaction responsible for the loss of Al^{3+} ions from the film to the electrolyte is reaction (2.10), and not reaction (2.11) [99, 100]. Furthermore, the chemical dissolution rate is very low compared to the rate of reaction (2.10) which takes place under the influence of the electric field [97–99]. Thus, during the growth of porous anodic film, the anodizing efficiency η_a , defined as the ratio between the current used for oxide formation over the current provided to the anode, is lower than 1. Experimental conditions favoring low anodizing efficiencies for aluminum anodizing are low electrolyte pH and low current densities [50]. Regarding porous anodizing of titanium and other valve metals, a low anodizing efficiency can be achieved by adding fluoride ions to the electrolyte [11, 101–104].

Transport numbers

Compared to transport number studies of barrier anodic oxide film growth, transport number studies for porous anodic oxide films must take into account the reduced efficiency of film formation to correctly evaluate in which proportion reactions (2.7) and (2.8) occur. Marker experiments performed for porous anodic film formation on aluminum revealed that the inert marker was located at the oxide/electrolyte interface. This suggests that all outwardly migrating Al^{3+} cations are lost in the electrolyte [105]. If all migrating Al^{3+} cations are lost to the electrolyte, the cation transport number t_c is such that $t_c = 1 - \eta_a$. The anodizing efficiency may be calculated by measuring the charge and the amount of oxygen anions in the anodic film. Using nuclear reaction analysis, Garcia-Vergara *et al.* reported efficiency values of 0.67, 0.85 and 0.92 for anodizing in phosphoric acid at current densities of 5, 15 and 35 mA cm^{-2} respectively [106]. This would correspond to cation transport numbers of 0.33, 0.15 and 0.08 at the corresponding current densities. Anodizing efficiencies calculated by Houser and Hebert [107] allows calculating a cation transport number, decreasing from 0.4 to 0.3 between 5 and 20 mA cm^{-2} .

Comparison with usual cation transport numbers obtained for dense barrier anodic alumina suggests either that the cation transport number is significantly different in barrier and porous anodic alumina, featuring a decrease with increasing current density (the opposite trend to what is generally observed for barrier anodic alumina), or that the anodizing

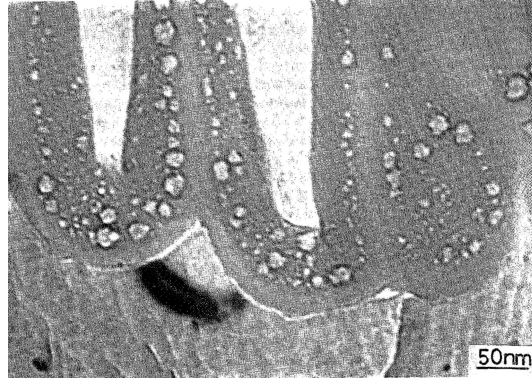


Figure 2.17: Transmission electron micrographs of a porous anodic alumina cross section formed in phosphoric acid, after exposure to the electron beam for 4 min. Reproduced from reference 105.

efficiency and cation transport numbers are not correlated to each other.

Incorporation of electrolyte species

Similarly to incorporation of electrolyte species during dense barrier anodizing, anion incorporation occurs during porous anodizing as well. This also results in a duplex structure of the anodic film, the electrolyte species being incorporated in the barrier layer at the oxide/electrolyte interface, while oxide flow (see section 2.3.4) contributes to the duplex structure to be conserved in the pore walls as well. The duplex structure can be seen in Figure 2.17, which shows a cross-sectional transmission electron micrograph of a porous film formed on aluminum in phosphoric acid. The duplex structure has been revealed by electron beam induced crystallization of the inner uncontaminated alumina layer.

Like for dense barrier anodizing, the relative thickness of the contaminated oxide depends on the electrolyte anion. The relative thickness of contaminated alumina formed in chromic acid, phosphoric acid, oxalic acid and sulphuric acid are, respectively, 0, 70, 90 and 95 % [108,109]. These ratios are more or less independent of the anodizing voltage, at least for phosphoric acid [110].

The relative contaminated thickness depends on the migration rate of the electrolyte species in the alumina. The absence of chromate ions

in the anodic film is due to the fact that chromate-containing electrolyte species migrate outward when incorporated in dense barrier anodic films [111]. Thus, because no oxide is formed at the oxide/electrolyte interface during porous anodizing, no chromate species are present in the anodic film. Interestingly, at a given current density, the steady-state voltage, hence the interpore distance and diameter (see section 2.3.2) for anodic alumina decreases for films formed in chromic acid, phosphoric acid, oxalic acid and sulphuric acid. This could mean that anion incorporation is a key factor in determining the steady-state geometry of porous anodic films.

Regarding the amounts of incorporated electrolyte species, the contaminated layer contains about 6–8 wt.% phosphate, 2.4 wt.% oxalate and 12–14 wt.% sulphate anion species for typical anodizing conditions in phosphoric, oxalic and sulphuric acid, respectively [50]. The incorporated amounts in phosphoric acid increase slightly with current density, which might be related with a dependence of the incorporated amounts on the electric field [110].

Internal stress

Few stress measurements for porous anodizing have been reported. More particularly, no data is available for porous anodizing of other metals than aluminum.

Bradhurst and Leach reported stress measurements for aluminum anodizing in sulfuric acid at a current density of 1 mA cm^{-2} . The stress was initially tensile, and a tensile-to-compressive transition occurred at a thickness of about $10 \mu\text{m}$ [55].

Wüthrich measured the stress during and after growth of porous anodic alumina formed in phosphoric acid at 0.5 mA cm^{-2} [56]. Growth stresses were compressive during the barrier layer growth stage, went through a compressive maximum just before the cell voltage maximum was reached, and were subsequently lower during the porous layer growth stage. On the other hand, open-circuit stresses were tensile during the initial barrier layer growth and were compressive during the porous layer growth, once the voltage plateau had been reached.

The first systematic study on the dependence of internal stresses on experimental conditions during porous anodizing of aluminum in sulfuric acid were performed by Moon and Pyun [62,112] and Benjamin and

2. State of the art

Table 2.5: Stress sign (C = compressive, T = tensile) during the barrier layer growth stage / porous layer growth stage reported by Moon and Pyun [62,112] and Benjamin and Khalid [113] for porous Al anodizing in H_2SO_4 .

H_2SO_4 concentration (mol l^{-1})	current density (mA cm^{-2})				
	2	5	10	15	20
0.5	C/C	C/T	C/T	C/T	T/T
1.75	T/T	C/C	C/C	T/T	C/T
3	C/C	C/C	C/C	C/C	T/T

Khalid [113]. While for some experimental conditions, they observed the same behavior than Wüthrich, i.e. compressive stress during barrier layer growth stage and tensile stress during the porous layer growth stage, they also measured tensile or compressive stress only during both stages depending on the experimental conditions. No systematic influence of the current density nor the electrolyte concentration was evident, as shown in Table 2.5.

It should be mentioned that no stress values are reported in those studies.

Porous anodizing of aluminum alloys

In industrial applications, aluminum alloys rather than pure aluminum are being anodized. Similarly to studies for barrier anodic films, model metastable binary alloys obtained by sputtering have mainly been anodized. The behavior of an alloying element during porous anodizing is very similar to its behavior during dense barrier anodizing. Enrichment of alloyed elements also occurs at the alloy/oxide interface of relatively dilute alloys. The enrichment is then followed by oxidation and incorporation of the alloying element in the anodic oxide film.

In the case of aluminum-copper alloys, copper oxide increases the electronic conductivity of the anodic film, and oxygen gas bubbles are generated within the film (reaction (2.12)). This leads to film cracking and subsequent rapid healing by current density concentration. This in turn results in an irregular porous oxide morphology compared to usual porous films on aluminum [114]. Oxygen generation also reduces the

ionic efficiency [115].

2.3.2 Dependence of the morphology on the anodizing conditions

The dependence of the porous oxide morphology on the anodizing conditions is described in this section. First, we outline the morphology dependence of disordered porous anodic alumina. Second, the morphology dependence of ordered porous anodic alumina is discussed. Third, the morphology dependence of porous and nanotubular anodic oxide films on other valve metals is presented. Note that this section reports on the steady-state morphology of these films.

Disordered porous anodic alumina

The first reports on the morphology of porous anodic films on aluminum are from the early fifties. The nanometer-scaled features could be resolved thanks to the development of electron microscopy. Keller, Hunter and Robinson were able to “see” the porous oxide cells, and one pore in each cell [91]. They established the equivalence between cell diameter and the distance between the pores (interpore distance). They also reported the proportionality between cell diameter and voltage for potentiostatic anodizing. Reported proportionality constant were dependent on the electrolyte, from 1.6 nm V^{-1} in sulfuric acid to 2.0 nm V^{-1} in oxalic and phosphoric acid solutions. Much higher ratios have been reported since.

Wood, O’Sullivan and Vaszko [92], and O’Sullivan and Wood [93] measured ratios of 2.7, 2.5 and 2.8 nm V^{-1} for sulfuric, oxalic and phosphoric acids respectively. Ebihara, Takahashi and Nagayama [116, 117] reported the cell diameter dependence on voltage for a wide range of galvanostatic anodizing conditions, and compared it to data reported by other authors for potentiostatic anodizing. Their results are reprinted in Figure 2.18. Obviously, the cell diameter is voltage-dependent, whether potentiostatic or galvanostatic anodizing is performed. A piecewise linear relationship between the cell diameter d_c and the voltage U was proposed:

$$d_c = \begin{cases} 14.5 + 2.00 U & \text{if } U \leq 20 \text{ V}, \\ -1.70 + 2.81 U & \text{if } U \geq 20 \text{ V} \end{cases} \quad (2.26)$$

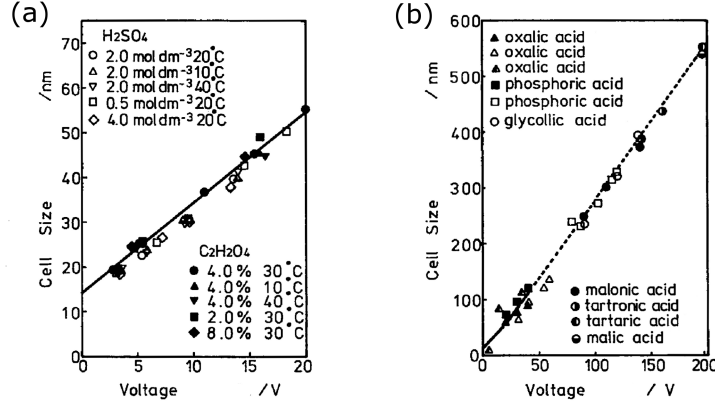


Figure 2.18: Dependence of the cell diameter on the voltage reported by various authors for different electrolytes and anodizing conditions. (a) data from Ebihara, Takahashi and Nagayama [116, 117] (b) data from, among others, references 91 and [93]. Reproduced from reference 117.

The latter relationship between anodizing voltage and cell diameter also fits (± 10 nm) more recent data reported by Ono and Masuko [118].

Other factors than the voltage have been found to influence the cell diameter. A recent study has shown that the cell diameter at a given anodizing voltage could be decreased by reducing the aluminum grain size [119]. For grain size $d_g > \frac{1}{2}2.5 U$, the cell diameter is well predicted by Equation (2.26). For $d_g < \frac{1}{2}2.5 U$, every aluminum grain is associated with an oxide cell, thus $d_c \approx d_g$. This result indicates that other factors than the anodizing voltage have to be accounted for to model the dependence of the oxide morphology on experimental conditions.

The pore diameter d_p also seems to be controlled by the anodizing voltage as numerous studies pointed out. A ratio of 1 nm V^{-1} between the pore diameter and the anodizing voltage is usually reported for phosphoric and sulfuric acid anodizing [93, 120]. However, Ebihara *et al.* report a constant pore diameter of 12 and 18 nm, respectively in sulfuric and oxalic acid, for anodizing voltages smaller than 20 V. Above 20 V, the pore diameter is proportional to the voltage, with a proportionality con-

stant of 1 nm V^{-1} [116, 117]. Ono and Masuko obtained ratios of about 1 nm V^{-1} in chromic, oxalic and sulfuric acid, while in phosphoric acid, the ratio was of 1.5 nm/V . The same ratio was obtained by Friedman and Menon in phosphoric acid [121].

The higher ratio in phosphoric acid can be attributed to its higher chemical dissolution rate of alumina, compared to other electrolytes. This effect is expected to be predominant if the pore diameter is measured far from the pore base, at the oxide / electrolyte interface [122]. The outer pore diameter also increases with temperature [122] and electrolyte concentration [95], both parameters increasing the chemical dissolution rate.

Finally, similarly to the cell diameter, decreasing the aluminum grain size may decrease the pore diameter, in otherwise similar conditions [119].

The barrier layer thickness is proportional to the anodizing voltage, similarly to dense barrier anodic films. This is a consequence of the relative independence of the electric field on the barrier layer thickness, and on the current density for usual anodizing conditions. Usual ratios of barrier layer thickness over anodizing voltage are 1.0 nm V^{-1} for films formed potentiostatically in phosphoric acid [92, 93].

Ebihara *et al.* reported decreasing barrier layer thickness over voltage ratios for films formed in sulphuric acid, from 1.4 nm V^{-1} to 0.9 nm V^{-1} between 5 and 18 V [116]. They also reported a similar decrease in oxalic acid, from 1.6 nm V^{-1} to 1.1 nm V^{-1} between 5 and 40 V [117]. The reported decrease of the proportionality constant between barrier layer thickness and voltage is due to the fact that increasing the voltage increases the current density during the steady-state growth stage [116, 117]. If the ionic current density increases, the field also increases, hence the proportionality constant between barrier layer thickness and voltage, which is equal to the inverse of the field, decreases.

The porosity of the oxide, p , is equal to the ratio of the surface occupied by pores over the total oxide surface. Ono and Masuko propose that:

$$p = (d_p/d_c)^2 \quad (2.27)$$

Porosity is found to decrease with increasing anodizing voltage in potentiostatic [118] and galvanostatic [116, 117] conditions for various elec-

2. State of the art

trolytes. The porosity is typically of 10 % to 20 % but can be as large as 80 % for films formed at very low voltage (< 5 V).

Because the anodizing potential is constant once the steady-state porous oxide growth stage is reached (stage IV in Fig. 2.16), the thickness of the barrier layer and the cell and pore diameters do not change with time anymore. On the other hand, the thickness of the porous layer increases at a constant rate [123]. To a first approximation, the thickness of the porous layer is simply a function of the charge, through Faraday's law, Eq. (2.17). More precisely, the porous layer growth rate will also depend on the anodizing efficiency, and the porosity (which modifies the density in Faraday's law). The efficiency increases and the porosity decreases with increasing current density. The porous oxide thickness per unit charge increases therefore slightly with the current density [116].

Although the porous oxide thickness increases linearly with time, there exists a maximum attainable thickness, due to the chemical oxide dissolution. For extended anodizing times, the outermost part of the pore collapses, as it has been exposed for the longest time to the electrolyte. A further oxide thickness increase is therefore practically limited, although aluminum metal conversion into an oxide continues to occur. Typical maximum thicknesses are about 20 μm to 100 μm , depending on the precise electrolyte dissolution rate [124].

Ordered porous alumina

Ordered porous anodic oxide films are characterized by the small standard deviation of the distribution of pore and cell diameters. For such ordered films, the morphology-controlling factors are the same than for disordered films. The mean proportionality constant between voltage and cell diameter is equal to 2.81 nm V^{-1} , the cell diameter being however slightly larger than the predicted value in phosphoric acid, and slightly smaller in sulfuric and oxalic acid [6].

The porous oxide growth rate is time invariant, up to a maximum thickness at which the growth rate is reduced to zero [125], in a similar way than for disordered porous films.

In recent years, there has been considerable research effort on new synthesis routes to obtain ordered porous anodic oxide films, in order to get

rid of the disadvantages of classical processes, such as long anodizing times (up to several days), or to access other pore morphologies. Examples of other routes include hard anodization, which consists in anodizing at high voltages and current densities and low temperatures [126], hard anodization in galvanostatic conditions [127] and constant current anodization, i.e. galvanostatic anodisation in concentrated sulphuric acid [128].

For those routes, the porous oxide morphology does not depend on anodizing conditions in the same way than for the conventional “mild anodizing” route. For instance, the proportionality constant between cell diameter and voltage is different for “mild anodizing” and hard or constant current anodization. This is illustrated on Figure 2.19.

As stated previously, only specific anodizing conditions lead to ordered porous anodic oxide films. The purity of the aluminum is important, and using aluminum of purity lower than 99.99% results in decreased pore ordering [129]. Long-range order is promoted by large aluminum grain size, attained by extensive annealing in nitrogen ambient [7]. To obtain ordered films, the aluminum surface must be of relatively low roughness. Low substrate roughness is usually achieved by electropolishing [5, 7]. Furthermore, the ordering can be significantly improved by performing a first anodizing step, followed by selective oxide dissolution, which leaves on the substrate an initial topography that “guides” the pores during the second anodizing step [8, 130].

During anodizing, the homogeneity of the electrolyte has to be guaranteed by vigorous steering [7]. The electrolyte is generally also cooled down to avoid chemical dissolution of the oxide [7]. Only specific voltage values, which depend on the electrolyte, the electrolyte concentration and its temperature, allow obtaining ordered porous films [6, 131]. A common feature of these ordered porous films, formed in different electrolytes at different voltages, is that the volume expansion factor, defined as the ratio of produced alumina thickness over consumed aluminum thickness, is always about 1.4 [6] and that their porosity is always about 10% [131]. In such conditions, the number of Al^{3+} ions lost in the electrolyte compared to the number of oxidized Al is always about 23%. The anodizing efficiency is therefore equal to 77% [131].

Other interpore distances than the ones accessible via “mild” anodizing can be attained by pre-patterning the aluminum substrate [3]. The pre-patterning can be done using an SiC mold (nanoimprint lithogra-

2. State of the art

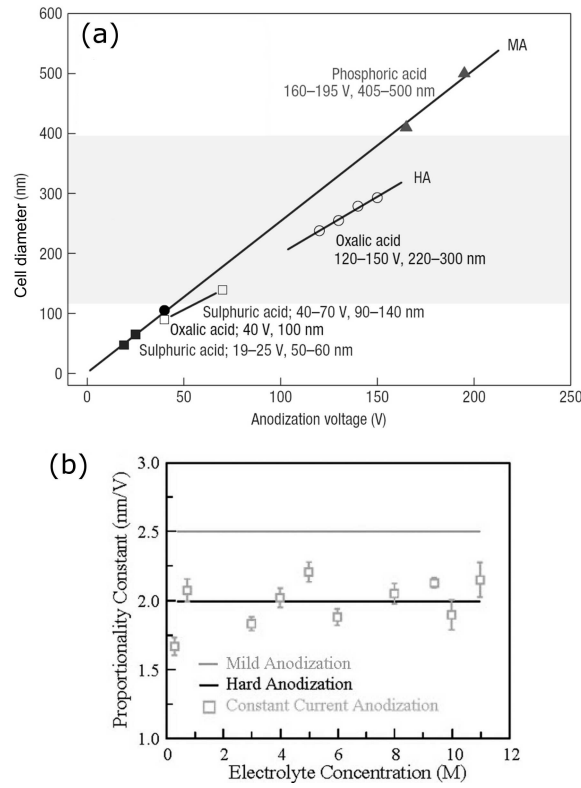


Figure 2.19: Differences between conventional “mild”, hard, and constant current anodization in conditions leading to ordered porous anodic alumina. (a) Dependence of cell diameter on anodizing voltage. Filled symbols indicate conventional “mild anodizing” conditions (MA), open symbols indicate hard anodization conditions (HA). (b) Proportionality constant between voltage and cell diameter as a function of sulfuric acid electrolyte concentration, with proportionality constant of other processes indicated for reference. Reproduced from references 126 and 128.

phy) [3,132], electron beam lithography [9], or focused ion beam lithography [94]. Another way of accessing intermediate pore morphologies is to mix electrolytes, for instance, oxalic and sulfuric acid [95].

As to the mechanism of self-ordering of porous anodic alumina, internal stress in the oxide has been proposed to be a key factor [131]. This is supported by the fact that the same volume expansion factor is obtained for ordered layers grown in different electrolytes [10,131]. This would assume the major stress contribution is the volume expansion of aluminum into alumina. Most of the stress measurements performed on dense barrier anodic films however indicate that this is not the case. Another result potentially indicating the key role of stress is that the pore ordering can be modified by applying an external tensile stress to the aluminum/alumina system [133].

Porous and nanotubular oxides on other valve metals

The recent synthesis of porous anodic films on titanium and other valve metals generated a lot of research efforts. It is questionable if the mechanisms of growth of these films are similar to the growth mechanisms of porous anodic alumina. Most results indicate that the morphology of porous anodic oxide films on titanium and other valve metals changes with experimental conditions in the same way than for porous anodic alumina, indicating that the same fundamental mechanisms form the porosity.

Similarly to porous anodic alumina, a prerequisite for the formation of porous anodic titania, zirconia, tantalum, and niobia is that the anodizing efficiency is smaller than 1. This can be achieved by adding fluoride ions to the electrolyte [11,101–104].

The pore and cell diameters increase linearly with the voltage [134–136]. The dissolving action of the electrolyte increases the pore diameter with time, as does a higher fluoride concentration [103,135]. The cell diameter also depends on the electrolyte composition. For porous anodic titania, the ratio between pore distance and voltage increased with increasing water content of ethylene glycol/ NH_4F electrolytes [137].

Remarkably, depending on the anodizing conditions, the anodic oxide films may either be nanoporous or nanotubular. The nanotubular morphology is illustrated on Figure 2.20. This kind of morphology is

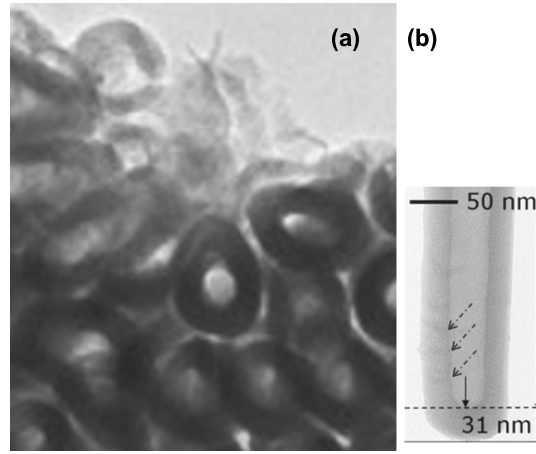


Figure 2.20: Transmission electron micrographs of nanotubular anodic oxide film on titanium (a) surface view, (b) cross-section view. Reproduced from reference 140.

predominant in the case of titania, but either nanoporous or nanotubular layers have been synthesized in the case of anodic film growth on zirconia [136], Ti-Nb [138] and Ti-Al alloys [139].

For anodic zirconia, the obtained morphology depends on the water content of the electrolyte: above a critical water content the layer is nanotubular rather than nanoporous. For Ti-Al alloys anodizing, either decreasing the aluminum content, or increasing the anodizing potential resulted in a tubular morphology, rather than a nanoporous one.

The mechanism put forward to explain the formation of nanotubes rather than nanopores, is that the cell boundaries have a higher solubility than the remainder of the oxide. This may be due to the higher fluoride content of the cell boundaries [138]. The higher fluoride content of the oxide making up the cell boundaries is expected from the faster migration rate of F^- anions compared to O^{2-} anions. The latter is due to the smaller ionic radius of F^- (see section 2.2.4 and Fig. 2.13).

Nanotubular anodic alumina has also been synthesized by taking advantage of the higher dissolution rate of the cell boundaries. This required a chemical etching step after the usual synthesis of nanoporous alumina [141].

All the described similarities between porous anodic alumina and

porous anodic oxides of other valve metals suggest that their formation mechanism is the same.

2.3.3 Pore nucleation

The present section presents the various models that have been proposed so far to explain the appearance of pores in anodic oxide films and the transition from a barrier oxide to a porous one. Some of these models are qualitative, and aim at an understanding of the basic physical mechanisms responsible for pore initiation. Other (complex) models aim at predicting the morphology of porous anodic films.

Pre-existing pattern

Early work on the growth mechanism of porous anodic alumina was based on bulk aluminum. To improve the oxide homogeneity as in industrial processes and facilitate microscopic observation, the aluminum was electropolished prior to anodizing. Electropolishing is known to produce ridges on the aluminum surface [142, 143]. Transmission electron microscopy on oxide films grown galvanostatically in phosphoric acid revealed that thicker oxide grows above these ridges during the initial barrier layer growth (rising voltage stage) [108, 144]. Pore growth then proceeds once sufficiently thick oxide grew above the ridges, with pores rearranging afterwards [93, 108].

This has led to the distinction between so-called “incipient pores” and “major pores”. The first type of pores keep the spatial distribution of the ridges produced by electropolishing, while the second one result from steady-state pore growth and have a larger interpore spacing. This three-step process of dense oxide growth, appearance of incipient pores and the rearrangement and growth of major pores is shown on transmission electron micrographs on Figure 2.21.

Two questions arise from the proposed pore initiation mechanism. The first one relates to the fact that thicker oxide grows above the ridges produced by electropolishing, while the voltage is still increasing at a constant rate during galvanostatic anodizing. This implies that the conduction properties of the oxide formed above the ridges should be different than from the remainder of the barrier oxide. The second question is whether porous films will form on non-electropolished substrates.

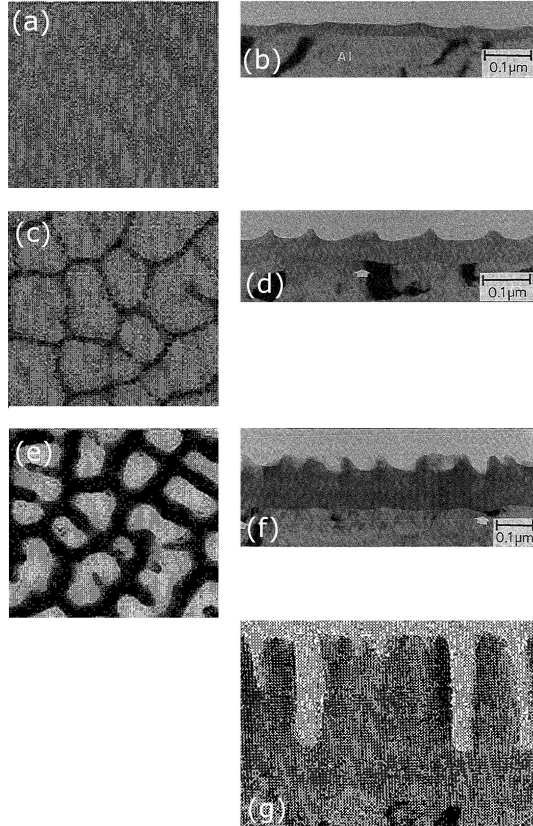


Figure 2.21: Transmission electron micrographs of stripped films (a,c,e) and corresponding cross-sections (b,d,f) of anodic alumina grown at a constant current density of 5 mA/cm^2 in 0.4 mol/L phosphoric acid. Incipient pores appear in (e,f). (g) Film grown during 300 s, well into the voltage plateau. All micrographs are of same magnification. Reproduced from reference 145.

Regarding the non-homogeneous oxide conduction properties, Thompson and Wood assumed that the oxide formed above the ridges would contain a high density of flaws, leading to film cracking and a subsequent increase of the local current density to heal the cracks [108]. The flaws would originate from the segregation to the ridges of impurities in the aluminum during electropolishing. Shimizu *et al.* assumed local oxide cracking above metal ridges, hence rapid oxide growth at these locations [145]. Wu, Zhang and Hebert suggested that the potential distribution resulting from the geometry of the metal/oxide interface causes the oxide to preferentially thicken above the ridges [146]. This last hypothesis, which they supported with model calculations, is also confirmed experimentally. Indeed, the growth rate of porous oxide films is 2 to 7 % faster on large convex aluminum regions relative to the growth rate on flat regions. This last result is independent of the preparation procedure to obtain a curved topography nor the aluminum source [147]. This points to the absence of effect from defects or impurities on the growth rate at ridges.

Regarding pore nucleation when the aluminum surface is not electropolished, pores always appear, whatever the surface treatment prior to anodizing. Porous anodic alumina has also been obtained on chemically or mechanically polished aluminum substrates. Furthermore, aluminum deposited by physical vapor processes such as electron-beam evaporation or sputtering can also be anodized into porous alumina [69], even though the initial surface is of relatively low roughness. Final proof against the requirement of a pre-patterned surface is provided by Masuda *et al.*, who showed that when aluminum is imprinted with missing indents, the missing indent leaving a perfectly flat aluminum surface, pores do nucleate and grow at the location where the indent was initially missing [148]. Therefore, while electropolishing produces an initial surface topography which might allow incipient pores to appear, it seems it is not required for the development of major pores.

Perturbation analysis models

Several authors have attempted to predict pore initiation by performing so-called perturbation analysis. Perturbation analysis has mainly been used to predict morphological instabilities during epitaxial growth of thin films [149]. The principle of such an analysis is to perturb the

2. State of the art

equations governing the motion of interfaces, typically by adding a small sinusoidal term to the coordinates of the interfaces, and calculate under which conditions the perturbation amplifies.

Two complementary approaches exist. The first one consists in calculating the energy difference between the perturbed and unperturbed base state. When the energy difference is positive, the perturbation is not energetically favored, and it will be damped. When the energy difference is negative, the perturbation will amplify, if the kinetics of the system allows it to. The second approach consists in introducing the perturbation terms into the kinetics of interface motion. A mathematical analysis then allows to check under which conditions the perturbation will be amplified.

Both kind of approaches have been used to attempt to explain pore initiation in anodic films on valve metals. An energetics-based approach taking into account the contributions of surface energy and stress was proposed as a qualitative explanation for pore initiation in anodic titanium, although it was not confirmed that the predicted perturbation wavelength had the correct order of magnitude [150].

On the other hand, several authors have used the kinetics-based approach, introducing the perturbation terms into the equations describing the evolution of the metal/oxide and oxide/electrolyte interfaces [151–154]. Thamida and Chang considered the destabilizing effect of field-assisted dissolution (see section 2.3.4) at the oxide/electrolyte interface and metal oxidation at the metal/oxide interface in their analysis. Singh *et al.* argued that a cut-off mechanism was needed, and they proposed the dependence of the activation energies of the reactions on surface energy and elastic stress to provide such cut-off [152, 154]. This model was further extended to incorporate non-linear oxide conduction [155] or oxygen migration [156]. Yang considered the competing effects of the electric field and interfacial diffusion at the metal/oxide interface to be responsible for a particular wavelength selection at that interface [153]. Recent developments on the mechanisms of pore growth suggest that field-assisted dissolution does not control the porous oxide morphology. The basic assumption behind these analyses being wrong, they cannot help explaining the transition from a dense barrier oxide to a porous oxide.

2.3.4 Pore growth

In this section, the different models accounting for pore growth are reviewed. Key features of models are the prediction of the steady-state geometry, i.e. the invariance of pore and cell diameter, and of the barrier layer thickness. Two major mechanisms have been proposed in the anodizing literature. Historically, it was thought that the invariance of the geometry was due to oxide removal at the pore bottom by oxide dissolution. Only recently has this mechanism been rejected. There is now a large consensus on the fact that oxide growth proceeds by oxide creep, the viscous flow of oxide from the barrier layer to the pore walls keeping the steady-state geometry invariant.

Oxide dissolution at the pore base

Early studies on the morphology of porous anodic alumina have proposed oxide dissolution to be responsible for porous oxide growth. For instance, in the early work of Keller, Hunter and Robinson [91], it is already stated that “nonporous coatings form in electrolytes that possess no ability to dissolve the oxide, while porous coatings are formed in electrolytes that exert appreciable solvent action on the oxide”. These authors actually suggested that the (chemical) dissolution was due to the temperature and H^+ concentration rise at the bottom of the pore. Calculations have later shown that the temperature rise due to Joule heating was negligible in most cases [97,98].

A field-assisted oxide dissolution mechanism was proposed by Hoar and Mott [157], and later refined by Diggle *et al.* [158]. The mechanism was further supported by O’Sullivan and Wood to qualitatively explain the dependence of the porous layers morphology on anodizing conditions [93]. This mechanism has been subsequently cited in the literature to explain pore growth in anodic alumina.

Several models assuming rate equation characteristic for field-assisted oxide dissolution have been developed to explain the dependence of the porous oxide morphology on experimental conditions. Parkhutik and Shershulsky [96] took into account the electric field distribution in the oxide and included field-assisted dissolution and oxidation reactions at the oxide/electrolyte interface as boundary conditions to model the steady-state pore geometry. The rate of field-assisted dissolution is modeled as being pH-dependent and has an exponential dependence on the field.

2. State of the art

This model predicts a linear dependence of cell diameter on anodizing voltage.

Thamida and Chang were also able to reproduce the linear dependence between voltage and cell diameter by performing a perturbation analysis of the equations describing the movement of the interfaces, which were also governed by field-dependent oxide deposition and dissolution [151]. Singh *et al.* further extended previous models by taking into account a dependence of the activation energies of oxide deposition and dissolution on interfacial energy and elastic stress [152,154]. Their model predicts ordered hexagonal pore arrays for a range of volume expansion factors close to the one observed for ordered porous films [6].

A recent attempt to experimentally validate the models of Parkhutik and Shershulsky [96], Thamida and Chang [151] or Singh *et al.* [152,154] concluded that none of these models is able to predict experimental results [159]. This is due to the fact that these models assume pore formation by field-assisted dissolution while this mechanism has been recently rejected.

Viscous flow of oxide

Until 2006, field-assisted dissolution was the widely accepted mechanism for pore growth, and the steady-state pore geometry was rationalized in terms of a self-regulating competition between oxide growth at the metal/oxide interface and oxide dissolution at the oxide/electrolyte interface. Although a few discrepancies were reported in the literature, no satisfying mechanism was proposed.

Such a discrepancy is that no oxygen from the oxide ends up in the electrolyte, except for the low amounts resulting from chemical, open-circuit dissolution. This was determined by measuring the amounts of ^{18}O in the oxide before and after anodizing in an ^{18}O -depleted electrolyte following a short anodizing step in an ^{18}O -enriched electrolyte [99,100].

Another discrepancy is that much higher volume expansion factors, i.e. ratios of produced oxide thickness over the corresponding thickness of consumed aluminum, were measured for porous anodizing compared to barrier anodizing [6,10,160]. The ratio of thicknesses of grown alumina Δh_{ox} over consumed aluminum $-\Delta h_{Al}$ can be calculated from Faraday's

law, Eqs. (2.17) and (2.19):

$$\frac{\Delta h_{ox}}{-\Delta h_{Al}} = \eta_a \frac{M_{ox}/(\rho_{ox} z_{ox})}{M_M/(\rho_M z_M)} \quad (2.28)$$

For dense barrier alumina, $\eta_a = 1$, $\rho_{ox} = 3.1 \text{ g/cm}^3$, $M_{ox} = 102 \text{ g/mol}$, $z_{ox} = 6$, the volume expansion factor is equal to 1.65. For porous anodic alumina, $\eta_a \approx 0.6$, the volume expansion factor should be equal to 0.99. However, reported values are in the range 1.3 to 1.6 [6,160]. Pore growth by expansion of film material from the barrier layer to the pore walls was suggested by Garcia-Vergara *et al.* by comparing volume expansion factors and anodizing efficiencies of porous anodic alumina formed in sulfuric and phosphoric acid electrolytes with the ones for dense anodic alumina formed in ammonium pentaborate electrolyte [69].

A final discrepancy was found by modeling the electrical potential distribution in a steady-state porous oxide geometry. Indeed, Houser and Hebert found that additional transport processes than high-field ionic transport were necessary in order to keep the steady-state porous oxide geometry invariant [161].

The distribution of tungsten in tracer experiments, in which a thin tungsten layer is deposited in a sputter-deposited aluminum layer, was found to be consistent with transport of oxide by flow [162,163]. The distribution of tungsten in porous anodic alumina formed in phosphoric acid at 5 mA cm^{-2} is shown in a transmission electron micrograph in Figure 2.22. The expected tungsten distribution in a porous oxide film formed by field-assisted dissolution, or in a porous oxide film formed by flow are shown in Figure 2.23.

Tungsten tracer experiments performed in other electrolytes yielding porous anodic alumina have shown that oxide flow is the pore growth mechanism in sulphuric acid [165], oxalic and malonic acid [166], but that field-assisted dissolution is responsible for pore growth in alkaline borax [164] and chromic acid [167] electrolytes. Porous anodic films formed in chromic acid contain no electrolyte species, compared to films formed in sulphuric, oxalic, and phosphoric acid, which contain acid anions in the outer part of the film [109,167]. This may point to the influence of electrolyte anion incorporation in determining the oxide flow properties.

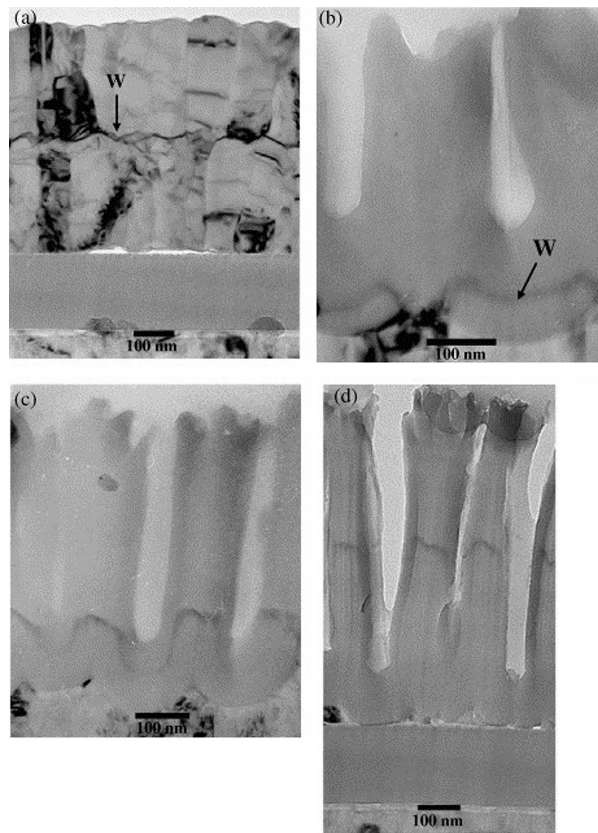


Figure 2.22: Transmission electron micrographs of (a) aluminum deposited by sputtering, incorporating a tungsten tracer layer, and anodized for 180 s (b), 240 s (c) and 350 s (d) at 5 mA/cm^2 in 0.4 mol/L phosphoric acid. Reproduced from reference 163.

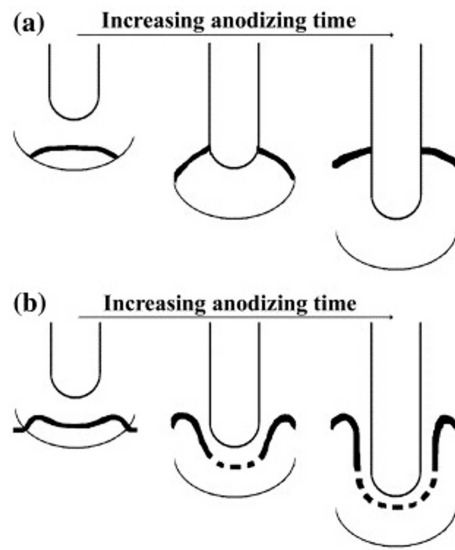


Figure 2.23: Illustration of the behavior of tungsten tracer species incorporated into porous anodic films on aluminum in case of pore growth by (a) field-assisted dissolution or (b) oxide flow. Reproduced from reference 164.

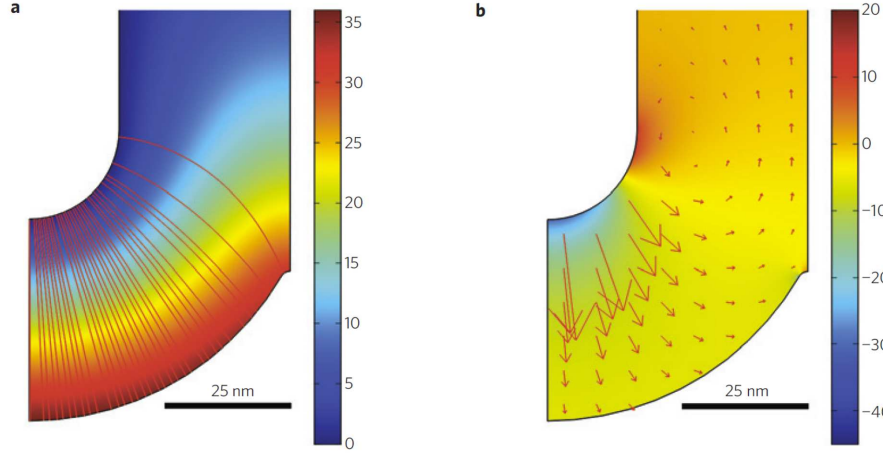


Figure 2.24: Predicted (a) current lines and electrical potential distribution (in volts) and (b) dimensionless hydrostatic stress and oxide velocity vectors from modeling oxide growth by electric-field driven ionic transport coupled with oxide viscous flow. Reproduced from reference 107.

Further conclusive evidence for oxide flow was recently presented by Houser and Hebert in a seminal paper in *Nature Materials* [107]. These authors incorporated viscous flow in their model for calculating the interface velocities on the basis of the electrical potential distribution in porous anodic oxide films [107,161]. Their simulation results were able to quantitatively reproduce the distribution of tungsten compared to the tracer experiments described above.

Furthermore, their model predicts the (non-dimensional) stress distribution in the oxide film. At the film/electrolyte interface, the predicted stress is compressive, presumably because of anion adsorption. At the oxide cell boundary, the predicted stress is tensile, which is consistent with the microscopic observation of voids at cell boundaries and triple junctions under specific anodizing conditions [168]. Figure 2.24 shows the predicted electrical potential and (dimensionless) stress in the porous oxide.

Although the formation mechanism of porous oxide films on other valve metals has been studied less extensively than on aluminum, tung-

sten tracer experiments [169] and volume expansion factor measurements [170] performed for anodic titania nanotubes formation are also consistent with porosity development by oxide flow. In that case however, the porosity separating the tubes may be formed by dissolution of the cell boundaries, as described previously.

2.4 Breakdown of dense anodic oxide films

In section 2.2, the mechanisms of dense anodic film growth were presented. In section 2.3, we saw that the initial growth of a dense anodic film could be followed by the growth of a porous one. In this section, we will see that the growth of a dense anodic oxide film can also be terminated by breakdown. Breakdown, when occurring, either limits the attainable anodic oxide film thickness before the number of “imperfections” in the film increases dramatically [73, 171, 172], or limits the thickness of the anodic film in the sense that it will not further thicken [13, 84, 172–176]. Note that in the first case, the anodic film can be further thickened, but due to the defects it will not be homogeneous anymore.

Few investigators have made a systematic distinction between these two types of breakdowns, except for Jouve and Derradji [177] and Di Quarto *et al.* [172, 178]. Di Quarto used the terminology of mechanical and electrical breakdown, but here we will rather term these breakdown events as type-I and type-II breakdown. Type-I and type-II breakdown are not mutually exclusive. Indeed, once type-I breakdown occurred, the film usually continues to grow, until type-II breakdown occurs. However, once type-II breakdown occurred, type-I breakdown will not occur anymore.

First, the general breakdown phenomenology is discussed. Secondly, the specific physico-chemical processes occurring in anodic oxide films during their breakdown are discussed in detail. Thirdly, the dependence of breakdown on anodizing conditions is presented. Finally, qualitative and quantitative models describing breakdown are presented and their validity is discussed in the light of some experimental observations from the literature.

2.4.1 Breakdown phenomenology

During galvanostatic anodizing, type-II breakdown is usually detected by rapid voltage fluctuations [179]. On the other hand, type-I breakdown is indicated by a decrease of the derivative of voltage versus time. This is illustrated in Figure 2.25 for type-II breakdown (Fig.2.25(a)), and type-I breakdown followed by type-II breakdown (Fig.2.25(b)). Note that a change of the slope of the voltage versus time curve does not always in-

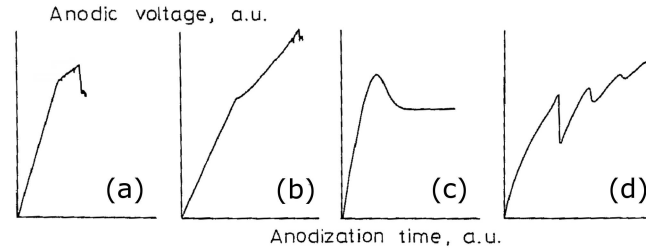


Figure 2.25: Schematic voltage evolution during galvanostatic anodizing of a valve metal in case of (a) type-II breakdown and (b) type-I breakdown, followed by type-II breakdown. Not to be confused with (c) porous film formation nor (d) cyclic oxide growth / dissolution during silicon anodizing. Reproduced from reference 181.

dicate breakdown [171]. Moreover, a voltage plateau may also indicate that the anodic film is porous (Fig. 2.25(c)). Finally, voltage oscillations such as those observed during silicon anodizing in aqueous acidic electrolytes indicate cyclic oxide growth and dissolution, not breakdown (Fig. 2.25(d)) [180].

Type-I breakdown has only been reported so far on anodic oxides of titanium [171, 177], zirconium [172] and tungsten [178]. For these metals, it does not occur systematically in all electrolytes, nor all current densities.

Once type-I breakdown occurs, the oxide film is damaged locally, with holes in anodic titania [177, 182], cracks in anodic zirconia [172] and tungsten oxide [183]. In the case of anodic titania, these defects have been associated to the growth of anatase crystals 10 to 20 nm in size in the amorphous titania matrix [177, 182]. The decrease of the slope of the voltage - time curve has been attributed to oxygen evolution, which results from the increase of the electronic conductivity of the oxide film associated with crystallization [73].

In the case of anodic zirconia and tungsten oxide, the cracks have been attributed to a build-up of stress with increasing oxide thickness, eventually causing oxide failure and cracking [172, 178]. The decrease of the slope of the voltage-time curves has been attributed to a decrease of the anodizing efficiency.

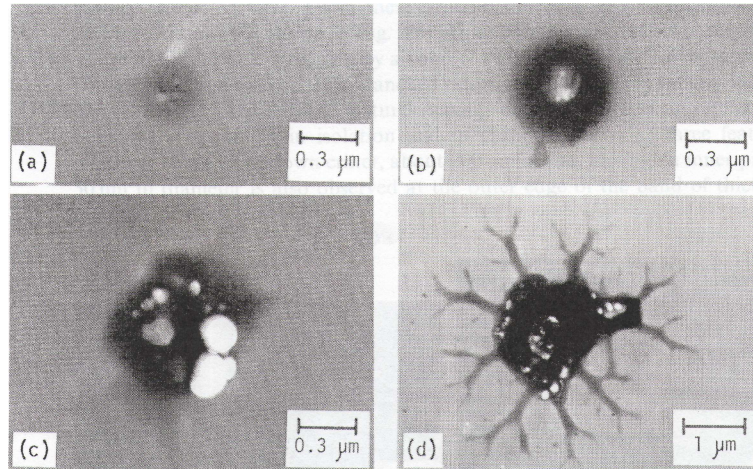


Figure 2.26: Transmission electron micrographs of stripped anodic alumina showing the sequence of events leading to type-II breakdown: (a,b) local overgrowth ; (c) local film evaporation and healing resulting in the radial propagation of cracks (d). Reproduced from reference 176.

Type-II breakdown has been reported to occur for all anodic oxides. For amorphous anodic oxides, such as the oxides of aluminum and tantalum, crystalline oxide has been detected after type-II breakdown at the location of the breakdown events [184]. Type-II breakdown is also accompanied by audible noise and sparking on the anode [179,185]. Sparks actually start to appear a few volts below the actual breakdown voltage, which is usually defined as the maximum voltage attainable [181,185]. A rigorous distinction between the first spark voltage and the breakdown voltage has not always been made [181].

Most investigators also report oxygen evolution on the anode slightly before breakdown occurred [173,176,179]. The local character of type-II breakdown has been emphasized by Shimizu *et al.*, who reported on successive sparking and short bursts of gas (probably oxygen), followed by local oxide overgrowth, oxide evaporation due to thermal effects, and subsequent oxide healing. Subsequent crack propagation leads to generalized oxide breakdown [176]. The sequence of these events which are distributed over the whole anode surface is illustrated in Figure 2.26.

Today, the question still remains unanswered whether local oxide

overgrowth, crystallization, oxygen evolution, and light emission (sparking) are either the cause or a consequence of breakdown. These phenomena are discussed in the next section.

2.4.2 Phenomena related to the breakdown

Breakdown during the growth of anodic oxide films is associated with various phenomena, namely local oxide crystallization, oxygen evolution at the film surface or within the film, and light emission.

Crystallization

Vermilyea [186] first reported on obtaining crystalline anodic tantalum oxide at low temperatures, although he did not relate it to breakdown at the time. An electric field had to be maintained in the oxide, which was done by holding the potential constant for several minutes (potentiostatic aging). Crystallization caused cracking of the oxide. Cracking of potentiostatically aged anodic tantalum oxide was later confirmed by Jackson [187]. Crystallization also caused film blistering and partial delamination as illustrated in Figure 2.27. Habazaki *et al.* observed crystallization during potentiostatic aging of anodic niobium oxide. Crystallization resulted in oxide blistering [188].

The location of the crystallization indicates that crystal precursors originate from the native oxide [188]. The native oxide seems to be a precursor for crystallization in anodic alumina as well, as relatively ordered (i.e. more readily crystallizable, as determined by differential thermal analysis) anodic alumina grows there [189]. The crystal growth occurs by new oxide growth, rather than by phase transformation [188]. This does not exclude that the crystal nuclei form by phase transformation.

Leach and Pearson associated such crystallization with low oxide growth rates (hence the potentiostatic aging, during which very slow oxide growth may occur), which they associated with low cation transport numbers [175]. Low cation transport numbers mean that the oxide grows predominantly at the oxide / metal interface. The resulting epitaxial oxide growth and high compressive stresses would then favor the growth of crystalline oxide.

Regarding type-I breakdown, Dyer and Leach detected crystalline oxide

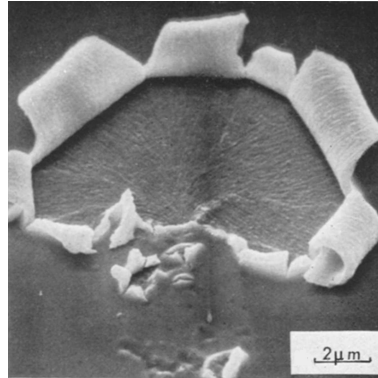


Figure 2.27: Blisters and cracks in anodic tantalum oxide films resulting from oxide crystallization. Scanning electron micrograph of a film anodized in 85 °C nitric acid at 120 V for 16 min. Reproduced from reference 187.

in anodic titania after breakdown occurred. Subsequent oxygen evolution occurred on the crystallites [171]. Transmission electron microscopy located cavities in the oxide film in which oxygen evolution occurred [73]. These cavities were located near anatase nanocrystals, which developed at the location of the native oxide film [73].

Yahalom and Zahavi showed that after type-II breakdown occurred, anodic films on aluminum and tantalum were partially crystalline, whereas they were amorphous prior to breakdown [184]. They assumed that internal stress builds up with increasing oxide thickness, resulting in oxide cracking. High current density and temperature oxide growth in the crack would then result in crystallization. They also put forward the hypothesis that crystallization of the amorphous oxide would be driven by high compressive stress in the anodic film.

Li *et al.* detected crystalline oxide in anodic alumina formed galvanostatically well before type-II breakdown occurred. Small amounts of crystalline oxide were already detected in the oxide at 200 V, whereas breakdown occurred only at 420 V [173]. These authors proposed that the oxide crystals act as precursors for breakdown.

In conclusion, although breakdown of anodic oxide films and crys-

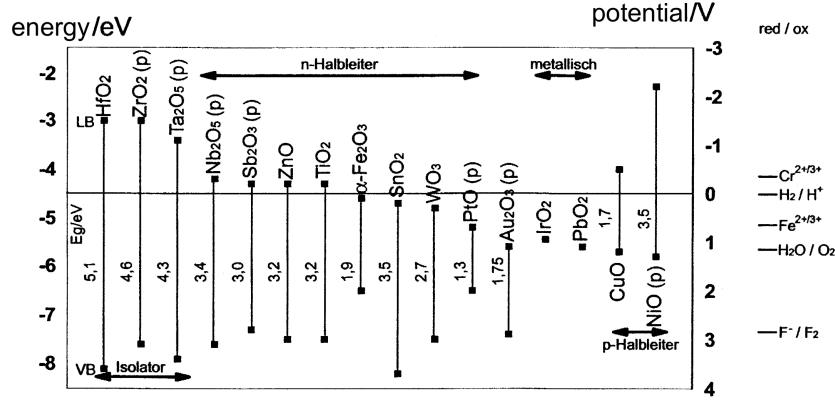


Figure 2.28: Band structure of passive films for insulating, semiconducting and metallic oxide films. Not on the figure, alumina has a reported bandgap of about 8 eV [20]. Reproduced from reference 190.

tallization seem to be closely related, no conclusive evidence exists as to which one occurs first. Whether or not crystallization associated with breakdown occurs by the same mechanism than crystallization during potentiostatic aging of the oxide film is still an open question.

Oxygen evolution

The breakdown of anodic oxide films has also been associated with oxygen evolution on the anode surface. Oxygen evolution, introduced in section 2.2.2, is an oxidation reaction which involves electron transfer (reaction (2.12)):



Thus, for this reaction to occur on either the anodic film surface, or within the film itself, the film must be an electronic conductor.

Classification of oxide films on the basis of their insulating, semiconducting or metallic character has been made (see Figure 2.28), and revealed that most oxides that can be grown anodically are insulating, with the notable exception of TiO₂ which is a n-type semiconductor [190].

However, during the growth of anodic oxide films, the electronic conductivity is not only dependent on the intrinsic solid-state properties of

2. State of the art

the oxide. Firstly, if the oxide is assumed to be an ideal semiconductor, a Schottky barrier is present at the oxide / electrolyte interface [191]. Secondly, anodic oxide films are usually amorphous, so that the band gap is actually a mobility gap, with localized states present in the gap [190,191]. Thirdly, the presence of defects in the anodic film, such as vacancies and electrolyte species, are also expected to modify the band structure of the anodic film [190]. And finally, the situation is expected to be even more complex when an electric field is present in the oxide, during its growth. For instance in the case of anodic titania, the electronic properties such as donor concentration are strongly dependent on oxide thickness, film formation rate and substrate grain orientation [192,193]. Thus, the possibility for oxygen evolution to occur is determined by a variety of complex factors.

Regarding the mechanism of electron transfer within the film, resonant tunnelling of electrons has been proposed. This would require a sufficient number of states within the film [194]. For anodic titania, oxygen vacancies have been proposed to act as quantum wells, where electrons hop from one well to the other [195].

Oxygen evolution can occur on the surface of anodic films, but also within anodic films. Oxygen bubbles produced within anodic oxide films have been reported during the anodizing of aluminum alloys, principally Al-Cu [87,196], but also Al-Cr [197], Al-Fe [198] and Al-Zr [39] alloys. It has also been reported during anodizing of titanium and its alloys [73,84,199], and tantalum-copper alloys [200]. Oxygen bubbles produced within the film are responsible for circular or ellipsoidal cavities in the anodic oxide film. Typical cavities are 50 nm x 50 nm to 200 nm in size but cavities smaller than 5 nm have also been reported [87].

Oxygen evolution within the films has been attributed to the formation of regions of high electronic conductivity. These regions were identified as nanocrystals in an amorphous oxide matrix, e.g. anatase for anodic titania or cubic zirconia in an amorphous zirconia matrix [39,73,84]. Locally high electronic conductivity has also been attributed to the formation of clusters of a semiconducting oxide such as CuO during Al-Cu alloys anodizing [87].

The presence of gas bubbles within the anodic oxide film is thought to lead to film disruption. Indeed, the stress resulting from the presence of high-pressure gas might be significant. The pressure of the gas has

usually been estimated using the Young-Laplace equation:

$$\Delta p = \gamma(R_1^{-1} + R_2^{-1}) \quad (2.29)$$

with Δp the pressure difference across the bubble interface, γ the surface tension, and R_1, R_2 the principal radii of curvature. Typical values for anodic oxide films are $\gamma = 1 \text{ N m}^{-1}$, $R_1 = 25 \text{ nm}$ to 100 nm and $R_2 = 25 \text{ nm}$. The typical pressure is then 80 MPa to 50 MPa . Smaller bubbles of 5 nm diameter may be pressurized to 800 MPa . Damaged appearance of the oxide surface has sometimes been attributed to oxygen generation within the anodic oxide film [87].

Luminescence

It has been known for a long time that during anodizing, light emission accompanies oxide growth [201,202]. This phenomenon has mainly been studied for aluminum anodizing, since the emission has been reported to be more intense than during anodizing of other valve metals.

For aluminum anodizing in inorganic electrolytes, the luminescence intensity has been found to be strongly dependent on the surface preparation. The intensity is higher for as-received or degreased aluminum surfaces, while it is slightly reduced for chemically polished samples and nearly zero for electro-polished samples [203–206].

The purity of the aluminum is also an important factor since Mn, Eu, Tb, or Dy doping increase the luminescence intensity, while Zn decreases it. The luminescence intensity is not affected by Cr, Cu, Fe, or Mg [204]. For anodic alumina films formed on chemically polished or as-received samples, the luminescence intensity increases with temperature, and is independent of electrolyte concentration or current density [204]. The luminescence intensity L increases with the anodic alumina film thickness h_{ox} [203, 205, 207], and in some cases, it has been shown to follow approximately the relationship:

$$L = a(\exp(bh_{ox}) - 1) \quad (2.30)$$

where a is proportional to the current density, and b is a constant [203, 208]. Note that more recent results obtained on pure aluminum anodized in inorganic electrolytes indicate that the luminescence intensity is independent of the current density [204, 207]. These conflicting

2. State of the art

results could be due to the fact that the electrolyte nature (organic or inorganic), which has not been given much consideration in early studies, fundamentally modifies the characteristics of the luminescence [203].

The exponential increase of the luminescence with oxide thickness (and in some cases with current density) has been taken as evidence that luminescence is caused by collision excitation of electrons in the anodic oxide film, these electrons originating from incorporated anions or metallic impurities in the anodic film [209].

The latter mechanism has been rejected by Shimizu and Tajima, at least for high-purity aluminum anodizing in inorganic electrolytes, since the macroscopically uniform luminescence was found to actually occur locally at flaws in the oxide film [205]. This contradicts the hypothesis of a uniform electronic current in the film. The concentration of flaws in the anodic film, defined as defects where the oxide growth appears to be inhibited, was found to increase with oxide film thickness, and be dependent on the pretreatment. Anodic alumina grown on as-received, chemically polished, and electro-polished specimens had a flaw concentration of about $2 \times 10^8 \text{ cm}^{-2}$, $3 \times 10^7 \text{ cm}^{-2}$, and $1 \times 10^5 \text{ cm}^{-2}$, respectively [205]. These flaws are possibly associated with γ -alumina nanocrystals [206].

When type-II breakdown occurs, the luminescence intensity further increases and sparks are visible on the oxide surface [173]. Similarly to the luminescence occurring during “normal” film growth, it is still a matter of debate whether the sparks are caused by some process occurring at flaws, or recombination of electrons from avalanche processes. Sparking has also been attributed to current discharges through oxygen gas bubbles generated at the surface [210].

2.4.3 Dependence of the breakdown on the anodizing conditions

The breakdown voltage may depend on experimental conditions during anodizing. The breakdown voltage is dependent on the metal anodized, the current density, and the electrolyte composition. On the other hand, it does not depend on the electrolyte temperature, stirring rate, and sample history.

Influence of the substrate

Regarding type-I breakdown, no study was found to compare systematically the voltage at which breakdown occurred for different metals. It seems however to occur at a lower voltage during titanium (≈ 10 V to 70 V) and tungsten anodizing (≈ 50 V to 70 V) than during zirconium anodizing (≈ 100 V to 250 V). For the breakdown of titanium, using an analytical grade rather than a technical grade Ti substrate increases the breakdown voltage by 4 to 6 V. However, it was not clear whether the effect was due to the purity or the structure of the titanium grains [177].

Wood and Pearson reported type-II breakdown voltages of respectively 190, 210, 235, and 295 V for niobium, tantalum, aluminum, and zirconium, anodized in 3% ammonium tartrate. Alwitt and Vijn reported breakdown voltages of 190, 275, 350, and 315 V for the same oxides grown in the same conditions [210]. Alwitt and Vijn correlated the increase in breakdown voltage with increasing bandgap values. This could mean that breakdown is an electronic phenomena. However, as Alwitt and Vijn pointed out, breakdown also correlates with the thermodynamic stability of the oxide, since the bandgap is a monotonic function of the enthalpy of formation [211]. However, no conclusion could be formulated regarding a classification of the breakdown voltage of these anodic oxides based on their intrinsic properties, since the order of increasing breakdown voltages of these oxides depend on the electrolyte resistivity (see Figure 2.29).

Influence of the current density

A pronounced effect of the current density on the breakdown voltage has been reported for type-I breakdown. During zirconium anodizing, the breakdown voltage V_I was found to follow a logarithmic dependence on current density j :

$$V_I = A_I + B_I \log j \quad (2.31)$$

where A_I and B_I are constants depending on the electrolyte. For zirconium and titanium anodizing, $B_I > 0$ and A_I and B_I are independent of the electrolyte concentration, but for tungsten anodizing, $B_I < 0$ and A_I decreases with increasing electrolyte concentration [172, 177, 178]. It should be noted that increasing the acid concentration led to a con-

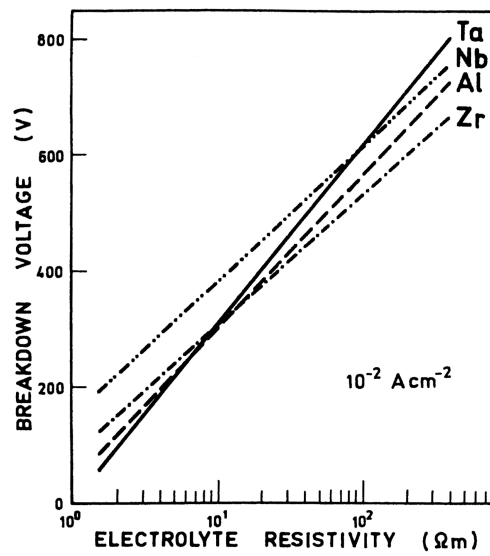


Figure 2.29: Dependence of type-II breakdown voltage on the logarithm of electrolyte resistivity for Ta, Nb, Al and Zr anodizing in solutions of ammonium salicylate in dimethylformamide. Reproduced from reference 212.

stant breakdown voltage above a critical current. Further increasing the electrolyte concentration resulted in the absence of type-I breakdown, probably because type-II breakdown occurred before [172].

The current density has however been reported to play only a moderate effect on the type-II breakdown voltage of anodic oxide films. The breakdown voltage decreases slightly with increasing current density for anodic niobia, tantalum, alumina, and zirconia [66, 172, 212]. For zirconium anodizing, a linear dependence of the breakdown voltage V_{II} on current density j has been reported:

$$V_{II} = A_{II} - B_{II} j \quad (2.32)$$

where A_{II} and B_{II} are positive constants depending on the electrolyte and its concentration [172].

Influence of the electrolyte

The electrolyte seems to be predominantly affecting type-II breakdown. Early studies have reported a logarithmic dependence of the breakdown voltage U_{II} on the electrolyte resistivity ρ_e [179]:

$$U_{II} = a_{II} + b_{II} \log \rho_e \quad (2.33)$$

where a_{II} and b_{II} are constants depending on the electrolyte composition and the anodized metal. This dependence has been confirmed later on by many other investigators [172, 212–215]. Parkhutik *et al.* suggested that the electrolyte resistivity dependence actually “hides” a more fundamental dependence on a property of the oxide/electrolyte interface, such as the amount of incorporated anions [181].

Indeed, Kato *et al.* showed that the electrolyte resistivity is not the only electrolyte parameter determining the breakdown voltage [216]. At constant resistivity, increasing the anion concentration or the electrolyte pH decreases the breakdown voltage, as illustrated on Figure 2.30. Finally it should be mentioned that the addition of thiourea in an ammonium pentaborate electrolyte has been reported to increase the type-II breakdown voltage of anodic alumina [217].

In conclusion the influence of the electrolyte on the breakdown voltage seems to be more complex than the simple logarithmic dependence of the breakdown voltage on the resistivity.

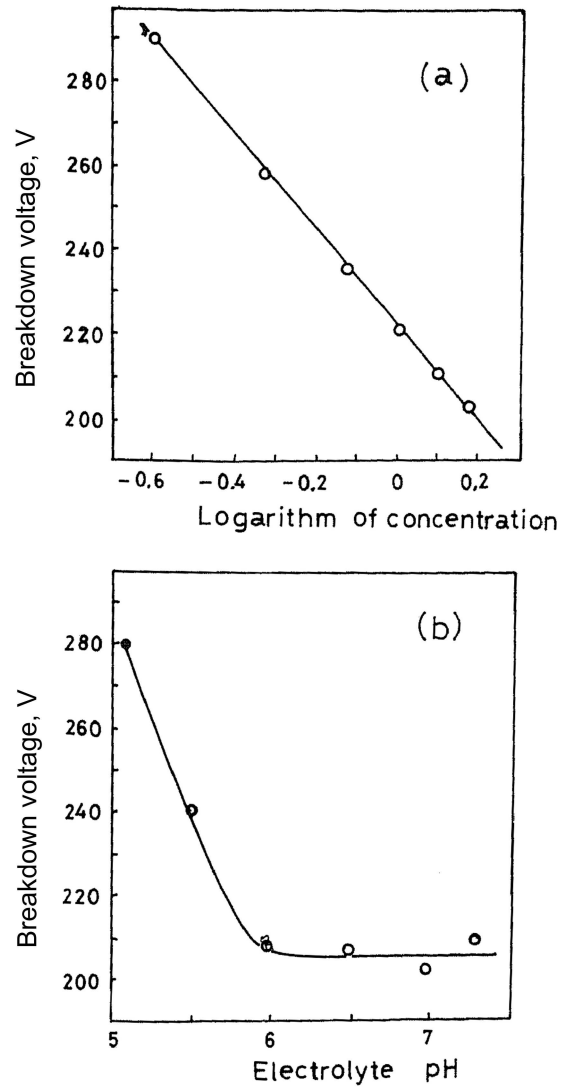


Figure 2.30: Dependence of type-II breakdown voltage on (a) the anion concentration in the electrolyte and (b) the electrolyte pH, at constant electrolyte resistivity for aluminum anodizing in various ammonium adipate solutions. Reproduced from references 181, 216.

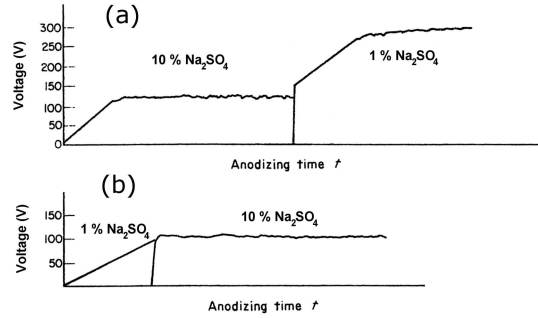


Figure 2.31: Voltage evolution for duplex tantalum anodizing at 25 mA cm^{-2} in (a) 10 % Na_2SO_4 electrolyte and then in 1 % Na_2SO_4 and (b) in 1 % Na_2SO_4 and then 10 % Na_2SO_4 . Adapted from reference 218.

Influence of other factors

The effect of other anodizing parameters on breakdown has been studied as well. For instance, type-II breakdown is relatively unaffected by the history of the film. If a valve metal is anodized in solution A until the breakdown voltage U_A , and the sample is then re-anodized in solution B in which the breakdown voltage is larger than in solution A ($U_A < U_B$), the voltage starts increasing again at a constant rate from U_A to U_B at which breakdown occurs [41,218,219]. This is illustrated on Figure 2.31 for tantalum anodizing at 25 mA cm^{-2} in Na_2SO_4 .

The anodizing temperature has also been reported to have a negligible effect on the type-II breakdown voltage [213,216,220]. However, it should be acknowledged that a change in the anodizing temperature is likely to modify both the properties of the electrolyte (for instance, by modifying the resistivity of the electrolyte) and the properties of the anodic oxide (for instance, by modifying the electric field strength). Therefore, it is not excluded that the absence of an apparent influence of the temperature on breakdown is due to self-canceling modifications in more fundamental properties.

Among other parameters, electrolyte stirring rate and anodizing interruptions have been reported not to affect type-II breakdown [66,179]. Such experiments have been conducted to allow dissipating heat in the

oxide, hence confirming that a uniform oxide temperature increase is not the origin of breakdown.

2.4.4 Models for the breakdown of anodic oxide films

Stress-driven breakdown models

Sato derived a model to explain the breakdown of passivity of anodic films, accounting for the role of internal stress in the passive film [221]. Although the applicability of such a model to growing, thick anodic oxide films is questionable, we briefly present it here. According to Sato, the film “pressure” or mean normal stress in the film p , considering electrostriction and surface tension, is equal to:

$$p = p_0 + \frac{\varepsilon(\varepsilon - 1)E^2}{8\pi} - \frac{\gamma}{h_{ox}} \quad (2.34)$$

where p_0 is the atmospheric pressure, ε is the oxide permittivity, and γ is the surface tension.

Although very small film thicknesses (< 0.5 nm) were not explicitly considered, it is obvious that in this model, the stress in the film increases with increasing oxide thickness. Hence, if a critical stress for breakdown exists, which should be lower than the first term in Equation (2.34), the increasing thickness of the oxide film finally leads to breakdown.

However, this model is contradicted by several experimental observations. Firstly, typical orders of magnitude for the first term (≈ 100 MPa) and surface tension (≈ 1 J m⁻²) are such that the calculated hydrostatic stress in the film is very large at low film thickness, and should even be larger than the stress attained at higher thicknesses, which supposedly lead to breakdown. Secondly, the film pressure does not change much once the film thickness becomes larger than about 20 nm, which is in contradiction with typical breakdown thicknesses of several hundreds of nanometers. Thirdly, it is well known that the contribution of electrostatic forces to the stress in anodic oxide films are usually small compared to the contribution of intrinsic stresses (see section 2.2.5).

Di Quarto *et al.* also suggested that internal stress in growing anodic oxide films on zirconium and tungsten could be larger than some critical value, leading to type-I breakdown of the oxide film [172, 178]. One of the hypotheses of this model is that the internal stress in the

oxide builds up with increasing oxide thickness. Aware of the fact that the average internal stress in anodic zirconia had been measured to be roughly independent of thickness, Di Quarto *et al.* further suggested that stress is not homogeneously distributed over the film thickness.

Electron avalanche model of Ikonopisov

Ikonopisov inferred that because the type-II breakdown voltage mainly depends on the nature of the anodized metal and the resistivity of the electrolyte, breakdown is controlled by electrochemical reactions at the oxide/electrolyte interface and depends on the solid-state properties of the oxide. He further assumed type-II breakdown to be similar to the breakdown of dry semiconductors, in that it is due to avalanche breakdown in the film.

While in the case of dry semiconductors the initial current originates from the cathode, in the case of type-II breakdown, the initial electrons would be injected into the film from the electrolyte [185]. The electronic current j_e then depends on the coordinate along the oxide thickness x , $x = 0$ being the oxide/electrolyte interface. The electronic current is maximum at the metal/oxide interface:

$$j_e(x = h_{ox}) = j_e(x = 0) \exp(reEh_{ox}/\xi_m) \quad (2.35)$$

where $r < 1$ is a constant, e is the electron charge, E is the electric field, and ξ_m is the threshold energy for impact ionization. Ikonopisov assumed that breakdown occurs if the electronic current exceeds a critical value $j_{e,B}$. Thus breakdown occurs if the oxide reaches a thickness $h_{ox,B}$ for which $j_e(h_{ox,B}) = j_{e,B}$. Since $U_B = E h_{ox,B}$, one obtains:

$$U_B = (\xi_m/re)(\ln j_{e,B} - \ln j_e(x = 0)) \quad (2.36)$$

Ikonopisov determined, at low electric fields, the dependence of $j_e(x = 0)$ on the electric field, temperature, and electrolyte resistivity ρ_e . The following expressions were obtained:

$$j_e(x = 0) = \alpha_1 \exp(\alpha_2 E^{1/2}) \quad (2.37)$$

$$\ln j_e(x = 0) \approx \beta_1/T + \beta_2 \quad (2.38)$$

$$j_e(x = 0) = \gamma_1 \rho_e^{-\gamma_2} \quad (2.39)$$

2. State of the art

Substituting Eq. (2.37) into Eq. (2.36) yields the following dependence of the electric breakdown voltage on electric field:

$$U_B = \frac{\xi_m}{re} (\ln j_{e,B} - \ln \alpha_1) - \frac{\xi_m}{re} \sqrt{E} \quad (2.40)$$

According to Ikonopisov, since the electric field increases weakly with current density, this equation accounts for the moderate decrease of U_B with increasing current density. Regarding the predicted evolution of the breakdown voltage with temperature, the following expression is obtained:

$$U_B \approx \frac{\xi_m}{re} (\ln j_{e,B} - \beta_1/T - \beta_2) \quad (2.41)$$

Thus the predicted breakdown voltage should depend on the electrolyte temperature, which contradicts experiments. However, Ikonopisov suggested that a temperature change should also modify the electrolyte conductivity, and the effect of temperature is thus more complicated to predict. Finally, the dependence of the breakdown voltage on the electrolyte resistivity is obtained:

$$U_B = \frac{\xi_m}{re} (\ln j_{e,B} - \ln \gamma_1 + \gamma_2 \ln \rho_e) \quad (2.42)$$

which is in agreement with the empirical relationship between breakdown voltage and electrolyte resistivity, Eq. (2.33).

This model has, however, been criticized by several investigators. The first concern is that during galvanostatic experiments, the total current density j should be equal to $j = j_i + j_e(x=0)$ where j_i is the ionic current density, which is used for oxide growth. Therefore, an increase of j_e with the oxide thickness should eventually decrease the oxide growth rate [181]. This concern might be unjustified since the predicted growth rate decrease would actually explain the maximum voltage and thickness that can be attained before breakdown occurs.

The second concern raised about Ikonopisov's model concerns the unrealistic value obtained for the coefficient ξ_m/re , which can be extracted by comparing Eq. (2.33) with Eq. (2.42). According to Shimizu, the mean free path of ionized electrons in the avalanche would be about 500 nm [222]. This value being of the same order of magnitude as the thickness of the anodic oxide film when breakdown occurs, it is unlikely

that any electron avalanche actually occurs. Hence, Shimizu concludes that Ikonopisov's model must be rejected.

Finally, although the theory of an electron avalanche would explain well the different experimental facts regarding breakdown, the origin of the electrons in Ikonopisov's model remains questionable according to Albella *et al.* [223]. In Ikonopisov's model, the electrons are injected from the electrolyte into the oxide conduction band by either a Fowler-Nordheim or Schottky mechanism. However, unless some specific (undisclosed) electrochemical reaction occurs, the electron injection properties of the electrolyte seems questionable [223].

Electron avalanche model of Albella *et al.*

In their model, Albella *et al.* assume that the electronic current in the oxide which leads to an electron avalanche actually originates from the species incorporated in the electrolyte. The latter act themselves as donor levels in the oxide energy gap, releasing electrons to the conduction band as a result of the strong electric field [41, 224, 225]. In their model, the total current density applied, j , consists of three terms:

$$j = j_1 + j_2 + j_e \quad (2.43)$$

where j_1 is the oxidation current, j_2 is the current density consumed by the electrolyte species incorporation, and j_e is the electronic current. j_2 is further assumed to be a fixed ratio of the oxidation current, i.e. $j_2 = \gamma_3 j_1$ with γ_3 a constant. Similarly to Ikonopisov's model, $j_e = j_{e,0} \exp(\alpha_3 x)$ with $j_{e,0}$ the primary electronic current density, α_3 the impact ionization coefficient and x the oxide thickness. Since the primary electronic current originates from incorporated species, $j_{e,0} = \gamma_4 j_2$ with γ_4 , a constant. Furthermore, the derivative of the voltage evolution, dV/dt is equal to:

$$\frac{dV}{dt} = \frac{1}{\rho_{ox}} \frac{E}{F} \left(\frac{M_1}{x_1 y_1} + \frac{M_2}{x_2 y_2} \right) \quad (2.44)$$

where ρ_{ox} is the oxide density, and M_1 and M_2 are the molecular weights of the oxide and the incorporated species respectively, while their corresponding anion and cation valences are x_1, y_1 and x_2, y_2 . Combining Eq. (2.44) with Eq. (2.43) and the above expressions for the current

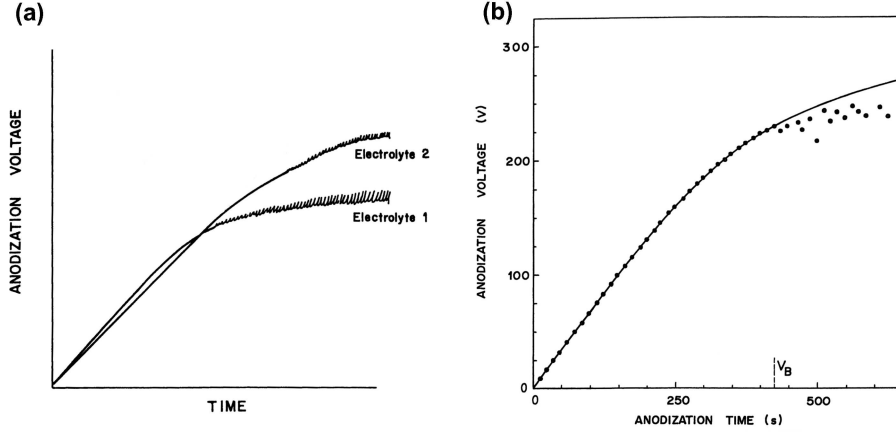


Figure 2.32: (a) Predicted voltage evolution for anodizing in an electrolyte with high anion incorporation (electrolyte 1) and low anion incorporation (electrolyte 2: $\gamma_{3,2} > \gamma_{3,1}$). (b) experimental and theoretical voltage evolution for tantalum anodizing in $1.2 \text{ mol l}^{-1} \text{ H}_3\text{PO}_4$. Reproduced from references 41, 225.

densities yields:

$$\frac{dV}{dt} = \frac{M_1 E}{x_1 y_1 \rho_{ox} F} j \frac{1 + (M_2 x_1 y_1) / (M_1 x_2 y_2) \gamma_3}{1 + \gamma_3 + \gamma_3 \gamma_4 \exp(\alpha_3 (AR) V)} \quad (2.45)$$

Assuming a constant field in the oxide, the integration of Eq. (2.45) yields:

$$V(t) = \frac{1 + A\gamma_3}{1 + \gamma_3} K j t - \frac{\gamma_3 \gamma_4}{1 + \gamma_3} \frac{E}{\alpha_3} (\exp(\alpha_3 V / E) - 1) \quad (2.46)$$

which according to Albella *et al.* is consistent with experimental data for tantalum anodizing, in which a gradual decrease of dV/dt is observed (see Figure 2.32).

The condition for breakdown is that the electronic current density reaches a certain fraction of the oxidation current density $j_e = \gamma_5 j_1$. Thus, the breakdown voltage V_B is given by [41]:

$$V_B = \frac{E}{\alpha_3} \ln \left(\frac{\gamma_5}{\gamma_3 \gamma_4} \right) \quad (2.47)$$

By fitting Eq. (2.46) on experimental voltage evolutions obtained in different electrolyte concentrations, an empirical relationship between γ and electrolyte concentration C was found:

$$\gamma_3 \approx aC^b \quad (2.48)$$

with a and b electrolyte dependent constants. Combining Eqs. (2.46) and (2.48) yields:

$$V_B \approx \frac{E}{\alpha_3} \left(\ln \left(\frac{\gamma^5}{\eta a} \right) - b \ln C \right) \quad (2.49)$$

which agrees with the experimental dependence of the breakdown voltage on the electrolyte concentration (or resistivity).

Although no criticism of this model has been found in the literature, a few discrepancies have been identified. One of these is that in the above calculation of the voltage evolution, a constant electric field was assumed. However, it is clear from the high-field model that if the ionic current density decreases as a result of an increase of the electronic current, the electric field will decrease as well. This effect is significant if the electronic current is comparable to the ionic current, as seems to be the case [226].

It also remains an open question if electron avalanche really occurs in anodic oxide films. As we have seen in section 2.4.2, the luminescence during the growth of anodic oxide films, which increases with increasing film thickness, has usually been taken as evidence that electron avalanche occurs in anodic oxide films. However, no luminescence occurs during the growth of anodic alumina on pure electropolished substrates, although breakdown terminates regular film growth for such anodic oxide films [173]. In fact, in the latter case, a large luminescence intensity has been measured after breakdown occurred [173].

2.5 Summary

In this chapter, technologically important applications using anodic oxide films were presented first. The growth of porous anodic oxide films, and the breakdown of anodic oxide films were identified as two processes of which an understanding could lead to major technological improvements for the surface treatment of aluminum and its alloys, nanotechnol-

2. State of the art

ogy applications, electrolytic capacitors, and to improve our understanding of high-temperature corrosion of zirconium and zirconium alloys.

The growth mechanisms of dense anodic oxide films were then presented. The rationale used to calculate the anodic oxide film thickness from the measured electrochemical variables was developed. Some of the growth peculiarities of dense anodic oxide film growth, potentially playing a role on the subsequent pore formation, or breakdown of anodic oxide films were also presented.

The current understanding of, on the one hand, pore nucleation and growth and, on the other hand, of breakdown processes in anodic oxide films was then presented. The dependence of the porous anodic film morphology and breakdown occurrence on the anodizing conditions were described. The state-of-the art models describing these dependencies were presented. We will later see how this thesis challenges these models and elucidates some of these experimental dependences.

As we have seen, internal stress has been proposed by some investigators to be a key factor both for pore nucleation and growth, as for breakdown. Whether or not this is the case will now be confronted experimentally with our *in situ* internal stress measurements during porous anodizing of aluminum and the breakdown of anodic zirconia.

Chapter 3

Experimental methods

In this chapter, the experimental methods used in this thesis are presented. We present the sample preparation details, describe the anodizing procedure, and provide the details of the *ex situ* characterization techniques used.

3.1 Sample preparation procedure

In this section, the sample preparation procedure relative to the use of a multi-beam optical sensor during thin film anodizing is described. Several constraints had to be taken into account when designing this experimental setup. Some constraints are related to the anodizing process itself, while others are imposed by the curvature measurement technique.

First of all, the experimental setup had to allow for optical access to the anode and the latter had to exhibit sufficient reflectivity. In order for anodizing to result in a curvature change, the sample had to have one single active surface only. As anodizing is intrinsically an irreversible process, the anode samples are single-use. Therefore, the experimental setup had to allow for easy replacement and reproducible positioning of the anode. The latter also had to be clamped at one end in order to achieve a cantilevered beam configuration, and be entirely immersed in the electrolyte up to the clamping point during anodizing. Finally, the whole experimental setup had to be massive enough to ensure mechanical stability.

Considering all requirements described above, the following configu-

3. Experimental methods

ration was selected:

1. Double-side polished silicon wafers, 380, 350, 250, or 180 μm thick, were used as substrate for the thin film anodes. Prior to the metalization step, a 400 to 600 nm thick SiO_2 layer was grown on both sides of the Si wafer by a wet oxidation process. This layer insulates the silicon from the electrolyte and the metallic layer in order to prevent leakage currents through the substrate during the anodizing.
2. A thin valve metal film, 200 to 1000 nm thick, was deposited on one face of the oxidized Si wafers. Metalization was carried out either by sputtering or by electron-beam evaporation. For sputtering, the pressure in the deposition chamber prior to sputtering was at most 4.7×10^{-5} Pa. For electron-beam evaporation, the pressure was typically 2.7×10^{-5} Pa. A summary of the different metallic films deposited is provided in Table 3.1.
3. The metalized wafers were then diced to make rectangular samples, approximately $5 \times 45 \text{ mm}^2$ in size. The wafer processing procedure is illustrated on Figure 3.1.
4. A small aluminum block ($4 \times 5 \times 6 \text{ mm}^3$) was glued on the metal layer on one end of the electrode using silver paste in order to provide electrical contact, as illustrated step-by-step on Figures 3.2(a)–(c).
5. It was found that, in some cases, the anodizing behavior of the metal, typically characterized by its cell voltage evolution, was different from the expected behavior. This was attributed to an electrical short-circuit between the metal and the silicon exposed by dicing. Therefore, in those problematic cases, an acetone lift-off was performed after the metalization to remove the metal from the parts of the wafer where the dicing was subsequently performed, as illustrated in Figure 3.3.
6. The end of the electrode with the attached aluminum contact was then clamped in Epofix resin cast in a Teflon mold. This is illustrated step-by-step on Figures 3.2(d), 3.2(e), 3.2(f), 3.4(a), 3.4(b) and 3.4(c). Specific two-part molds were fabricated, which allowed

Table 3.1: Summary of the characteristics of the deposited metallic films used in this thesis.

metal	deposition method	laboratory	composition (RBS)	thickness (nm)	internal stress in metal (MPa) ^a
Al (batch 1)	e-beam evaporation	Winfab (UCL)	Al	800	0
Al (batch 2)	e-beam evaporation	Winfab (UCL)	Al	800	-112
Al(Si, Cu)	sputtering	Winfab (UCL)	Al-1wt.%Si-0.7wt.%Cu	600	-220
Zr (batch 1)	sputtering	LARN (FUNDP)	-	235	-80
Zr (batch 2)	sputtering	LARN (FUNDP)	-	440	-40

^aFurther details on the measurement of the internal stress in the deposited metal are provided in section 4.2.

3. Experimental methods

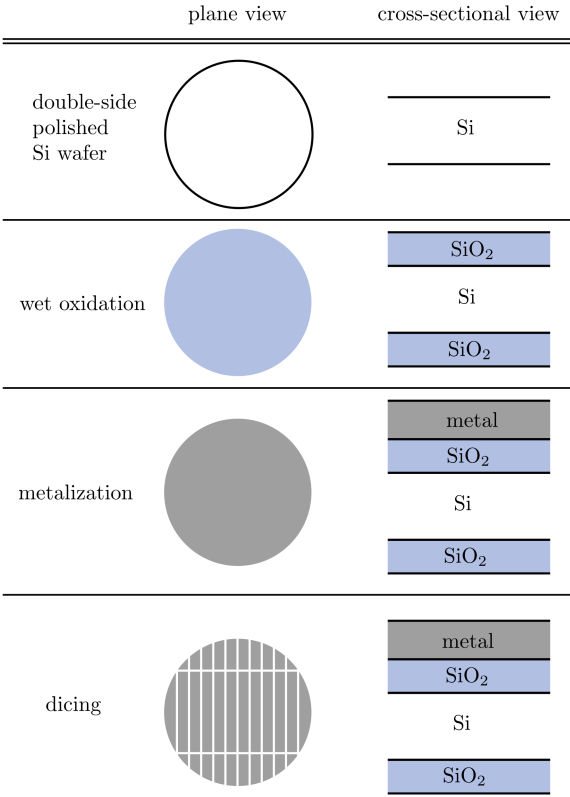


Figure 3.1: Illustration of the as-received silicon wafer sample preparation procedure.

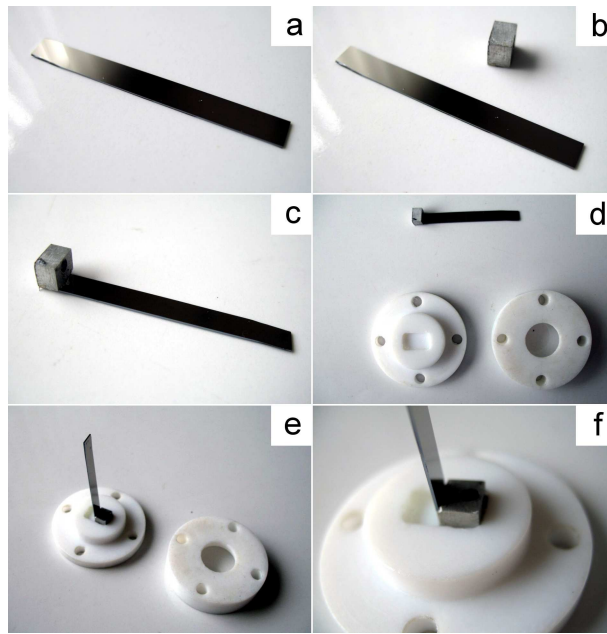


Figure 3.2: Illustration of the sample preparation procedure. Images *a* to *d* show the placement of the electrical contact on the sample. Images *e* and *f* show the placement of the sample in the Teflon moulds. Reproduced from [227].

3. Experimental methods

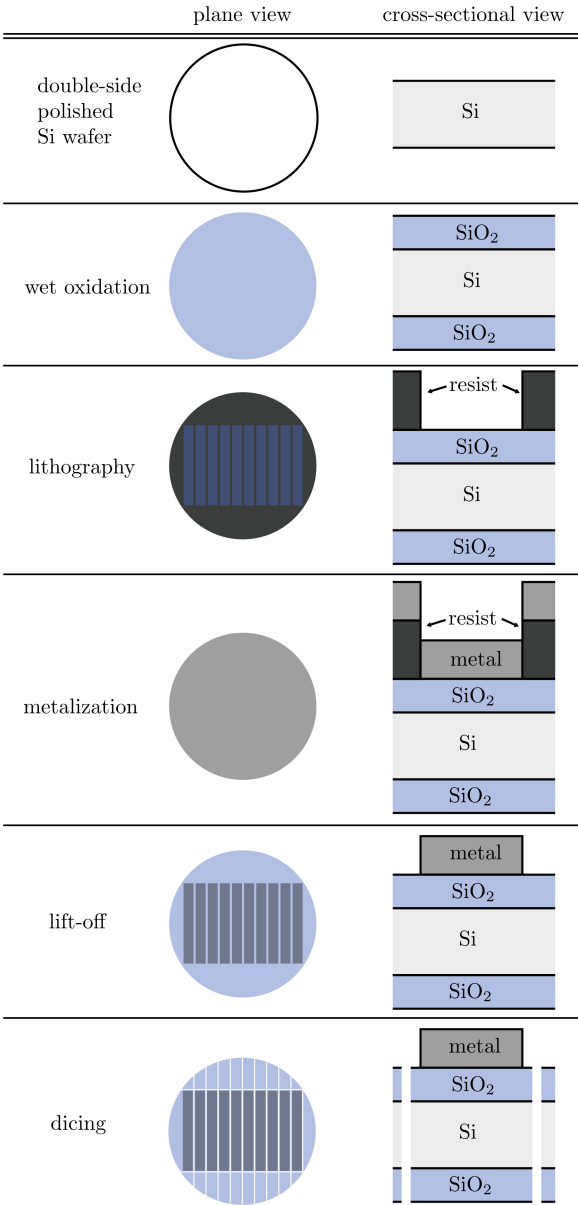


Figure 3.3: Illustration of the as-received silicon wafer sample preparation procedure when dicing is performed on non-metalized surfaces.

for easy sample preparation, reproducible sample positioning and complete insulation of the electrical contact.

7. When the resin had dried, the two parts of the mold were separated (Fig. 3.4(d) and 3.4(e)), the cantilevered sample being attached to the upper part. A hole was drilled in the aluminum block from the back of the sample to allow for connection to the power source using a banana plug (Fig. 3.4(f)).
8. The upper part of the Teflon mold containing the cantilevered anode was attached to a stainless steel sample holder using nylon screws, as illustrated on Figure 3.5(a) and 3.5(b).
9. The position of the laser source was then adjusted in order to achieve normal incidence of the laser beams on the sample surface, because in such conditions, the error on the curvature is small (see chapter 4). The array of beams was positioned parallel to the sample length in the center of the sample width.
10. After the experiment, the anode sample was cleaved at the point of anchoring in order to detach the sample from the resin block and save it for further *ex situ* characterization. The resin block could be withdrawn from the mold so that the molds were completely reusable. The Al contacts were easily recovered as well by fracturing the resin block. The spacing between the incident laser beams was then measured by measuring the spot spacings reflecting on a flat dielectric mirror in air. The length of the optical path between the sample and the CCD was also determined, by measuring the spacings reflecting on mirrors of 4 and 20 m radii of curvature. As we will see in the next chapter, both the incident spots spacings and optical path length must be known to calculate the sample curvature from the measured evolution of the reflected laser beam spacings.

3.2 *In situ* curvature monitoring during anodizing

Anodizing was carried out in an optical glass cell (Hellma), with a titanium plate as a cathode. For current supply and cell voltage monitor-

3. Experimental methods

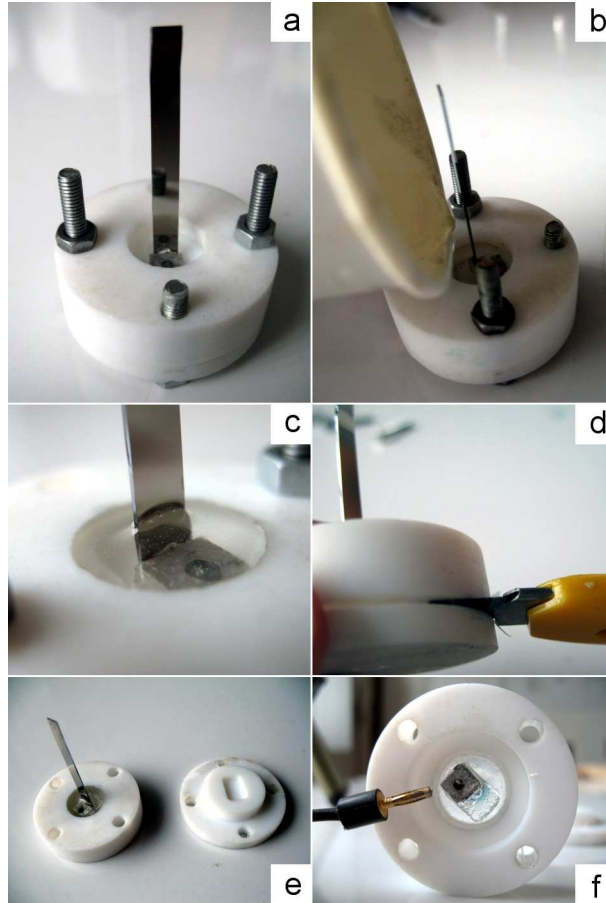


Figure 3.4: Illustration of the sample preparation procedure. Images *a* to *e* show the clamping of the lower end of the sample in epoxy resin. Image *f* shows the banana plug used to connect the sample to the power source. Reproduced from [227].

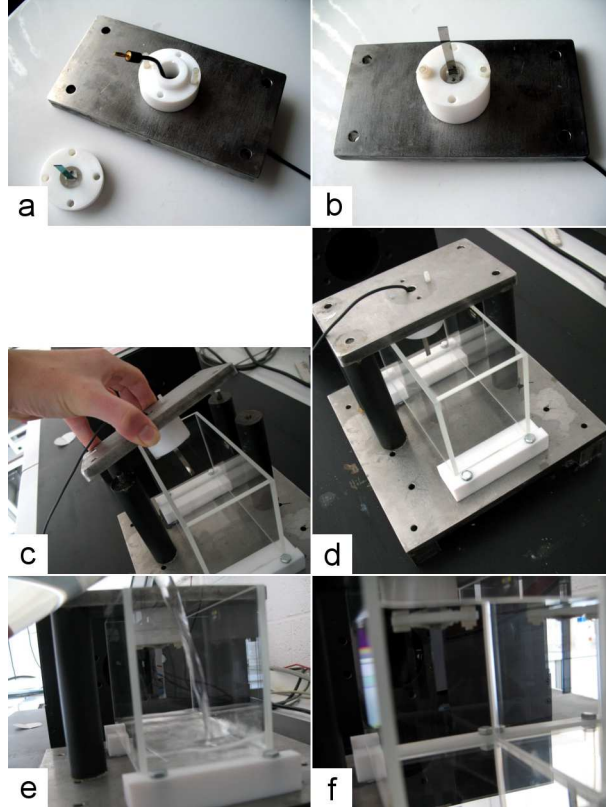


Figure 3.5: Illustration of the sample placement in the electrochemical cell. The sample is at first attached to a stainless-steel sample holder (pictures *a* and *b*). The latter is then secured to a fixed structure allowing for reproducible positioning with respect to the cell (pictures *c* and *d*). When the cell is filled with electrolyte, the sample is completely immersed up to the anchoring point (pictures *e* and *f*). Reproduced from [227].

3. Experimental methods

ing, a Keithley 2400 SourceMeter was used. A 2-electrodes setup was systematically used, and all the anodizing experiments were performed galvanostatically at current densities ranging from 0.5 to 21 mA cm⁻².

The volume of electrolyte was 500 ml. The electrolyte was filtered because it reduced the occurrence of optical perturbations during the curvature measurements. All the solutions were prepared from analytical grade reagents and twice-deionized water (resistivity higher than 18 MΩ cm). The electrolyte solutions used were 0.05 or 1 mol l⁻¹ sulfuric acid, 0.4 mol l⁻¹ phosphoric acid, or 0.01 mol l⁻¹ ammonium pentaborate. All the anodizing experiments were performed at room temperature.

A schematic of the entire experimental setup is shown in Figure 3.6. An horizontal configuration was selected, with a vertically aligned cantilever, in order to avoid possible oxygen accumulation on the anode. The MOS housing, to which all optical components were fixed, and the sample holder were attached to a steel plate. All parts, except the cell, were mechanically attached with stainless steel screws to ensure stability of the setup and robustness towards vibrations. The optical distance between the sample and the detector was about 80 cm. A PMMA box shield was used in order to reduce convection-induced perturbations of the laser beams. The sample holder, the electrochemical cell and the sample placement into the liquid containing cell are shown on Figure 3.5(c) - 3.5(f).

3.3 *Ex situ* characterization methods

In this section, the general experimental details of the *ex situ* characterization of our anodic oxide films are presented.

3.3.1 Scanning electron microscopy

Films surfaces and cross-sections were examined by scanning electron microscopy. Field-emission-gun equipped microscopes allowed examining the films without depositing a conductive coating on them, avoiding any possible artifacts. Cross-sections were prepared by propagating cracks through the silicon substrate. In areas where the crack is self propagating, the fracture planes are smooth and the morphology of the film is not affected. Two microscopes were used, a Leo 982 FEG-SEM and a

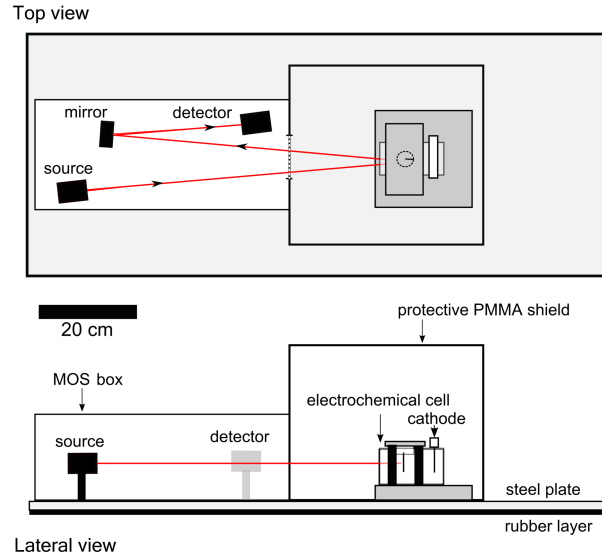


Figure 3.6: Schematic representation of our curvature measurement setup. Reproduced from [227].

Jeol Ultra55. The energy of the electron-beam was usually in the range 0.5 to 3 keV to avoid charging the oxide films.

Morphological data, such as film thicknesses, or pore spacings were measured on cross sectional micrographs. In the latter case, better results were obtained when measuring pore spacings from cross sectional micrographs than surface micrographs. The error bars reported on these morphological data represent the spread in data obtained at different locations on the samples.

3.3.2 Transmission electron microscopy

The crystalline structure of zirconium oxide films was determined by electron diffraction in a transmission electron microscope (TEM). In-plane freestanding oxide samples were prepared by chemical dissolution of the zirconium metal. Samples were first glued on copper grids with epoxy resin. A 10:45:45 mixture (volume ratio) of hydrofluoric acid:isopropyl alcohol:water was then used to separate the oxide films from their substrate [25]. The oxides were examined in a Leo 922 TEM,

3. Experimental methods

operating at 200 kV and equipped with a Köhler illuminator, ensuring minimal sample exposure to the electron beam in order to avoid any structural modification inside the TEM. Diffraction patterns corresponding to a sample surface of $1.13\text{ }\mu\text{m}^2$ were analyzed quantitatively using ProcessDiffraction software, allowing for an averaged radial representation of the diffraction intensities [228].

3.3.3 Atomic force microscopy

Atomic force microscopy was performed in tapping mode using high resolution silicon probes, with cantilevers having a free resonant frequency of 70 kHz and integrated tips with a specified apex radius of 2 nm and an aspect ratio of at least 4:1. In some specific cases, the lengthscales associated with an image were determined by calculating the radial power spectral density (PSD) for a given sample. This was done by first acquiring images of different scales, usually 0.1×0.1 , 0.3×0.3 , 1×1 and $3 \times 3\text{ }\mu\text{m}^2$, and the PSD was calculated on the entire analyzed scale range by merging the radially averaged PSDs calculated from the individual images [229]. The length scales associated with the spatial frequencies at which the correlation breaks occur were then calculated by performing a parametric fit of the PSD curve with a correlation function proposed by Palasantzas [230].

3.3.4 Chemical analysis of the solutions

Chemical analysis was used on the one hand to calculate the thickness of metal deposited for specific batches, after dissolving the metallic layer. On the other hand, it allowed quantifying the amount of cations ending in the electrolyte as a result of anodizing. The aluminum and zirconium ionic content of electrolytes were measured by inductively coupled plasma optical emission spectrometry (ICP-OES). Regarding zirconium anodizing, electrolytes were analyzed with a Varian 720-ES ICP-OES. The measurements were calibrated with solutions of 1, 3, 5, 10, 15 and $20\text{ }\mu\text{g l}^{-1}$ of Zr^{4+} . Only the signals provided by the 256.9 nm and the 257.1 nm emission wavelengths were used, because these gave the most sensitive signal at such small concentrations. The signals were recorded for about 200 seconds for each solution, and then averaged. Reported error bars correspond to the standard deviation of these average values.

For aluminum, the 167.0 nm emission wavelength was generally used, because of its higher sensitivity in the concentration range investigated.

3.4 Conclusion

To conclude, we have shown in this chapter the details of our sample preparation technique to measure the internal stress *in situ* during anodizing, described the setup used for curvature monitoring during thin film anodizing and provided the details of the characterization methods used.

Chapter 4

Measuring the internal stress during anodizing

In this chapter, we first show how the internal stress in a thin film can be calculated by measuring the curvature of the substrate to which it is attached. The validity of Stoney's equation, which relates the curvature and the internal stress in the film is discussed with respect to our specific sample geometry. We then show how Stoney's equation allows to calculate the internal stress in our anodic oxide films, if the internal stress in the deposited metal is known. Finally, we develop a constitutive equation to measure the curvature of a sample in a liquid with the multi-beam optical sensor.

4.1 Stoney equation

A thin film on a rigid substrate generally has a non-negligible amount of internal stress, due to its constrained volume change. When the film wants to expand (contract), but cannot because it is constrained by the substrate to which it is attached, the film is in compression (tension). Several experimental techniques have been developed to measure internal stresses present in thin films, starting as early as 1909, when Stoney developed a curvature-based technique to measure the stress in electrodeposited coatings [231]. This approach, which relies on measuring the stress-induced change in the curvature of an elastic substrate on which the thin film is growing, is very popular. Since 1909, several other

4. Measuring the internal stress during anodizing

approaches have nevertheless been used for measuring the stress in a thin film [232]. Another popular approach consists in measuring the changes in the lattice constants of the material from the shifting of peaks of X-ray or electron diffraction patterns [233]. Another new approach consists in measuring the deformation of micromachined structures [234].

The curvature measurement approach has the advantage of being easily performed *in situ* with a variety of systems, which is not necessarily straightforward with diffraction-based techniques. Moreover, the fact that the curvature can be directly converted into stress using Stoney's equation [231] — as long as a few requirements are met — is another asset of curvature-based methods. More rigorous versions of Stoney's equation are now available to accurately obtain the internal stress from curvature in “non-ideal” conditions, for instance, when the curvature is large [235], or the substrate is thin [236].

Stoney equation, which was originally derived in 1909 [231] has been re-demonstrated by numerous investigators, who progressively refined the necessary assumptions for this equation to be valid. Stoney's equation is usually written in the following form [237]:

$$\langle \sigma_f \rangle h_f = \frac{Y_s h_s^2}{6} \kappa \quad (4.1)$$

where $\langle \sigma_f \rangle$ and h_f are, respectively, the mean stress and thickness of the film, $Y_s = E_s/(1 - \nu_s)$ and h_s are, respectively, the biaxial modulus and thickness of the substrate (with E_s and ν_s the Young modulus and Poisson ratio), and κ is the sample curvature, which is equal to the inverse of the radius of curvature of the sample.

The following assumptions are made to obtain the equation ; these are further related to our experimental setup:

- The thickness of the substrate h_s to which the film is attached must be much larger than the thickness of the film h_f [238]. How large the thickness of the substrate must be depends on the biaxial modulus of the film compared to the modulus of the substrate. A ratio of h_f/h_s smaller than 1% ensures Stoney's equation is accurate, with less than 5% error over a wide range of moduli ratio [236, 239]. In our experiments, in the most unfavorable case, the substrates were 180 μm -thick, the film thickness being 650 nm. The ratio is then equal to 0.4 %: the thin film hypothesis is satisfied in this thesis.

- When using clamped cantilevers, the length of the cantilever L should be greater than its width b . When L/b is greater than 3, the error associated with the use of Stoney's equation is lower than 0.1 % [240]. Our samples being typically $5 \times 35 \text{ mm}^2$ in dimension, this condition is satisfied.
- The curvature of the substrate must be small. Above a critical curvature, the substrate does not deform isotropically anymore. The accuracy of Stoney's equation is better than 95 % if $\kappa < 2.2h_s/b$ [232]. In the most unfavorable case in our experiments, h_s was equal to $180 \mu\text{m}$ and b was equal to 5 mm . In that case, the largest measured curvature being $600 \text{ km}^{-1} < 15\,800 \text{ km}^{-1}$, the curvature is biaxial.
- The curvature must be measured far enough from the edges of the sample, including the clamp, otherwise, shear stresses in the film may come into play, and Stoney's equation is not valid. It is generally accepted that only a region approximately 5 times the sample thickness is affected near the substrate edges [241]. In our setup, the curvature is measured at about 2 mm from the sample edges, thus, even with our thickest $380 \mu\text{m}$ substrates, this is not expected to be an issue.
- The substrate must be homogeneous, isotropic and linear elastic. In our experiments, the substrates consisted of (100) Si, thus satisfying the isotropic and homogeneity assumptions. Furthermore, the stress induced in the substrate by the film, σ_s , is equal to $-3h_f/h_s\sigma_f$ [242]. During our experiments, the maximum measured stress was -2 GPa , in a film about 600 nm -thick, with a substrate $180 \mu\text{m}$ -thick. In that case, the stress induced by the bending is equal to 20 MPa , and the substrate deforms elastically.

4.2 Modified Stoney equation for anodizing

In the experiments performed during this thesis, a metallic thin film was deposited on the silicon wafers prior to anodizing. As a result of the deposition, such a film may be stressed. In that case, during anodizing, the curvature change of the sample comes from two distinct contributions. The first contribution comes from the increasing thickness of the

4. Measuring the internal stress during anodizing

stressed anodic oxide film, while the second comes from the decreasing thickness of the stressed metallic film which is being oxidized. Since as long as each film satisfies the assumption of Stoney's equation, which is the case here, the Stoney equation for the multilayer consisting of a thick substrate (subscript "s"), a metallic film (subscript "M") and an oxide (subscript "ox") is written:

$$\langle \sigma_{ox} \rangle h_{ox} + \langle \sigma_M \rangle h_M = \frac{Y_s h_s^2}{6} \kappa \quad (4.2)$$

with $\langle \sigma_i \rangle$, h_i , Y_s and κ the mean stress in the i^{th} layer, the thickness of the i^{th} layer, and the biaxial modulus of the substrate and the substrate curvature, respectively [239,242]. The derivative of Eq. (4.2) with respect to the oxide thickness h_{ox} is:

$$\frac{d\langle \sigma_{ox} \rangle}{dh_{ox}} h_{ox} + \langle \sigma_{ox} \rangle + \frac{d\langle \sigma_M \rangle}{dh_{ox}} h_M + \langle \sigma_M \rangle \frac{dh_M}{dh_{ox}} = \frac{Y_s h_s^2}{6} \frac{d\kappa}{dh_{ox}} \quad (4.3)$$

which is equal to:

$$\frac{d\langle \sigma_{ox} \rangle}{dh_{ox}} h_{ox} + \langle \sigma_{ox} \rangle + \frac{dh_M}{dh_{ox}} \left(\frac{d\langle \sigma_M \rangle}{dh_M} h_M + \langle \sigma_M \rangle \right) = \frac{Y_s h_s^2}{6} \frac{d\kappa}{dh_{ox}} \quad (4.4)$$

The mean stress in the i^{th} layer is, by definition, equal to:

$$\langle \sigma_i \rangle \equiv \frac{1}{h_i} \int_0^{h_i} \sigma_i dx \quad (4.5)$$

or equivalently:

$$\sigma_i = \frac{d\langle \sigma_i \rangle}{dh_i} h_i + \langle \sigma_i \rangle \quad (4.6)$$

with σ_i the incremental stress associated with an infinitesimal thickness change [243].

Combining Equations (4.4) and (4.6) then yields:

$$\sigma_{ox} + \frac{dh_M}{dh_{ox}} \sigma_M = \frac{Y_s h_s^2}{6} \frac{d\kappa}{dh_{ox}} \quad (4.7)$$

Dividing Equations (1.18) and (1.20) allows to obtain the following expression for the proportionality factor between metal and oxide thickness rate of change:

$$\frac{dh_M}{dh_{ox}} = \frac{-1}{\eta_a} \frac{M_M}{M_{ox}} \frac{\rho_{ox} z_{ox}}{\rho_M z_M} \equiv -(PBR) \quad (4.8)$$

where η_a , M , ρ , z_M and z_{ox} are the anodizing efficiency, the molecular weight, the density, the number of electrons per oxidized metal atom and the number of electrons per oxide stoichiometric unit, respectively. PBR is the Pilling-Bedworth ratio.

By combining Equations (4.7) and (4.8), the incremental internal stress in the oxide σ_{ox} can be calculated from the derivative of the curvature with respect to the oxide thickness:

$$\sigma_{ox} = \frac{Y_s h_s^2}{6} \frac{d\kappa}{dh_{ox}} + (PBR)\sigma_M \quad (4.9)$$

Instantaneous internal stress changes in the oxide can therefore be detected by slope changes in plots of $\frac{Y_s h_s^2}{6} \Delta\kappa$ versus oxide thickness if PBR and σ_M do not change. We define $\Delta\kappa \equiv \kappa - \kappa_0$, with κ_0 the curvature of the sample before anodizing starts (calculated by averaging the curvature during 25 s prior to anodizing). We also define the stress-thickness product:

$$\text{Stress-thickness product} \equiv \frac{Y_s h_s^2}{6} \Delta\kappa \quad (4.10)$$

The oxide thickness h_{ox} was either calculated from the cell voltage evolution (Equation (1.16)), by using either literature or calculated values for the anodizing ratio, or by using Faraday's law (Equation (1.18)). Details of the methods used to calculate h_{ox} are given in chapters 5 and 6.

As representing the stress-thickness product versus calculated oxide thickness rely on assumptions regarding the oxide growth rate, incremental internal stress changes in the oxide have routinely been detected from representations of more fundamental variables. The stress-thickness product evolution was used. From Equation (4.9):

$$\frac{Y_s h_s^2}{6} \frac{d\kappa}{dt} = \sigma_{ox} \frac{dh_{ox}}{dt} - (PBR)\sigma_M \frac{dh_{ox}}{dt} \quad (4.11)$$

Thus, changes of the slope of the stress-thickness product versus time may indicate a change in the incremental internal stress in the oxide σ_{ox} , if the oxide growth rate, the Pilling-Bedworth ratio and the incremental stress in the metal do not change.

The stress resulting from deposition of the metal, prior to anodizing, must be known. This stress has been evaluated by measuring the curvature change induced by the chemical dissolution of the deposited metallic

4. Measuring the internal stress during anodizing

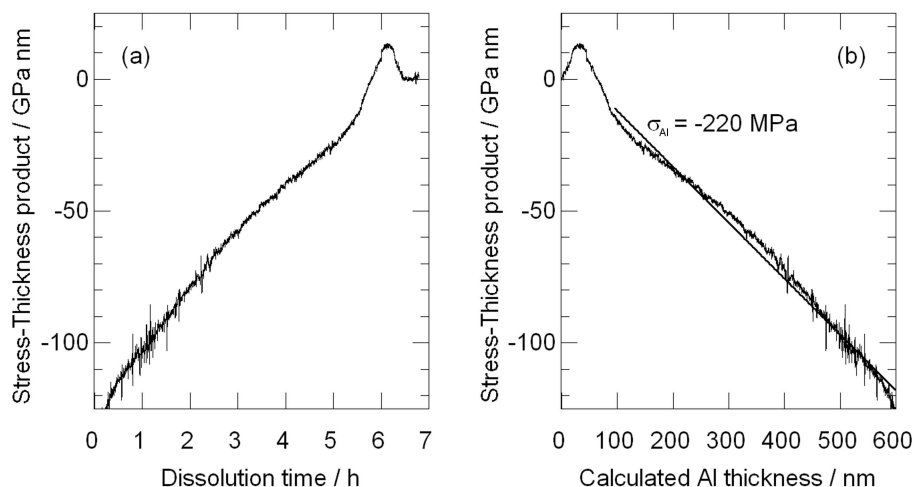


Figure 4.1: (a) Stress-thickness product evolution during sputtered aluminum alloy film dissolution in 0.4 mol l^{-1} phosphoric acid at room temperature. (b) Stress-thickness product as a function of aluminum film thickness, calculated by assuming a constant dissolution rate.

film. For aluminum films, this was done by continuously measuring the curvature change during dissolution of the film in 0.4 mol l^{-1} phosphoric acid. In that case, not only the mean internal stress in the aluminum film, but also the internal stress profile in the film are obtained, as illustrated on Figure 4.1. The stress-thickness product as a function of the metallic film thickness, which was calculated in this case by assuming a constant dissolution rate, is very similar to the general aspect of the stress-thickness product measured during Al sputtering, featuring a tensile then compressive internal stress corresponding to different film growth stages [244].

The mean internal stress in the zirconium films was determined by measuring the curvature change resulting from complete film dissolution in a 10:45:45 mixture (volume ratio) of hydrofluoric acid:isopropyl alcohol:water. Due to the presence of hydrofluoric acid in the solution, the curvature of the sample could not be measured *in situ* during the dissolution of the metallic film in the latter case.

To illustrate the importance of correcting for the stress in the de-

posited metal, two aluminum films were anodized in 0.01 mol l^{-1} ammonium pentaborate at 5 mA cm^{-2} , and their curvature monitored *in situ*. One of the aluminum films had an internal stress of 210 MPa, while the other film had an internal stress of -86 MPa . Without correcting for the internal stress in the aluminum, the product of stress and thickness change of the oxide, calculated as:

$$\langle \sigma_{ox} \rangle \Delta h_{ox} = \frac{Y_s h_s^2}{6} \Delta \kappa \quad (4.12)$$

yields to Figure 4.2 (a). Although the experiments were performed in the same conditions, one could mistakenly conclude from Eq. (4.12) that the different slopes of the stress $\times$ thickness change curve indicate that the internal stress in the oxide film depends on the stress in the aluminum film. However, using Equation (4.2), the product of the internal stress and thickness change of the oxide is equal to:

$$\langle \sigma_{ox} \rangle \Delta h_{ox} = \frac{Y_s h_s^2}{6} \Delta \kappa - \langle \sigma_M \rangle \Delta h_M \quad (4.13)$$

where the thickness change of the aluminum film was calculated from Faraday's law (Equation (2.18)). Using Equation (4.13) to correct the data in Figure 4.2 (a), the evolution of the product of stress and thickness change of the oxide is nearly identical for both aluminum films.

4.3 Measuring the curvature

Now that the internal stress has been related to the curvature, the curvature of our samples must be accurately measured *in situ*. To accurately determine the curvature of a sample, a wide variety of methods exist. The main ones are interferometry, differential capacitance measurements, and laser beam deflection methods. Interferometry allows for measuring deflections of a single point of the sample from the relative variations of the optical path of a laser beam [71, 245]. The curvature value can be extracted from the deflection for a given experimental geometry, but the technique requires a very accurate sample positioning.

Differential capacitance methods measure the relative capacitance change of a capacitor in which the sample acts as one of the plates. This technique has a very high sensitivity [246], but its integration for use

4. Measuring the internal stress during anodizing

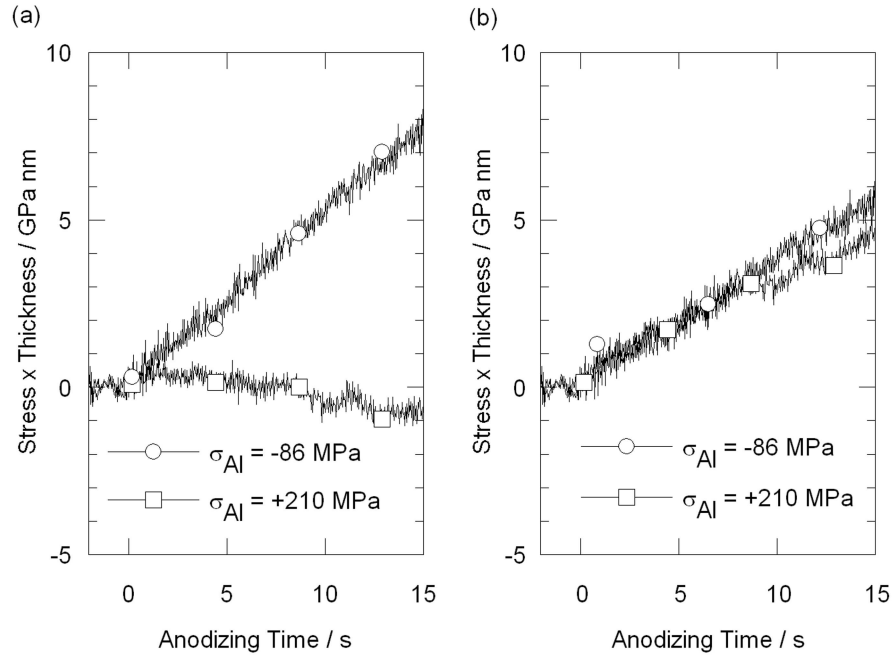


Figure 4.2: Evolution of the product of stress and thickness change of the oxide for aluminum anodizing in 0.01 mol l^{-1} ammonium pentaborate at 5 mA cm^{-2} . (a) Product of stress and thickness change of the oxide calculated from the curvature evolution without taking the internal stress in the metal into account (Eq. (4.12)), or (b) with taking the internal stress in the metal into account (Eq. (4.13)).

in a liquid environment is not straightforward, and generally requires a very specific design [247].

In laser deflection methods, the substrate curvature is deduced directly from the position of a reflected laser beam on a position-sensitive detector. This technique is the one that is most frequently being used, probably owing to its simplicity and versatility [60, 61, 248–253]. Some authors have used a scanning beam technique which allows for minimizing the sensitivity to displacements of the whole sample, at the detriment of time-resolution and vibration noise sensitivity [254–256].

4.3.1 The multiple beam optical sensor

A further improvement of the laser deflection technique came with the multi-beam optical sensor (MOS), introduced in 1996 by Floro and Chason [257] and inspired on the two-beams technique used by Kobeda and Irene [258]. In contrast to the single laser beam deflection technique, the MOS relies on the monitoring of the spacings between an array of laser beams reflected off the sample surface, and the position-sensitive detector has been replaced by a CCD camera allowing for faster acquisition rates. The curvature is deduced from the mean value of the differential spacings. The main advantage of using a multi-beam configuration instead of a single-beam one is a reduced sensitivity towards vibrations [259], while maintaining a high time-resolution. Vibrations of the sample, laser source or detector are expected to affect every laser beam in the same manner, so that the instantaneous spacings are expected to be virtually unaffected.

The multi-beam technique has already proven successful for *in situ* monitoring of the stresses generated in metal or ceramic thin films deposited in vacuum by chemical vapor deposition [260], physical vapor deposition [243] or molecular beam epitaxy [261]. Due to the recently increased interest in stress-related phenomena in liquid environments, the MOS technique starts being used for these systems as well [262–264]. For the latter, as opposed to vacuum or low pressure applications, laser beam refraction at the air/liquid interface is a complicating factor [265, 266], even when the incident beams are normal to the air/liquid interface [267].

Furthermore, an important source of error that is most often neglected during MOS measurements, both in liquid and in vacuum en-

4. Measuring the internal stress during anodizing

vironments, is the possible loss of linearity between beam differential spacing and curvature when the curvature is large. Therefore, in the following section, we provide a more accurate general relationship to extract the curvature from MOS measurements in air, and compare its accuracy with the simplified, most widely used equation [257]. An equation is then proposed for the case when the sample is in a liquid environment, and its accuracy is discussed as well. These considerations allowed us to select a specific setup geometry. We finally provide practical experimental details, such as the measurement resolution.

4.3.2 Curvature determination in air

For the sake of simplicity, we will first consider the specific geometry in which the sample bends along one single direction (uniaxial bending) and the plane containing the incident beams is normal to the sample surface in the flat reference state and parallel to the direction of bending of the sample. Equivalently, the incident and reflected beams are coplanar, which authorizes a 2D approach of the problem.

This geometry, which might be unattainable due to the finite size of the CCD and the laser source, can be rationalized in terms of the projection of the beams on a specific plane. This is discussed in a second part.

Uniaxial bending

The equations are hereafter derived for two laser beams, but the development can be extended to any number of beams by grouping them in pairs. As a first step, we will consider the reference state in which the two beams are reflected on a flat surface. As illustrated on Figure 4.3, we call A_i the point of incidence of the i^{th} beam on the surface and A_0 the point of clamping of the sample. The i^{th} beam is reflected off the sample and reaches the detector at B_i . We define the normal to the flat sample surface, which is used as a reference axis for expressing angles, at A_1 .

The reflected beams are normal to the detector surface in order to maximize the measured spacing, and we call O_1 the geometrical intersection of the reference axis with the plane of the detector. We also define the virtual point C_2 as the intersection of the 2^{nd} beam with the reference axis. The i^{th} incident beam makes an angle α_i with the reference

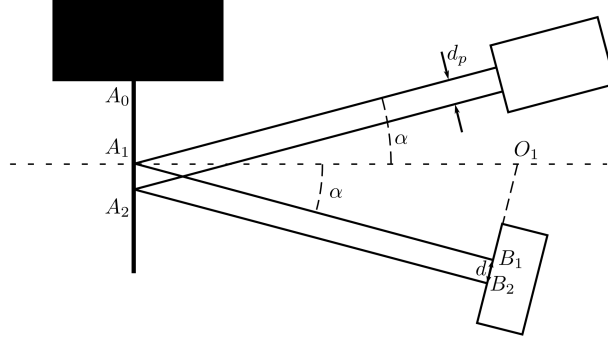


Figure 4.3: Illustration of the lengths and angles characterising the setup geometry in the case of two beams reflecting off a flat surface in air.

axis, and the i^{th} reflected beam makes an angle β_i with the reference axis. The spacing between the parallel incident beams is d_p . Because the incident beams are parallel, $\alpha_1 = \alpha_2 = \alpha$. Furthermore, as the sample surface is flat and normal to the reference axis, $\beta_1 = \beta_2 = \alpha$. Considering the $A_1O_1B_1$, $C_2O_1B_2$ and $C_2A_2A_1$ triangles, we can write the following geometrical relations:

$$\|O_1B_1\| = \|A_1O_1\| \sin \alpha \quad (4.14)$$

$$\|O_1B_2\| = \|C_2O_1\| \sin \alpha \quad (4.15)$$

$$\|A_1C_2\| = \|A_1A_2\| / \tan \alpha \quad (4.16)$$

$$\|A_1A_2\| = d_p / \cos \alpha \quad (4.17)$$

Therefore, in the flat reference state:

$$\|C_2O_1\| = \|A_1O_1\| + \|A_1C_2\| = \|A_1O_1\| + d_p / \sin \alpha \quad (4.18)$$

and the spacing between the two reflected beams on the detector d is given by:

$$d = \|O_1B_2\| - \|O_1B_1\| = d_p \quad (4.19)$$

Considering right triangles, we can write:

$$\frac{1}{\kappa^2} = (\|A_0 A_1\| + h_1)^2 + \left(\frac{1}{\kappa} - b_1\right)^2 \quad (4.20)$$

$$\frac{1}{\kappa^2} = \left(\|A_0 A_1\| + \frac{d_p}{\cos \alpha} + h_2\right)^2 + \left(\frac{1}{\kappa} - b_2\right)^2 \quad (4.21)$$

with $b_i = \|A_i A'_i\| \cos \alpha$ and $h_i = b_i \tan \alpha$. Equation (4.20) and (4.21) allow for calculating the displacement of the incidence point of the beams. The distance between the beams on the detector, $d = \|B'_1 B'_2\|$, can be expressed as a function of $\beta_i = \alpha + 2\delta_i$:

$$d = \frac{(\|A_1 O_1\| + b_2) \tan \beta_2 + h_2 + d_p / \cos \alpha}{\cos \alpha + \sin \alpha \tan \beta_2} - \frac{(\|A_1 O_1\| + b_1) \tan \beta_1 + h_1}{\cos \alpha + \sin \alpha \tan \beta_1} \quad (4.22)$$

We further need to link the curvature of the substrate to β_i . We use the fact that $\tan \delta_i$ is dependent on the sample curvature:

$$\tan \delta_1 = \frac{\|A_0 A_1\| + b_1 \tan \alpha}{1/\kappa - b_1} \quad (4.23)$$

$$\tan \delta_2 = \frac{\|A_0 A_1\| + b_2 \tan \alpha + d_p / \cos \alpha}{1/\kappa - b_2} \quad (4.24)$$

Thus, the spacing d between the reflected beams depends on the sample curvature and on the setup geometry, the latter being determined by the clamp to beam distance $\|A_0 A_1\|$, the angle of incidence α , the spacing between incident beams d_p and the distance between the sample and the detector through $\|A_1 O_1\|$.

Assuming angles are small enough to use the small angle approximation and to allow $A'_i = A_i$, this then yields the following simplified expression linking reflected spot spacing to curvature:

$$d = d_p \left(1 + \frac{2L}{\cos \alpha} \kappa\right) \quad (4.25)$$

or, equivalently:

$$\kappa = \frac{d - d_p}{d_p} \frac{\cos \alpha}{2L} \quad (4.26)$$

Equation (4.26), which was first presented with the introduction of the multi-beam optical sensor [257], is currently still the most used one

4. Measuring the internal stress during anodizing

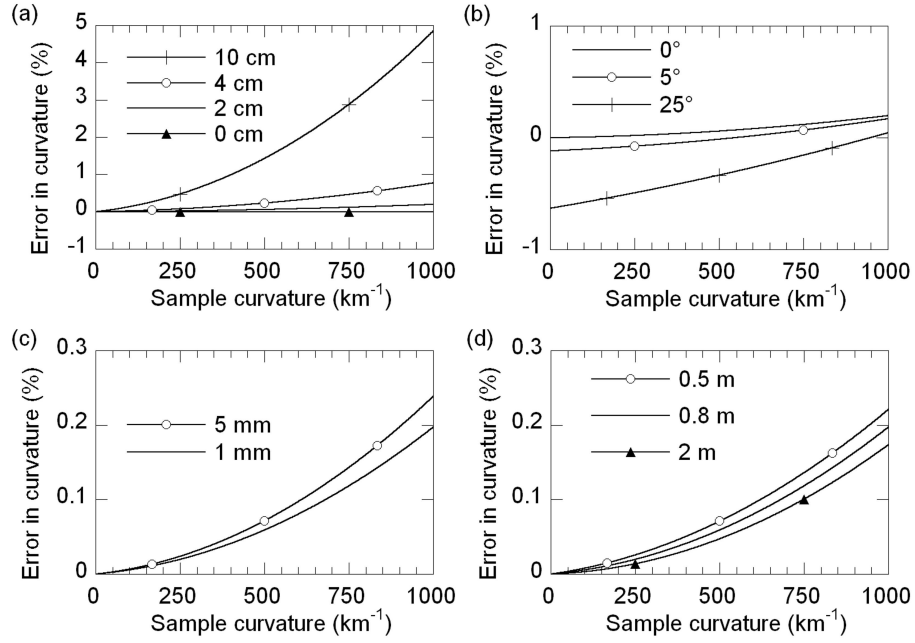


Figure 4.5: Relative error on calculated curvature when using Equation (4.26), as a function of sample curvature in air. The reference geometry is given by $\|A_0A_1\| = 2\text{ cm}$, $\alpha = 0^\circ$, $d_p = 1\text{ mm}$, and $\|A_1O_1\| = 0.8\text{ m}$. The following instrument parameters have been considered: (a) clamp to beam distance $\|A_0A_1\|$ (b) incidence angle α (c) spacing between the incident beams d_p (d) sample to detector distance $\|A_1O_1\|/\cos \alpha$.

in the literature to convert differential spot spacings to curvature from MOS measurements.

However, due to the underlying small angle approximation, an error is made when using Equation (4.26), instead of the exact Equations (4.20)-(4.24). This is illustrated for some selected but relevant cases in Figure 4.5 as a function of the sample curvature, by varying typical values of the instrumental parameters characterizing the setup geometry. The reference geometry that determines the value of the invariant parameters corresponds to our own setup ($\|A_0A_1\| = 2 \text{ cm}$, $\alpha = 0^\circ$, $d_p = 1 \text{ mm}$, and $\|A_1O_1\| = 0.8 \text{ m}$). Increasing the distance between the sample clamp and the incident beam (Fig. 4.5 (a)) increases the relative error, and the error increases with the sample curvature. Keeping the distance between the clamp and the beam below 4 cm will ensure the error is below 1 % up to a curvature of 1000 km^{-1} . Increasing the incident angle of the beams (Fig. 4.5 (b)) increases the maximum relative error, but its value is below 1 % for incident angles as large as 25° . Note however that at such large incident angles, another source of error on the measurement of curvature might arise from the astigmatism of the beams [268]. Increasing the distance between the incident beams (Fig. 4.5 (c)), or decreasing the distance between the sample and the detector (Fig. 4.5 (d)), both increase the relative error on the calculated curvature, but the maximum error is around 0.2 %.

Thus, if curvature measurements are performed at normal incidence and the clamp to beam distance is below 4 cm, the maximum relative error on the curvature calculated from Eq. (4.26) will be limited, on the order of 1 %. Unless a very specific geometry is being used, it is therefore reasonable to use Equation (4.26). In this thesis, Eq. (4.26) has been used to calibrate the setup, i.e. evaluate d_p and L by measuring the spot spacings with mirrors with a known curvature.

Note that in the cases where the substrate of interest is already curved before a film is grown on it, a relative form of Equation (4.26) will rather be used:

$$\Delta\kappa = \kappa - \kappa_0 = \frac{\Delta d \cos \alpha}{d_p} \frac{1}{2L} = \frac{(d - d_0) \cos \alpha}{d_p} \frac{1}{2L} \quad (4.27)$$

where κ_0 and d_0 are, respectively, the curvature and the beam spacing before the start of film growth. It should be noted that in the case of

4. Measuring the internal stress during anodizing

an initially curved substrate, $d_p = d_0$ in the denominator of Eq. (4.27) might lead to significant errors.

Extension to more complex geometries

In the above derivations, a specific geometry has been considered, characterized by a uniaxial bending of the sample and by the fact that the plane of incidence of the beams was normal to the sample surface in the flat reference state and parallel to the direction of bending. If the sample bends in two orthogonal directions, the above equations can still be used if the angles and distances are redefined by considering the projections of the beams on the planes of curvature. When a 2D array of laser beams is used for monitoring the curvature, two possibly different curvatures κ_x and κ_y will be extracted from the differential beam spacings in the horizontal and vertical directions respectively. In that case, the spacings and angles of incidence in the horizontal and vertical directions are independent.

Similarly to uniaxial bending, an adequate choice of the setup geometry will ensure the relative error on the calculated curvature to be below 1 % for curvatures up to 1000 km^{-1} . Measuring the curvature in two orthogonal directions allows to extract the stress in a film if the substrate is not isotropic, or if the stress in the film is not biaxial [269]. Because in this work, the curvature and the stress were biaxial, the curvature was only measured in one bending direction. Figure 4.6 further shows a typical experiment for which the curvature was measured in two orthogonal directions. This experiment illustrates that the curvature and the stress are indeed biaxial.

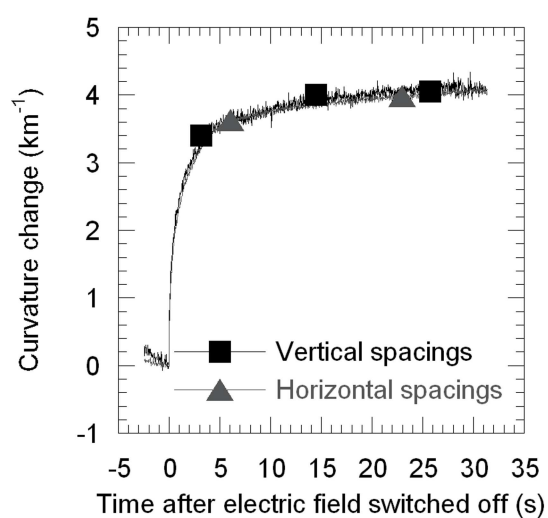


Figure 4.6: Tensile curvature change upon removal of the electric field in anodic zirconium oxide grown potentiostatically at 40 V for 2000 s, measured in both vertical and horizontal directions.

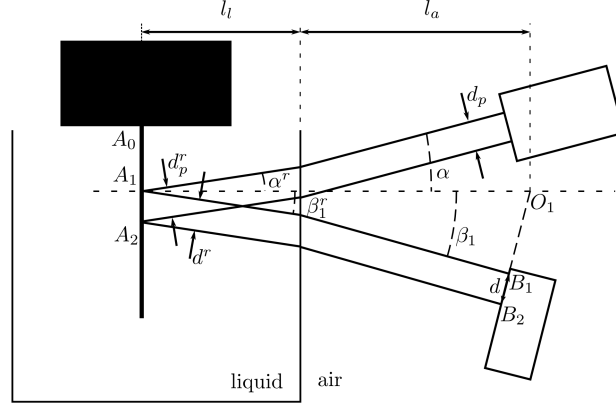


Figure 4.7: Illustration of the lengths and angles characterizing the setup geometry in the case of two beams reflecting off a flat surface inside a liquid.

4.3.3 Curvature determination in liquids

When the sample of which the curvature has to be monitored is placed in a liquid, Equation (4.26) needs to be corrected to take into account the refraction of the laser beams at the liquid/air interface. Again, for simplicity, we will consider the simplified geometry in which the sample experiences uniaxial bending and all the beams are coplanar with the direction of bending. For more complex geometries, the same reasoning is valid for the horizontal and vertical components of the beam deflection. Again, we will first consider the flat reference state before calculating how curvature modifies the spacing of the reflected beams.

We first consider the case in which the liquid containing cell window is parallel to the flat sample surface. As illustrated on Figure 4.7, a portion of the laser beams travel through the liquid, with refractive index n_{liq} , and one portion travels through air. We assume the cell window to be thin enough, to be able to neglect refraction at the liquid/glass and glass/air interfaces. Similarly to the previous derivation, we define the point of anchoring of the cantilevered sample as A_0 , and the points of incidence of the two beams on the surface A_1 and A_2 . As before, O_1 is

the geometrical intersection of the normal to the sample surface in the flat reference state with the plane of the detector.

The effective angle of incidence of the beams on the sample is now α^r , which, due to refraction, differs from the angle of incidence of the beams on the cell window, α . The reflection angles of the beams measured inside the liquid are β_1^r and β_2^r . The following relations link, for a flat sample, the spacing between the parallel incident and reflected beams inside the liquid (d_p^r and d^r , respectively) and the angles between the beams and the reference axis:

$$\sin \alpha = n_{liq} \sin \alpha^r \quad (4.28)$$

$$\sin \beta_i = n_{liq} \sin \beta_i^r \quad (4.29)$$

$$d_p^r \cos \alpha = d_p \cos \alpha^r \quad (4.30)$$

$$d^r \cos \beta_1 = d \cos \beta_1^r \quad (4.31)$$

$$d_p^r = d^r \quad (4.32)$$

$$\alpha^r = \beta_i^r \quad (4.33)$$

Therefore, $d = d_p$, as expected. In other words, if the beams are perpendicular to the CCD plane when the flat sample is in air, they will also be so when the sample is inside a liquid.

When the sample becomes curved, as illustrated on Figure 4.8, Equations (4.28)-(4.30) remain valid to calculate the modification of the angle and beam spacing induced by the refraction at the air/liquid interface. Similarly to curvature measurements in air, the following equations need to be solved to calculate the horizontal and vertical displacement b_i and h_i of the points of incidence of the beams on the sample:

$$\frac{1}{\kappa^2} = (\|A_0 A_1^r\| + h_1)^2 + \left(\frac{1}{\kappa} - b_1\right)^2 \quad (4.34)$$

$$\frac{1}{\kappa^2} = \left(\|A_0 A_1^r\| + \frac{d_p^r}{\cos \alpha^r} + h_2\right)^2 + \left(\frac{1}{\kappa} - b_2\right)^2 \quad (4.35)$$

$$h_i = b_i \tan \alpha^r \quad (4.36)$$

$$\|A_0 A_1^r\| = \|A_0 A_1\| - l_l (\tan \alpha - \tan \alpha^r) \quad (4.37)$$

while the following equations allow calculating the angle of the reflected

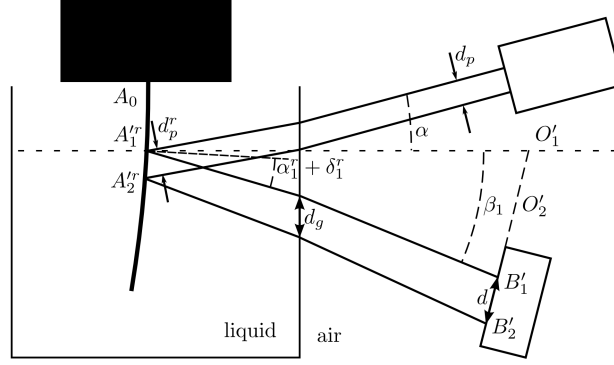


Figure 4.8: Illustration of the lengths and angles characterizing the setup geometry in the case of two beams reflected on a curved surface in a liquid.

beams from the curvature:

$$\beta_i^r = \alpha^r + 2\delta_i^r \quad (4.38)$$

$$\tan \delta_1^r = \frac{\|A_0 A_1^r\| + b_1 \tan \alpha^r}{1/\kappa - b_1} \quad (4.39)$$

$$\tan \delta_2^r = \frac{\|A_0 A_1^r\| + b_2 \tan \alpha^r + d_p^r / \cos \alpha^r}{1/\kappa - b_2} \quad (4.40)$$

Finally, the spacing between the reflected beams is equal to:

$$d = \frac{l_a \tan \beta_2 + (l_l + b_2) \tan \beta_2^r + h_2 + d_p^r / \cos \alpha^r}{\cos \alpha + \sin \alpha \tan \beta_2} - \frac{l_a \tan \beta_1 + (l_l + b_1) \tan \beta_1^r + h_1}{\cos \alpha + \sin \alpha \tan \beta_1} \quad (4.41)$$

where l_l and l_a are, respectively, the flat sample to cell window distance and the distance between the window and O_1 .

Assuming $l_l \ll l_a$, and using the small-angle approximation yields the

following simpler equation to calculate the sample curvature from the spacing between the beams:

$$\kappa = \frac{(d - d_p)}{d_p} \frac{\cos \alpha}{2Ln_{liq}} \quad (4.42)$$

This equation is formally very similar to Equation (4.26) for curvature measurements in air, but includes a correction factor equal to $1/n_{liq}$. This correction factor is the same as the one found by Lang and Seo for the single-beam technique [267]. In practice this means that, for a given curvature change of the sample, the resulting measured change in the beam spacing will be amplified by a factor n_{liq} , which is equivalent to increasing the sample to CCD distance and hence, the sensitivity of the measurement.

The error made when calculating the curvature from Equation (4.42) instead of the accurate set of equations (4.28)-(4.30), (4.34)-(4.41), is represented in Figure 4.9 as a function of the sample curvature for different measurement geometries. The reference geometry that determines the value of the invariant parameters, corresponds to our own experimental setup ($\|A_0A_1\| = 2\text{ cm}$, $\alpha = 0^\circ$, $d_p = 1\text{ mm}$, $l_l = 2\text{ cm}$ and $\|A_1O_1\| = 0.8\text{ m}$). It can be seen that the relative error of curvature associated with the use of the simplified equation is generally more important when the sample is inside a liquid than when the sample is in air. For instance, increasing the incidence angle from 0 to 25° increases the error by only 0.6% in air (Fig.4.5 (b)), while if the sample is in a liquid, the error increases to values between 2 and 5% in the 0 to 1000 km^{-1} curvature range (Fig.4.9 (b)). Similarly, increasing the distance between the sample clamp and the incident beam (Fig. 4.9 (a)) has a significant impact: for a curvature of 1000 km^{-1} , the error can be as large as 9% for a clamp to beam distance of 10 cm . At the same time, keeping the distance between the clamp and the beam below 4 cm will ensure the error is below 1% . Incident angles greater than 5° increase the maximum relative error, but the error is below 1% for smaller angles. Increasing the distance between the cell window and the sample (Fig. 4.9 (c)) can result in errors larger than 10% , if the reflected beams travel a non-negligible distance in liquid. Finally, decreasing the distance between the sample and the detector (Fig. 4.9 (d)) results in an increase of the relative error on the calculated curvature, but the maximum error is of

4. Measuring the internal stress during anodizing

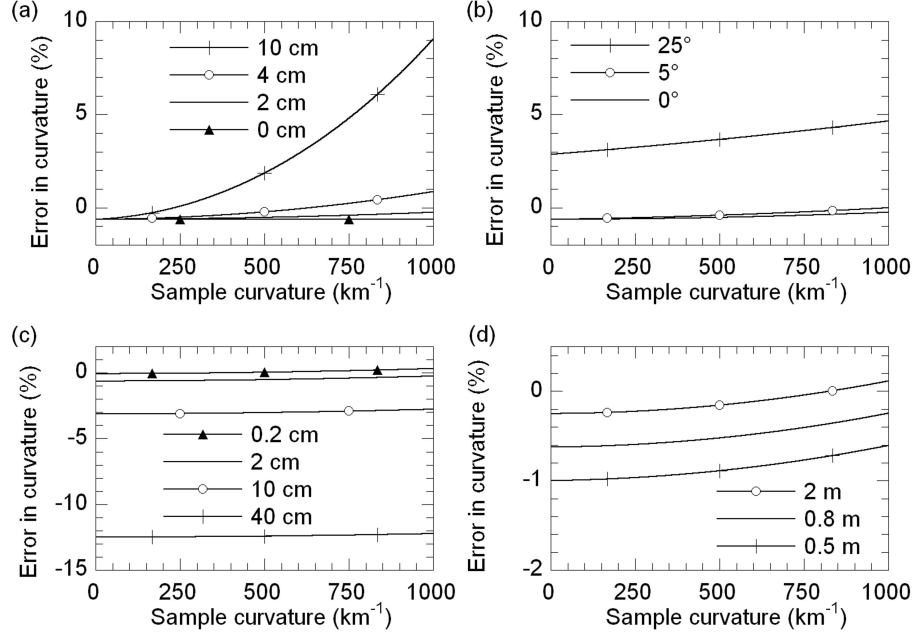


Figure 4.9: Relative error on calculated curvature when using Equation (4.42), as a function of the sample curvature in water. The reference geometry is given by $\|A_0A_1\| = 2 \text{ cm}$, $\alpha = 0^\circ$, $d_p = 1 \text{ mm}$, $l_l = 2 \text{ cm}$ and $\|A_1O_1\| = 0.8 \text{ m}$. The following instrumental parameters have been considered: (a) clamp to beam distance $\|A_0A_1\|$ (b) incidence angle α (c) distance between flat sample and cell window l_l (d) sample to detector distance $\|A_1O_1\|$.

1 % for a distance of 0.5 m.

Thus, if curvature measurements are performed at normal incidence, if the clamp to beam distance is below 4 cm, and if the length of the optical path of the reflected beams in the liquid is sufficiently small relative to the optical path length in air, the maximum relative error on the curvature calculated from Eq. (4.42) will be of the order of 1% only. Therefore, unless a very specific geometry is used, it is therefore reasonable to use Equation (4.42). It should be noted, however, that using Equation (4.26) instead of (4.42) will lead to a relative error of at least $1 - n_{liq}$, which in the case of water would represent a 33 % error.

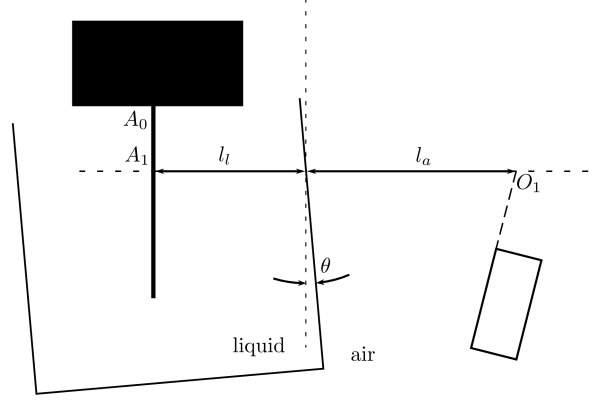


Figure 4.10: Definition of the misalignment angle θ .

In the above derivations, a setup was considered for which the cell window was parallel to the flat sample surface. When this is not the case, the angles α^r and β_i^r depend explicitly on the misorientation of the window, characterized by a misalignment angle θ . We define θ as the angle between the cell window and a perpendicular to the reference axis, as illustrated on Figure 4.10. If the cell window is rotated by an angle θ relative to the sample surface, Equations (4.28)-(4.30), (4.37), and (4.41) have to be modified as follows:

$$\sin(\alpha - \theta) = n_{liq} \sin(\alpha^r - \theta) \quad (4.43)$$

$$\sin(\beta_i + \theta) = n_{liq} \sin(\beta_i^r + \theta) \quad (4.44)$$

$$d_p^r \cos(\alpha - \theta) = d_p \cos(\alpha^r - \theta) \quad (4.45)$$

$$\|A_0 A_1^r\| = \|A_0 A_1\| - l_l \left(\frac{\tan \alpha - \tan \alpha^r (1 + \tan \alpha \tan \theta)}{(1 + \tan \alpha \tan \theta)(1 + \tan \alpha^r \tan \theta)} \right) \quad (4.46)$$

$$d = \frac{l_a \tan \beta_2 + (\cos \theta - \sin \theta \tan \beta_2)(x_1 + d_g)}{\cos \alpha + \sin \alpha \tan \beta_2} - \frac{l_a \tan \beta_1 + (\cos \theta - \sin \theta \tan \beta_1)x_1}{\cos \alpha + \sin \alpha \tan \beta_1} \quad (4.47)$$

where d_g is the spacing of the reflected beams on the cell window, and

4. Measuring the internal stress during anodizing

x_1 and g_1 are defined as follows:

$$x_1 = (b_1 + l_l)(\cos \theta \tan(\beta_1^r + \theta) - \sin \theta) + h_1(\sin \theta \tan(\beta_1^r + \theta) + \cos \theta) \quad (4.48)$$

$$g_1 = (b_1 + l_l) \cos \theta \tan(\beta_1^r + \theta) + h_1 \sin \theta \tan(\beta_1^r + \theta) \quad (4.49)$$

$$d_g = \left(\frac{b_2 - b_1}{\cos \theta} + x_2 \tan \theta \right) (\tan(\alpha_r - \theta) + \tan(\beta_2^r + \theta)) + ((b_1 + l_l) \cos \theta + h_1 \sin \theta) (\tan(\beta_2^r + \theta) - \tan(\beta_1^r + \theta)) + x_2 \quad (4.50)$$

$$x_2 = \cos \theta ((b_2 - b_1)(\tan \alpha^r - \tan \theta)) + \frac{d_p^r}{\cos \alpha^r} \quad (4.51)$$

The effect of misorientation is shown in Figure 4.11 for our own setup geometry, in which the incident beam is normal to the flat sample surface. It can be seen that any misorientation is likely to introduce large errors if Equation (4.42) is used to calculate curvature values smaller than 10 km^{-1} . It is anticipated that the error will become even more important if the incidence angle is not zero, so that any misalignment of the cell should therefore be avoided.

4.3.4 Resolution limiting factors in liquids

In this section, some sources of perturbations and experimental artifacts associated with optical curvature measurements in liquids are discussed, these perturbations having been observed during our anodizing experiments. Some guidelines are proposed to avoid such perturbations.

With our experimental setup, an absolute curvature resolution of 0.12 km^{-1} could be attained routinely, corresponding to a radius of curvature of 8 km. The resolution was calculated as two times the experimental standard deviation for the curvature signal during baseline recording, an example of which is illustrated in Figure 4.12. It is important to note that, according to the Stoney equation, the resolution of a given curvature measurement setup in terms of stress is determined not only by the curvature resolution, but also by the characteristics of the substrate. Indeed, the smallest stress variation that can be measured in a film of given thickness will depend strongly on the thickness (squared) of the substrate, as well as on its relevant elastic modulus. Hence, increasing the overall stress resolution can be achieved by either increasing

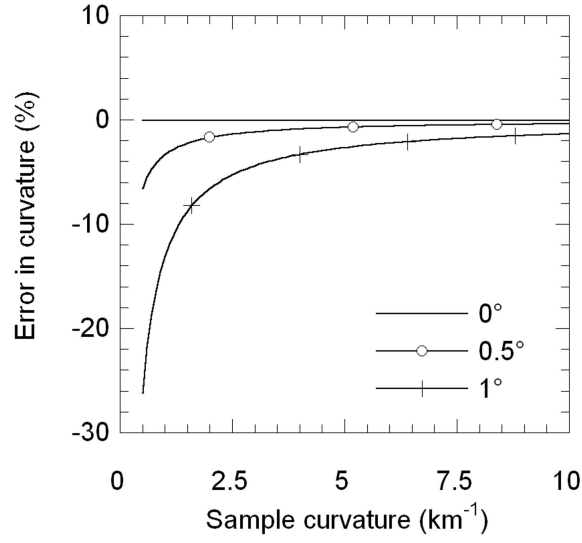


Figure 4.11: Error made when calculating the curvature from Eq. (4.42) for different misalignment angles θ . The reference geometry is characterized by the following parameters: clamp to beam distance $\|A_0A_1\| = 4$ cm, incidence angle $\alpha = 0^\circ$, spacing between incident beams $d_p = 1$ mm, refractive index of the liquid $n_{liq} = 1.33$, sample to cell distance $l_l = 5$ cm and reflected beam optical length in air $l_a = 0.95$ m.

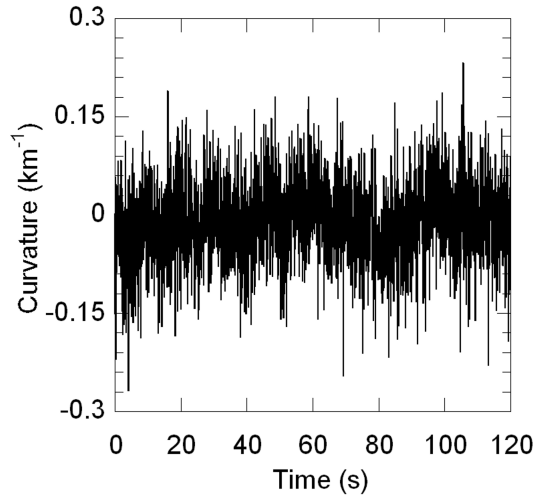


Figure 4.12: Typical example of curvature baseline recording, showing a standard deviation of 0.06 km^{-1} .

the distance between the sample and the detector (thus improving the curvature resolution), or by decreasing the thickness or the biaxial modulus of the elastic substrate (thus increasing the proportionality constant between stress and curvature).

In practice, the effective curvature resolution does not always correspond to the theoretical resolution calculated from the signal to noise ratio, but can be limited by additional optical perturbations. Generally speaking, such optical perturbations, i.e. local perturbations of the laser beams, are highly detrimental to the quality of the measurement. Possible sources of perturbations may include:

1. scattering of the beams on a dirt or scratch present on the cell window or on the detector filters, the latter generally being used for filtering out the ambient light in order to prevent saturation of the CCD detector ;
2. scattering of the beams on the sample surface due to roughening or due to specific surface reactions taking place, an example of which is oxygen or hydrogen evolution during electrochemical processes ;

3. convection effects inside the liquid due, for instance, to temperature gradients.

If one of the beams is scattered or deflected by a dirt or a scratch present on the cell window, on the sample surface or on the filters at the entrance of the detector, this may cause an artificial modification of the beam spacings. The advantage of monitoring a series of beams at the same time is that a perturbation of one of the beams can be easily detected by comparing the time-evolution of its position with the one of the other beams. Nonetheless, the cleanliness of all the components of the experimental setup is obviously crucial.

The reflection of the laser beams on the sample surface itself is generally complicated by a number of scattering issues. Besides surface roughening, which is intrinsically related to all thin film growth processes, water decomposition at the sample surface usually constitutes a more important scattering source during electrochemical processes. In the case of anodizing, oxygen bubbles may be formed on the electrode surface, randomly scattering the incident laser beams and thus preventing any curvature measurement. In order to address this problem, the curvature of our electrodes was measured from the electrically isolated backside of the sample. Double-side polished substrates have thus been used in order to ensure a good back-side reflectivity.

Convection effects can be visualized by speaking or shuffling close to the region located between the MOS detector housing and the liquid containing cell. This reproducibly leads to a series of marked peaks in the recorded beam spacings, as illustrated in Figure 4.13. This kind of effect is not encountered when the MOS device is connected directly to a vacuum deposition chamber, and therefore appears to be more problematic when the laser beams are crossing open-air or a liquid. Although the origin of this effect has not been studied extensively, it is likely that convection fluxes (natural or forced) induce local changes of the density of the medium (electrolyte or air) and therefore locally modify its refractive index. Such perturbations can be easily avoided by insulating the entire optical path of the laser beams from the environment. In our experimental setup, the cell as well as the optical path between the cell and the MOS housing were enclosed in a PMMA box in order to limit the influence of the convection fluxes due to natural convection.

An additional experimental perturbation manifested itself as an in-

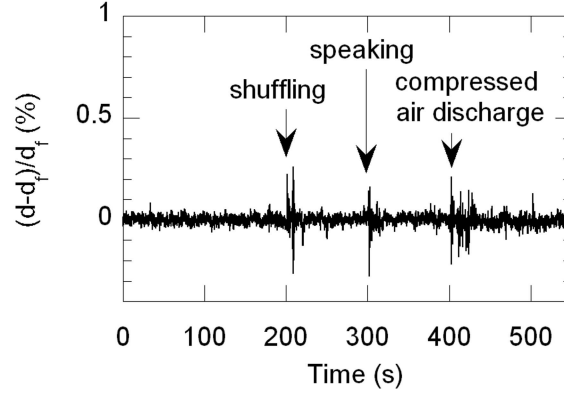


Figure 4.13: Illustration of the influence of convection effects on the differential spacings. An increase of the noise level is observed when convection effects are induced in the region between the detector and the cell by shuffling, speaking or discharging compressed air. Reproduced from [227].

crease followed by a decrease of the differential spacing. This perturbation was observed to propagate progressively either downward or upward from one pair of beams to the other, as illustrated in Figure 4.14. It is therefore likely that this effect is due to a solid particle, or a bubble crossing the path of the laser beams. During our experiments, it was found that this kind of perturbation could be almost completely avoided by filtering the liquid prior to the experiment.

4.4 Conclusion

To conclude, we have shown in this chapter the details of our experimental setup to measure the internal stress *in situ* during anodizing. We have shown how by measuring the curvature of cantilevers on one side of which a metallic film is anodized, the stress in the anodic film can be extracted, and explicitly stated the underlying requirements of the experimental setup. We have also shown how the curvature is calculated from the actual variable measured by our setup, i.e. the mean differential spacing. A simplified formula was derived to calculate the curvature when the sample is in a liquid, and its validity checked with respect to

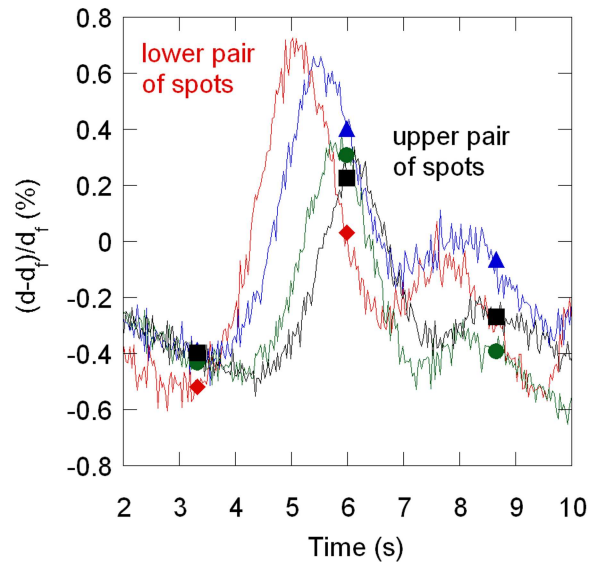


Figure 4.14: Time-evolution of the spacings between each pair of spots, corresponding to a particle-induced optical perturbation of the laser beams.

4. Measuring the internal stress during anodizing

our setup. Our results show that among other experimental details, the setup geometry should be provided when multiple beam optical sensor measurements are performed in liquids or when a specific geometry is used, in order to ensure reproducibility.

Chapter 5

Internal stress and porous anodic oxides

In this chapter, the role of internal stress on the development of porosity in anodic oxide films is studied.

First, we studied the role of internal stress on the initiation of porosity. As we have seen in section 2.3, the growth of porous anodic oxide films takes place through two distinct stages. The first one is the growth of a dense barrier oxide layer. The second one is the growth of a porous layer.

We show that by monitoring the curvature evolution during aluminum anodizing, the initiation of porosity can be detected very precisely. The increase in the rate of curvature change, which allows the detection of porosity initiation, will be shown to be consistent with pore growth by oxide flow from the barrier to the porous layer. We then specifically investigated the role of stress on pore initiation in anodic oxides. The hypothesis that pore initiation minimizes the sum of surface and strain energy of the system was not validated. Instead, we show that the pore initiation and the selection of the cell diameter result from the minimization of the sum of surface and electrostatic energy. This mechanism is supported by morphological data taken from our anodic alumina films, as well as from data from the literature for porous anodic alumina and anodic titania films.

Second, we report on the dependence of internal stress in anodic alumina on experimental conditions. By simultaneously determining the

internal stress and the kinetics of oxide film growth, the oxide viscosity could be estimated for the first time for anodic alumina at room temperature in the presence of large ionic currents.

5.1 Experimental details

For the experiments performed in this chapter, two types of aluminum films were used. The first type concerns pure aluminum films, deposited 800 nm-thick by electron-beam evaporation from 99.99 % pure granulated base material onto our oxidized silicon substrates. The aluminum, deposited in two different batches, had an internal growth stress of either 0 or -112 MPa following deposition, as measured by monitoring the curvature during dissolution of the Al film in phosphoric acid.

Anodizing experiments were also performed on an aluminum-silicon-copper alloy (further denoted Al(Si, Cu)). The silicon and copper content were 1 % and 0.7 %, respectively. The alloy was deposited 600 nm-thick by sputtering, and the internal stress in the metallic film was measured to be -220 MPa. This alloy, which is commonly used in the microelectronics industry, was originally used to investigate on the influence of the aluminum purity on the internal stress evolution.

Anodizing of the Al films was performed galvanostatically in either 0.4 mol l^{-1} phosphoric acid (H_3PO_4) or 1.0 mol l^{-1} sulfuric acid (H_2SO_4). Anodizing of the Al(Si, Cu) films was performed galvanostatically in 1.0 mol l^{-1} sulfuric acid. All experiments were performed at room temperature.

The internal stress in the oxide σ_{ox} was calculated from the slope of the stress-thickness product (defined as $(1/6)Y_s h_s^2 \Delta\kappa$, see section 4.2) versus oxide thickness using Equation (4.9):

$$\sigma_{ox} = \frac{Y_s h_s^2}{6} \frac{d\kappa}{dh_{ox}} + (PBR)\sigma_M \quad (4.9)$$

During the initial barrier layer growth stage, the oxide thickness h_{ox} was calculated from the anodizing voltage. For phosphoric acid anodizing, the dependence of the anodizing ratio on the current density was determined. The anodizing ratio (reciprocal of the electric field) was calculated as the ratio of the measured barrier layer thickness to the voltage at the end of anodizing. For sulfuric acid anodizing, a constant anodizing ratio of 1.1 nm V^{-1} was assumed [270]. Indeed, the small thickness

of the barrier layer in H_2SO_4 caused the uncertainty on the measured anodizing ratio to be quite large.

During the porous layer growth stage, the thickness of the anodic oxide film was assumed to be proportional to time. The proportionality constant was evaluated by measuring the final thickness of the porous layer in a scanning electron microscope.

A Pilling-Bedworth ratio (*PBR*) of 1.02 was calculated by assuming an anodizing efficiency of 0.6. The latter value was recently confirmed experimentally by detailed *in situ* optical emission spectrometry [271].

5.2 The role of the internal stress on pore initiation

5.2.1 *In situ* detection of porosity initiation

The role of stress on pore initiation in anodic alumina was investigated. We found out that by monitoring the stress-induced curvature evolution *in situ* during aluminum anodizing, the moment of pore initiation can be precisely detected.

Figure 5.1 shows the simultaneous change in substrate curvature $\Delta\kappa$ and cell voltage evolution as a function of anodizing time for Al anodizing in H_2SO_4 at a current density of 5 mA cm^{-2} . The voltage-time (V - t) curve is characteristic for the early stages of porous aluminum anodizing. As we have seen in section 2.3, the initial linear rise in cell voltage corresponds to barrier layer growth, while the gradual reduction of the slope of the V - t curve can be associated with the initiation of porosity [272, 273]. It can be seen from Figure 5.1 that our *in situ* curvature measurements provide complementary information to the V - t curve.

When anodizing starts ($t = 0$), an instantaneous discontinuity in the curvature evolution appears. This can be attributed to an electrostrictive-induced stress component in the pre-existing native oxide. Indeed, from the curvature change of about -0.05 km^{-1} , which corresponds to a change of about -0.22 GPa nm of the stress-thickness product in the native oxide film, a native oxide thickness of 3 nm is calculated from Equation (2.23) (oxide relative permittivity $\varepsilon_r = 8$, Poisson ratio $\nu_{ox} = 0.25$ and electric field $E = 0.9 \text{ V nm}^{-1}$) [68].

The substrate curvature change then starts to increase at a constant rate in the compressive direction, up to a transition time at which the

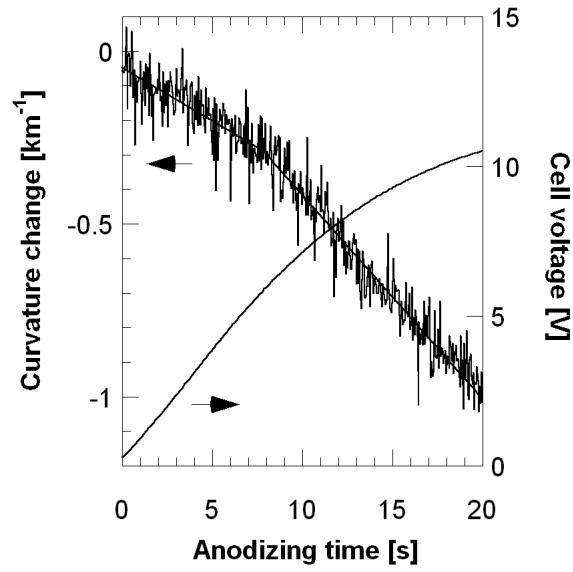


Figure 5.1: Curvature change and cell voltage evolution as a function of anodizing time for Al anodizing at 5 mA cm^{-2} in 1 mol l^{-1} sulfuric acid at 22°C .

rate of curvature change suddenly increases. The curvature transition time, calculated using a two-phase linear regression model fitting algorithm [274], is 7.9 ± 1.0 s, and the rate of curvature change increases by a factor of 1.9 ± 0.2 after the transition. At the transition time, the cell voltage reaches 6.0 V, which corresponds to a barrier oxide thickness of about 7 nm.

The observed increase of the rate of curvature change is believed to correspond to porosity initiation. This claimed influence of porosity initiation on the rate of curvature change can be inferred from the time derivative of the stress-thickness product, Equation (4.11):

$$\frac{Y_s h_s^2}{6} \frac{d\kappa}{dt} = \sigma_{ox} \frac{dh_{ox}}{dt} - (PBR)\sigma_M \frac{dh_{ox}}{dt} \quad (4.11)$$

where σ and h are, respectively, the stress and thickness, Y_s is the biaxial modulus of the silicon substrate and the subscripts “ox”, “s” and “M” refer to the oxide, the silicon substrate and the metal, respectively.

Thus, the rate of curvature change is equal to:

$$\frac{d\kappa}{dt} = \frac{6}{Y_s h_s^2} \frac{dh_{ox}}{dt} (\sigma_{ox} - (PBR)\sigma_M) \quad (5.1)$$

In this particular batch of aluminum, σ_M was measured to be zero. Therefore, an increase of the rate of curvature change is either due to an increase of the internal stress in the anodic film, or due to an increase of the oxide growth rate. Regarding an internal stress change in the oxide film upon porosity initiation, a stress decrease, rather than an increase, is expected. *In situ* stress measurements during vapor deposition of alumina have indeed shown that the increase of the porosity of the film decreases the internal stress, due to a decrease of its biaxial modulus [243]. Thus, an increase of the oxide growth rate is more likely.

Furthermore, from the values of cell voltage and anodic aluminum oxide thickness reported in reference 165, a growth rate increase of about 2.3 can be calculated. This is very close to our own measured increase (factor 1.9 ± 0.2) for the rate of curvature change. An increase of the oxide growth rate as porosity appears is consistent with growth of the porous layer by oxide flow. Such a growth rate increase would not be expected if the porous layer grew by dissolution of the oxide at the pore base. Indeed, under galvanostatic conditions, the volumetric rate of oxide production is expected to be constant during both barrier and porous

5. Internal stress and porous anodic oxides

layer growth. If field-assisted dissolution occurred, the rate of thickness change would be the same during barrier and porous layer growth since the pore volume would be created by loss of oxide material in the electrolyte. Oppositely, porous layer growth by oxide flow allows the oxide to thicken faster in the pore wall regions, which increases the oxide growth rate. It is the accumulation of oxide in the pore wall region that creates the pore volume in the latter case [69].

To confirm the appearance of porosity after the curvature transition time, *ex situ* atomic force microscopy (AFM) topographic images were acquired on surfaces anodized for different times. Anodizing was carried out in the same experimental conditions as above, and in each case, the curvature evolution was measured during anodizing in order to accurately identify the location of the curvature transition time. Figure 5.2 (a) and (c,e) show the topography of samples for which anodizing was interrupted before and after the curvature transition time, respectively. Due to the topography of the underlying aluminum grains, the porosity is best resolved when comparing the deflection of the AFM cantilever, which roughly corresponds to the spatial derivative of the topography (Fig. 5.2 (b), (d) and (f)). An additional small-scale feature can be seen on AFM images of samples anodized past the curvature transition.

To further quantify the size of these features, Figure 5.3 shows the obtained radial power spectral density curves for samples anodized in 1 mol l^{-1} H_2SO_4 for, respectively, 7 s, 14 s, 20 s and 35 s. The samples grown past the curvature transition time present two correlation breaks, while samples where the curvature transition time was not reached present only one correlation break. The first correlation break (λ_1), averaged over all four samples, is associated with a length scale of $290 \pm 20\text{ nm}$, while the second one (λ_2), when present, is associated with a length scale of $16 \pm 2\text{ nm}$.

Moreover, *ex situ* scanning electron microscopy of the surface and cross-section of the sample anodized for 35 s reveals that the oxide is indeed porous, and still sufficiently thin to reveal the topography of the underlying aluminum grains (Fig. 5.4). Pores were not observed on scanning electron micrographs (SEM) of samples where the curvature transition time was not yet reached. From the plane-view SEM micrographs, the mean pore diameter and the mean pore spacing are both on the order of 10 nm, while the mean aluminum grain size is about 200 nm.

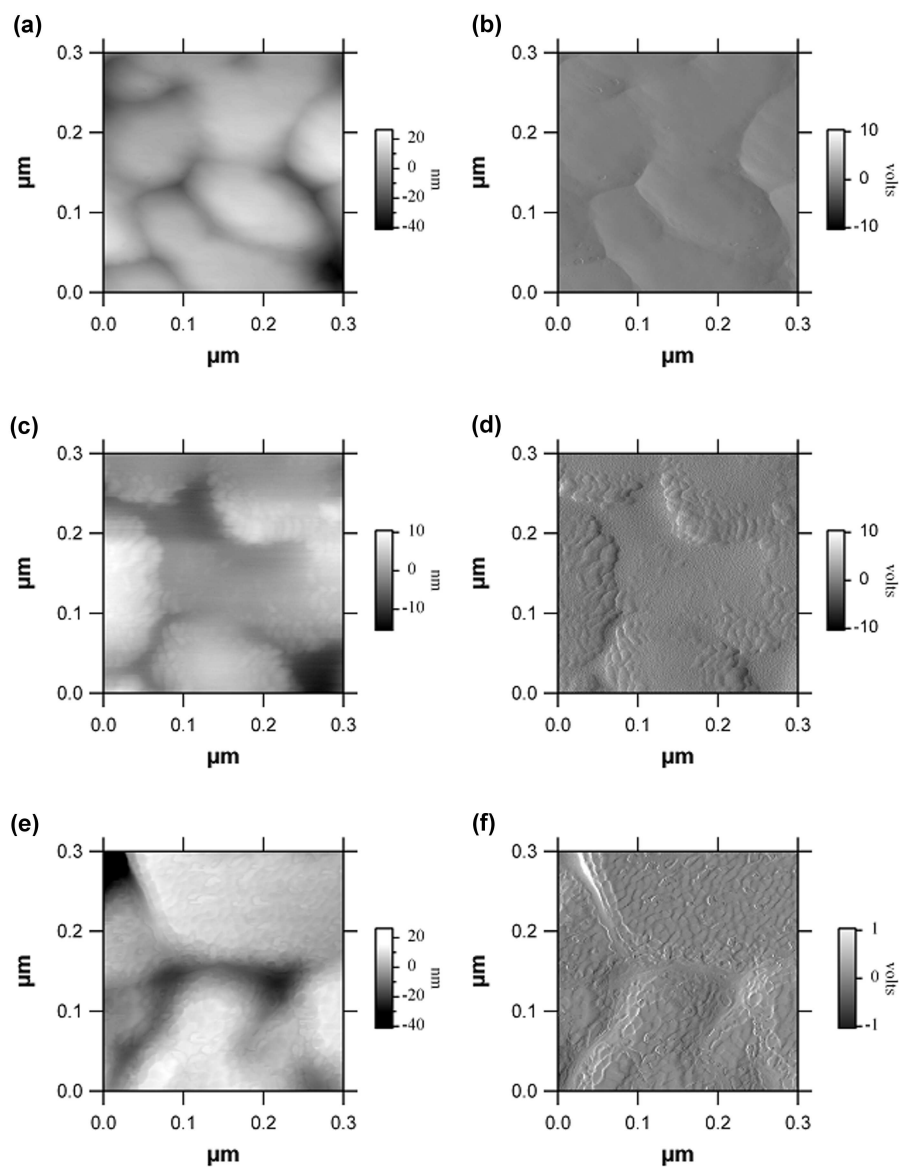


Figure 5.2: AFM images of Al samples anodized at 5 mA cm^{-2} in 1 mol l^{-1} sulfuric acid for (a,b) 7 s, (b,d) 14 s, and (e,f) 35 s. Topography is shown in (a), (c) and (e) and AFM cantilever deflection, in volts in (b), (d) and (f).

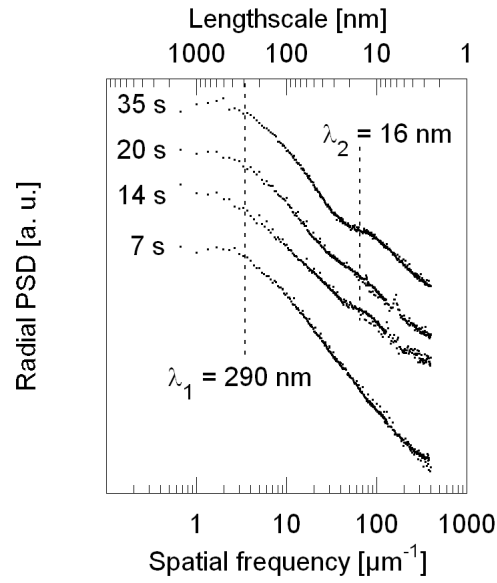


Figure 5.3: Radial power spectral density of Al samples anodized at 5 mA cm^{-2} in 1 mol l^{-1} sulfuric acid for different times. Only samples for which two linear regimes of curvature change versus time could be identified have two correlation breaks (λ_1 and λ_2), as indicated by the dashed lines. The curves were shifted vertically for clarity.

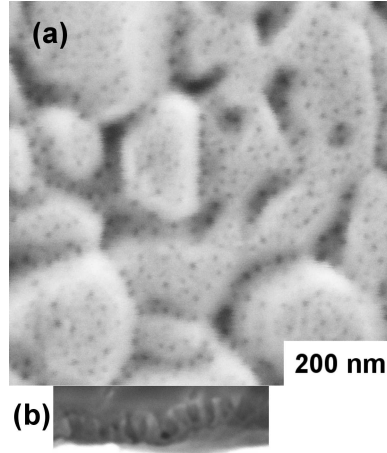


Figure 5.4: Scanning electron micrographs of the surface (a) and cross-section (b) of an Al sample anodized in 1 mol l^{-1} sulfuric acid at 5 mA cm^{-2} during 35 s. The same scale bar applies to both images.

From these dimensions, we can conclude that the presence of the first correlation break revealed by AFM reflects the underlying aluminum grain morphology, while the second correlation break can be associated with the appearance of porosity. From the cross-sectional micrograph in Figure 5.4(b), both the oxide / electrolyte and metal / oxide interface show a roughness about 10 nm wavelength. It must be acknowledged that no experiment could confirm which of the metal / oxide or oxide / electrolyte interface is the first one for which the roughness increases. The stability analysis performed in the next section shows that the oxide / electrolyte interface is the one at which the wavelength is selected. This suggests that the roughness increase of the metal / oxide interface is a consequence of the roughness increase at the oxide / electrolyte interface.

The detection of the moment at which porosity initiation occurs allowed to evaluate the growth time of the porous layer. This allowed in turn the evaluation of the porous layer growth rate (see section 5.3). Figure 5.5 (a) shows the simultaneous stress-thickness product and the cell voltage evolution for Al(Si, Cu) anodizing in 1 mol l^{-1} sulfuric acid at 1 mA cm^{-2} . The stress-thickness product features two slope changes. At the first transition, which occurs at a time t_i , the magnitude of the slope

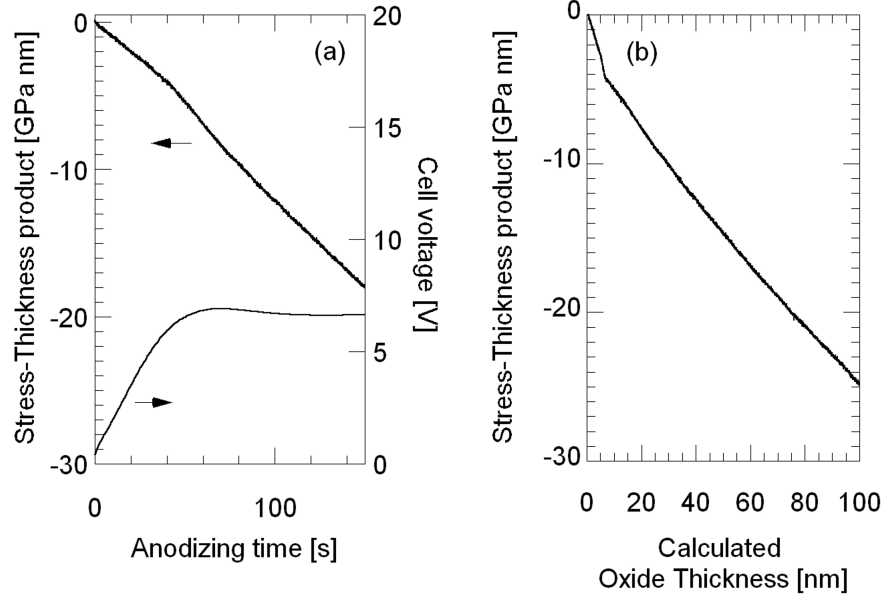


Figure 5.5: Stress-thickness product and voltage evolution for Al(Si,Cu) anodizing in sulfuric acid

increases, while at the second transition, the magnitude of the slope decreases. The first transition is associated with porosity initiation.

The oxide thickness h_{ox} can therefore be calculated in the following way:

$$h_{ox} = h_{ox,b} + h_{ox,p} \quad (5.2)$$

with $h_{ox,b}$ and $h_{ox,p}$ the thicknesses of the barrier and porous layer, respectively. The thickness of the barrier layer is calculated from the cell voltage using Equation (2.16):

$$h_{ox,b} = V(AR) \quad (2.16)$$

with V the cell voltage and (AR) the anodizing ratio which is assumed to be constant and equal to 1.1 nm V^{-1} . The thickness of the porous layer is assumed equal to:

$$h_{ox,p} = \begin{cases} 0 & \text{if } t < t_i, \\ K(t - t_i) & \text{if } t \geq t_i \end{cases} \quad (5.3)$$

with t the anodizing time ($t = 0$ when anodizing starts) and K a constant which has been evaluated by measuring the porous layer thickness on scanning electron micrographs of a sample cross-section.

It should be noted that the oxide thickness calculated in this way may not be accurate for anodizing times close to t_i . Nevertheless, two distinct internal stress regimes can be identified from the two different slopes of the curve in Figure 5.5. The first regime is characteristic for the barrier layer growth stage, while the second regime is characteristic for the porous layer growth stage. The stress decrease by a factor 2.0 in the porous layer growth stage can be attributed to a decrease of the biaxial modulus of the alumina film, induced by porosity [243]. Indeed, a decrease of stress by a factor 2.0 can be expected for a porosity of about 0.25, which is consistent with typical values reported for aluminum anodizing in sulfuric acid at 1 mA cm^{-2} [116, 118]. If the stress decrease in Figure 5.5(b) can be fully attributed to a porosity-induced decrease of the biaxial modulus, the stress in the barrier layer is expected to be the same whether the anodic oxide film is porous or not, except probably around t_i . Therefore, only stress values for the initial barrier layer growth stage are subsequently reported.

5.2.2 Stability analysis of the barrier oxide film

As we have seen in section 2.3.3, no model is available today for predicting the dependence of the morphology of porous oxide layers on experimental conditions. This is probably due to the fact that these models assume pore formation occurs by field-assisted dissolution, which is not the case. A model which would be able to predict the dependence of the porous layer morphology on anodizing conditions would also shed a light on the origin of porosity initiation, and hence on the transition from the dense barrier oxide to a porous oxide, since the associated increase in oxide surface area alone is energetically not favorable.

An attempt for such a model has recently been proposed by Raja *et al.* [150], who suggested, based on earlier seminal work by Asaro and Tiller [275], that internal stresses in anodic oxides are responsible for the initiation of porosity and the associated selection of pore spacing. Their suggestion is based on the well-documented observation that in several cases, an initially flat growing thin film may start to develop surface roughness, the length-scale of which is selected by the internal

5. Internal stress and porous anodic oxides

stress in the layer [149]. In such a case, an initially flat surface of the solid is energetically unstable against perturbations if the characteristic wavelength of the perturbation is greater than a critical value λ_c , the latter being defined as the wavelength at which the sum of the surface and strain energies is the same in the flat and the perturbed state.

By balancing the increase in surface area with the resulting decrease in strain energy, the critical perturbation wavelength λ_c can be expressed for an isotropic solid and small perturbation amplitudes as [239,275,276]:

$$\lambda_c = \frac{\pi Y \gamma}{(1 + \nu) \sigma^2} \quad (5.4)$$

where Y is the biaxial modulus of the solid, ν its Poisson ratio, γ its surface energy, and σ is the internal biaxial stress. Note that Equation (5.4) rigorously applies to a semi-infinite solid. However, for our multilayers consisting of a thick silicon substrate, an aluminum film and anodic alumina, the critical wavelength is still proportional to σ^{-2} :

$$\lambda_c = k \frac{\pi Y_{ox} \gamma}{(1 + \nu_{ox}) \sigma^2} \quad (5.5)$$

k being almost equal to 1 [276].

Besides strain energy, other energy terms can stabilize a perturbed surface as well, leading to a different expression for the critical wavelength λ_c than the one predicted by Equation (5.4) or (5.5). For instance, in the case of a parallel plate capacitor in vacuum over which an electric field E is present, the following expression was derived for λ_c [277]:

$$\lambda_c = \sqrt{\frac{4\pi^2 h \gamma}{\varepsilon_0 E^2}} \quad (5.6)$$

where h is the distance between the capacitor plates and ε_0 is the vacuum permittivity.

The parallel plate capacitor is conceptually similar to an anodic oxide film, as illustrated on Figure 5.6. Therefore, in the specific case of anodic oxide growth, during which relatively high electric fields on the order of 10^9 V/m are present, it can be anticipated that surface perturbations may be stabilized as well by the associated decrease in electrostatic energy. In such a case, the relevant critical perturbation wavelength for an

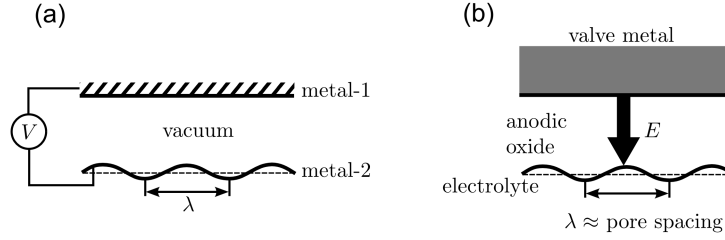


Figure 5.6: Conceptual similarities between (a) a parallel plate capacitor, with the surface perturbation of one of the metallic plates driven by an electric field [277], and (b) an anodic oxide, with a perturbed oxide/electrolyte interface, and through which an electric field E is present.

oxide dielectric with relative permittivity ε_r should then be equal to:

$$\lambda_c = \sqrt{\frac{4\pi^2 h_{ox} \gamma}{\varepsilon_0 \varepsilon_r E^2}} \quad (5.7)$$

where h_{ox} is the oxide thickness upon perturbation, corresponding to the thickness of the dense barrier layer (further denoted as $h_{ox,b}$).

The objective of this section is to verify whether the initiation of pores in anodic oxides films and the selection of a pore spacing during the growth of these films can be rationalized by either of the two generic model, Equations (5.5) or (5.7) that are known from the literature to govern the stabilization of surface perturbations. This was done by combining internal stress data, taken *in situ* at different current densities during galvanostatic anodizing of aluminum in sulfuric acid or phosphoric acid, with morphological data on pore spacing and barrier oxide thickness obtained from cross-sectional electron microscopy. Figure 5.7 illustrates the typical anodic oxide film morphology for Al anodizing in both H_2SO_4 and H_3PO_4 electrolytes.

The dependencies of the barrier layer thickness and pore spacing on current density are shown in Figure 5.8. It can be seen that, as expected, the barrier layer thickness and pore spacing are much smaller for the anodic oxides grown in sulfuric acid (Fig. 5.8(a)) than for the oxides grown in phosphoric acid (Fig. 5.8(b)). In both cases however, the barrier layer thickness and pore spacing increase with current density, and increase therefore with the anodizing voltage, as the steady-state

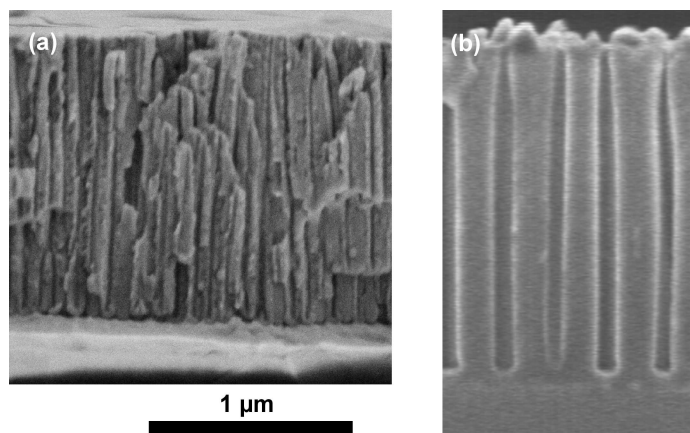


Figure 5.7: Cross-sectional scanning electron micrographs of Al films anodized at 50 mA cm^{-2} in $1.0 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ (a) and $0.4 \text{ mol l}^{-1} \text{ H}_3\text{PO}_4$ (b).

plateau voltage at which the anodic oxide films were grown increases with the current density, as shown in Figure 5.9(a).

The electric field in the oxide was calculated as the ratio between the steady-state voltage and the barrier layer thickness observed at the end of anodizing. It can be seen from Figure 5.9(b) that in H_3PO_4 the electric field increases from 0.85 to 0.95 V nm^{-1} in the current density range from 2.0 to 50 mA cm^{-2} . The trends reported for H_2SO_4 anodizing are very similar to those for H_3PO_4 anodizing. The electric field is however systematically 0.1 V nm^{-1} lower (except for one of the data points). Due to the smaller barrier layer thickness for anodizing in H_2SO_4 , the error on calculating the electric field is possibly higher compared to anodizing in H_3PO_4 . Note that the electric field values calculated for our porous anodic alumina films are consistent with typical values for Al anodizing [20].

Finally, the dependency of the internal stress during the initial barrier layer growth on current density is shown in Figure 5.10, for Al anodizing in phosphoric acid. Similarly to anodizing in sulfuric acid (Fig. 5.1), the internal stress during the initial barrier layer growth was found to remain constant in phosphoric acid as well, as illustrated in Figure 5.11. The stress was not measured during anodizing in H_2SO_4 for the samples in Figs. 5.8 and 5.9. However, as it will be seen in section 5.3,

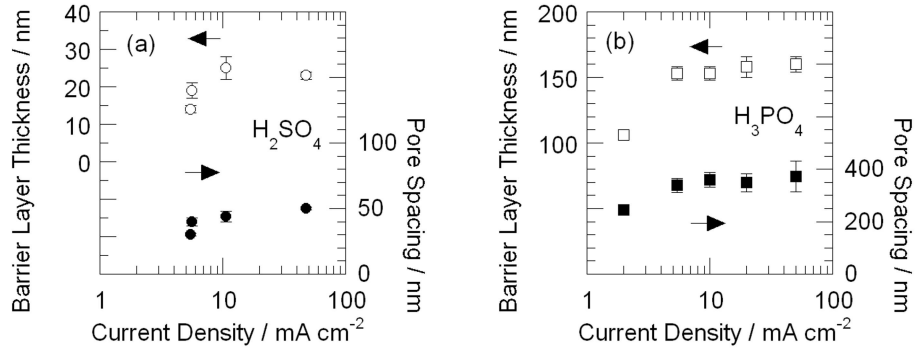


Figure 5.8: Dependence of barrier layer thickness and pore spacing on current density for Al anodizing in 1.0 mol l⁻¹ H₂SO₄ (a) and 0.4 mol l⁻¹ H₃PO₄ (b).

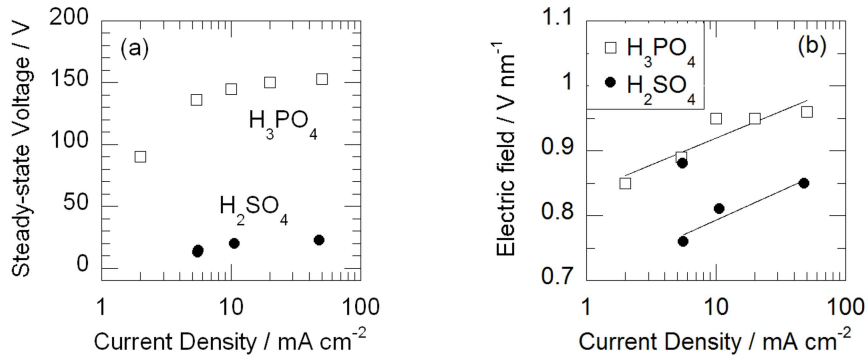


Figure 5.9: Dependence of (a) the steady state anodizing voltage and (b) the electric field in the barrier layer on the current density for Al anodizing in 1.0 mol l⁻¹ H₂SO₄ and 0.4 mol l⁻¹ H₃PO₄. The fit for H₂SO₄ excludes the out-of-fit data point.

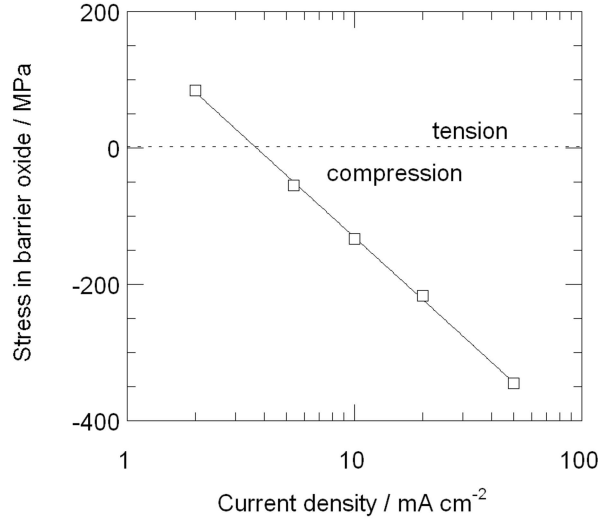


Figure 5.10: Dependence of the internal stress during the barrier layer growth stage on the current density for Al anodizing in $0.4 \text{ mol l}^{-1} \text{ H}_3\text{PO}_4$.

the same trend is found for sulfuric acid anodizing than for phosphoric acid anodizing.

It can be seen in Figure 5.10 that the internal stress value increases in the compressive direction with increasing current density. When the current density is lower than 3.6 mA cm^{-2} , the internal stress in the barrier oxide is tensile, while at higher current densities, the internal stress is compressive.

The very existence of a current density at about 3.6 mA cm^{-2} at which the internal stress in the barrier oxide is zero makes the hypothesis of an internal stress-induced perturbation unlikely. Indeed, from Equation (5.5), when the internal stress tends to zero, the pore spacing should become very large. However, this behavior is not observed given the continuous increase of pore spacing with current density (cfr. Figure 5.8). Furthermore, the tensile to compressive stress transition also implies that the proportionality between pore spacing and σ_{ox}^{-2} expected from Equation (5.5) for an internal stress-induced perturbation is not validated. This provides another indication that strain energy is

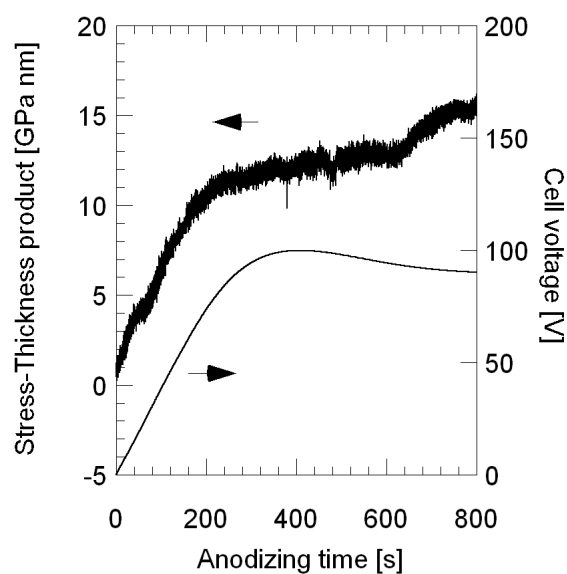


Figure 5.11: Stress-thickness product and cell voltage evolution for Al anodizing at 2 mA cm^{-2} in 0.4 mol l^{-1} phosphoric acid.

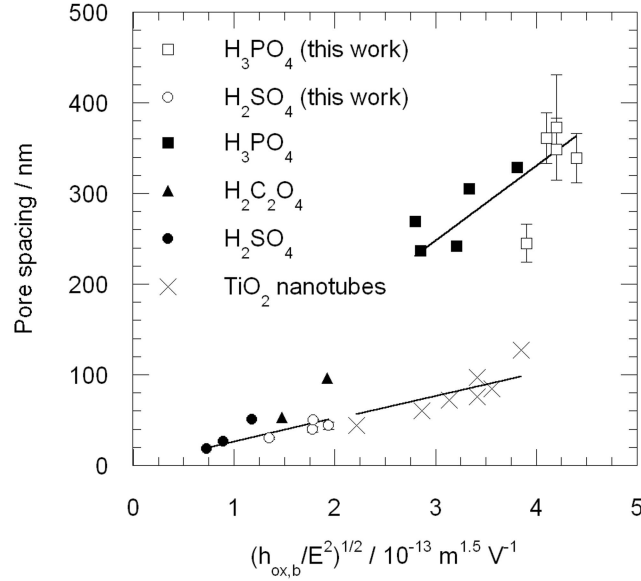


Figure 5.12: Dependence of measured pore spacing on measured ratio between the square root of barrier layer thickness ($h_{ox,b}$) and electrical field (E), compiled for a wide range of galvanostatic (this work) and potentiostatic anodizing conditions (H_3PO_4 [93], H_2SO_4 and $\text{H}_2\text{C}_2\text{O}_4$ [278], TiO_2 [137]). Linearity and slope values are consistent with Equation (5.7).

unlikely to be the factor controlling the pore spacing in anodic oxides.

However, in the case of an electrostatic energy-driven instability, Equation (5.7) predicts a linear proportionality between the pore spacing λ and $(h_{ox,b}/E^2)^{1/2}$, the slope being equal to $2\pi(\gamma(\epsilon_0\epsilon_r)^{-1})^{1/2}$. Such a correlation is represented in Figure 5.12, not only for our own porous anodic alumina films, but also for data sets compiled from the literature, including porous anodic alumina obtained in different electrolytes [93,278] and titania nanotubes [137], all these anodic oxides being grown potentiostatically.

It can be seen, first of all, that the proportionality predicted by Equation (5.7) between λ_c and $(h_{ox,b}/E^2)^{1/2}$ is indeed validated. More-

over, more quantitatively, Figure 5.12 also points to different slopes, i.e. different scaling factors determining the pore spacing in the different anodic oxides being considered.

Regarding these scaling factors, taking a relative permittivity (ϵ_r) of 9 and 55 for, respectively, anodic alumina [20] and anodic titania [63], and assuming that this value is independent of the electrolyte, values of the surface energy (γ) can then be calculated. For anodic alumina in phosphoric acid, oxalic acid and sulfuric acid, this gives γ -values of $1.38 \pm 0.22 \text{ J m}^{-2}$, 0.41 J m^{-2} , and $0.14 \pm 0.06 \text{ J m}^{-2}$, respectively. From the data set in Figure 5.12 on anodic titania, which concerns an electrolyte composed of ethylene glycol, hydrofluoric acid and water, the calculated surface energy is $0.80 \pm 0.25 \text{ J m}^{-2}$. The latter value is in agreement with the one reported for the anatase phase of titania (0.74 J m^{-2} [279]), while the ones calculated for anodic alumina can be considered realistic as well, despite the wide range of experimental values reported for alumina in the literature (from 0.03 J m^{-2} [280] to 1.52 J m^{-2} [281]).

Regarding the dependence revealed in Figure 5.12 of the surface energy for anodic alumina on the electrolyte used during anodizing, this can be attributed to the effect of ab- or ad-sorbed anions. Regarding the effect of absorption, a clear influence of sulphate content on the surface energy has been measured in reference 281. The surface energy of sulphate-contaminated alumina was found to be about 0.6 J m^{-2} lower than that of pure alumina. Regarding the effect of adsorption, Sato predicted that adsorbed anions tends to decrease surface energy [221]. In this respect, the difference in surface energy of anodic alumina in sulphuric or oxalic acid as compared to phosphoric acid can be taken as indicative for differences in the adsorption behavior of SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$ or PO_4^{3-} anions on the alumina surface during anodizing, which has been suggested to be strongly dependent on the valence of the adsorbed anion [111].

Furthermore, the obtained dependence of the surface energy on the type of anion in the electrolyte indicates that the instability leading to the formation of pores occurs at oxide/electrolyte interface. Indeed, while Equation (5.7) would still remain valid in the case of a surface perturbation at the metal/oxide interface, a dependence of the interfacial energy of the metal/oxide interface on the type of anions in the electrolyte is not anticipated. Indeed, the anodic oxide formed at this interface is relatively pure, as we have seen in section 2.3.

The rationalization presented here, stating that pore spacing selection arises more likely from the competition between surface and electrostatic energy, rather than from the contribution of strain energy terms, provides for the first time a rigorous and quantitative framework to understand why pores appear in anodic oxides and which parameters control their spacing. It should be acknowledged though that the experimentally observed steady-state pore spacing does not necessarily correspond to the critical wavelength λ_c , but rather to the fastest growing wavelength. This wavelength is proportional to λ_c , the proportionality constant depending on the exact transport mechanism [149,276,277,282]. Given the realistic values of surface energies obtained in the above analysis, it is expected that the transport mechanism allowing the perturbation to develop in the case of anodic oxide films is such that the proportionality factor is very close to one. Hence, the above used perturbation analysis, giving explicit expressions for λ_c (i.e. Eqs. (5.5) and (5.7)), is believed to keep its relevance when linked up with experimentally observed steady-state pore and tube spacings.

Finally, while the above energetic considerations rationalize the dependence of pore spacing on anodizing conditions, the kinetics of oxide growth must be considered as well. Indeed, while all parameters in Equations (5.7) are of the same order of magnitude when anodizing is performed in electrolytes yielding dense barrier anodic oxide films, no porous films forms. In fact, if surface perturbations appear in such electrolytes, an electric field increase at thinner oxide locations would cause enhanced oxide formation at the oxide / electrolyte interface, thus decaying the perturbation. On the other hand, because no oxide forms at the oxide / electrolyte interface in pore-forming electrolytes, surface perturbations can amplify.

5.3 The role of internal stress on pore growth

As we have seen in section 2.3, the growth of the porous layer in anodic oxide films occurs by oxide flow from the barrier layer to the porous layer. This mechanism is consistent with our observation of an increase in the rate of curvature change upon porosity initiation.

By performing simulations of the viscous flow of anodic alumina in an invariant geometry, Houser and Hebert found that the flow velocity

$\mathbf{v}$ was the highest in the radial direction of the pores, as illustrated in Figure 5.13 [107]. By approximating the flow as a radially directed flow in spherical coordinates, spreading from the pore bottom into the oxide ($\mathbf{v} = v_r \hat{\mathbf{r}}$) one obtains from Navier-Stokes equation that:

$$0 = \frac{1}{\eta} \frac{\partial \sigma}{\partial r} + 2 \frac{\partial^2 v_r}{\partial r^2} + \frac{4}{r} \frac{\partial v_r}{\partial r} - \frac{4}{r^2} v_r + \frac{1}{r^2} \left(\frac{\partial^2 v_r}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial v_r}{\partial \theta} \right) \quad (5.8)$$

where σ is the biaxial stress and η is the viscosity.

Taking order-of-magnitude estimates for the derivatives ($\partial/\partial r \sim 1/h_b$ and $\partial/\partial \theta \sim 0$) and $r \sim R$ where R is the oxide cell radius of curvature which is indicated in Figure 5.13, one obtains that:

$$\frac{1}{\eta} \frac{1}{v_r} \sigma h_b \sim 2 \left(1 + 2 \frac{h_b}{R} - 2 \left(\frac{h_b}{R} \right)^2 \right) \quad (5.9)$$

Because h_b and R are of the same order of magnitude, the viscosity can be estimated as:

$$\eta \sim \frac{\sigma h_b}{2 v_r} \quad (5.10)$$

The viscosity estimate from Equation (5.10) is formally similar to the “effective” viscosity, estimated from the “effective” stress σ_e and strain rate $\dot{\epsilon}$. Indeed, the constitutive law for Newtonian viscous flow is written:

$$\dot{\epsilon} = \frac{\sigma_e}{\eta_e} \quad (5.11)$$

where η_e is the “effective” oxide viscosity.

Considering the typical anodic oxide film morphology on Figure 5.14, the strain rate can be defined in first approximation as the ratio of the porous layer growth rate dh_p/dt to the barrier layer thickness h_b :

$$\dot{\epsilon} = \frac{1}{h_b} \frac{dh_p}{dt} \quad (5.12)$$

Combining Eqs. (5.11) and (5.12) yields:

$$\eta_e = \frac{\sigma_e h_b}{dh_p/dt} \quad (5.13)$$

Comparing Eq. (5.10) with Eq. (5.13) shows that the measured “effective” oxide viscosity provides a rough estimate of the actual oxide viscosity.

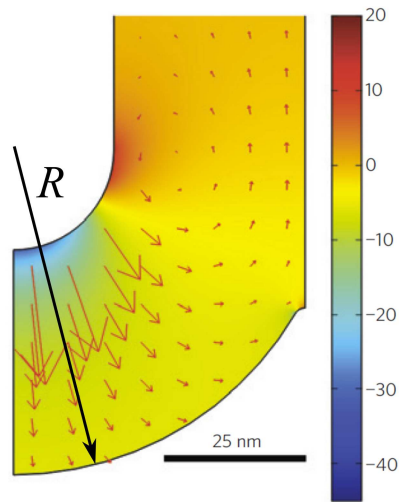


Figure 5.13: Predicted dimensionless hydrostatic stress and oxide velocity vectors from modeling oxide growth by electric-field driven ionic transport coupled with oxide viscous flow. Reproduced from reference 107.

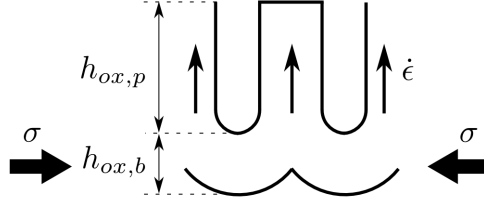


Figure 5.14: Schematic illustration of the porous anodic oxide film morphology considered. The thickness of the barrier and porous layer are h_b and h_p , respectively.

The reason for using an “effective” stress to estimate the effective viscosity is that a stress gradient is needed for material flow to occur. Indeed, a stress gradient creates a concentration gradient which is the actual driving force for mass transport. Such a stress gradient may exist despite a constant measured internal stress if, for instance, the stress is equal to zero at the unconstrained oxide / electrolyte interface [61].

Depending on the origin of stress gradients in the anodic oxide film, a change of sign of the internal stress in the barrier layer could imply that the direction of the flow changes. Our stress measurements indicate that the internal stress is not always of the same sign. Indeed, internal tensile stresses were measured for Al anodizing at low current densities, and Al(Si, Cu) anodizing, whereas the stress was compressive for Al anodizing at higher current densities as illustrated on Figure 5.15. Therefore, only the experiments for which the measured stress was compressive were considered first. All the experiments will however be considered later, when the electrostatic stress σ^{ES} will be used as the effective stress to calculate the oxide viscosity. In that case, stress gradients in the film are caused by electric field gradients.

The barrier layer thickness h_b was measured for phosphoric acid anodizing. On the other hand, it was assumed to be proportional to the plateau voltage for sulfuric acid anodizing ($AR = 1.1 \text{ nm V}^{-1}$). The growth rate of the porous layer dh_p/dt was calculated as the ratio of the thickness of the porous layer to the anodizing time during the porous layer growth. The time at which the porous layer starts growing was taken as the time at which the increase in the rate of curvature change

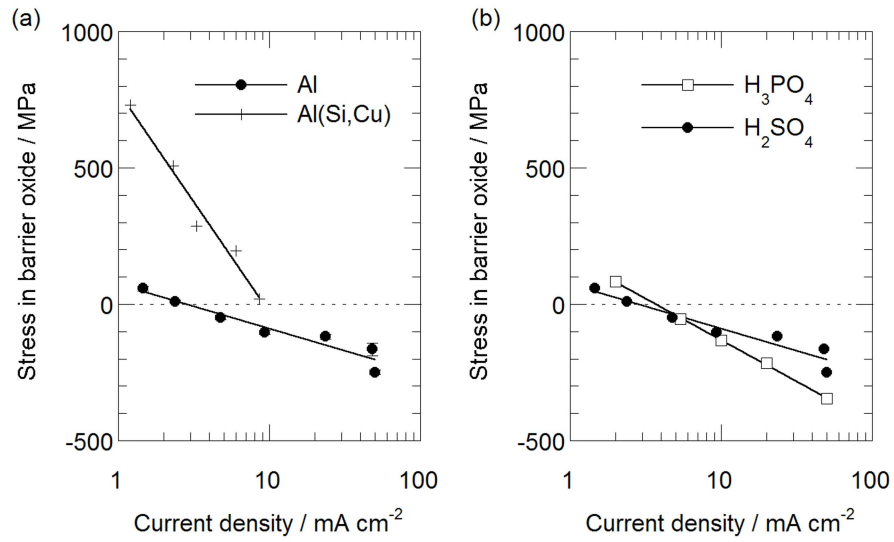


Figure 5.15: Dependence of stress during barrier layer growth stage on current density for (a) Al and Al(Si,Cu) anodizing in 1.0 mol l⁻¹ H₂SO₄ and (b) Al anodizing in 1.0 mol l⁻¹ H₂SO₄ and 0.4 mol l⁻¹ H₃PO₄.

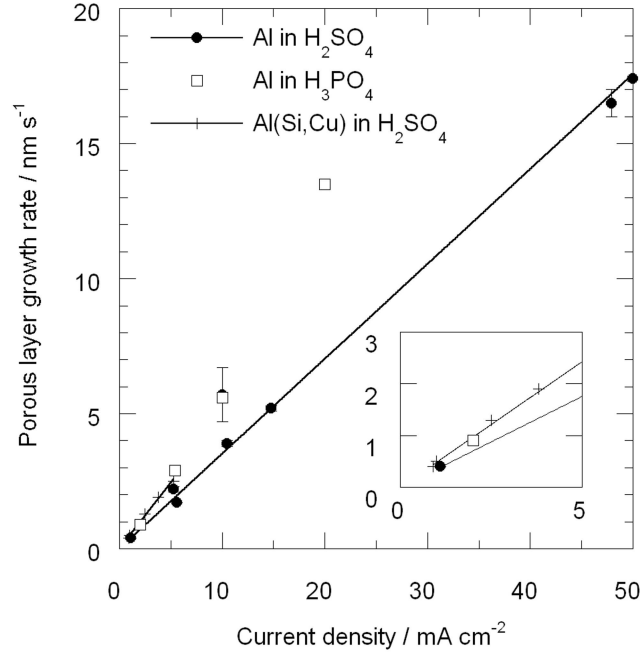


Figure 5.16: Growth rate of the porous layer for Al anodizing in $1.0 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ and $0.4 \text{ mol l}^{-1} \text{ H}_3\text{PO}_4$ and Al(Si,Cu) anodizing in $1.0 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$.

occurred, or as the time at which the voltage evolution was not linear anymore. The porous oxide thickness was measured from SEM cross-sections.

The samples anodized in sulfuric acid for which internal stress was measured were not anodized until the voltage reached a plateau. For these samples, the growth rate of the porous layer was assumed to be proportional to the current density. The proportionality ratio was calculated from the growth rate of the porous layer measured on another set of samples, anodized in sulfuric acid as well. The growth rate of the porous layer is shown in Figure 5.16 for Al anodizing in both H_3PO_4 and H_2SO_4 and Al(Si,Cu) anodizing in H_2SO_4 , as a function of the current density. The least square linear regression of the data in Figure 5.16 was used to calculate the growth rate of the porous layer for samples anodized in sulfuric acid.

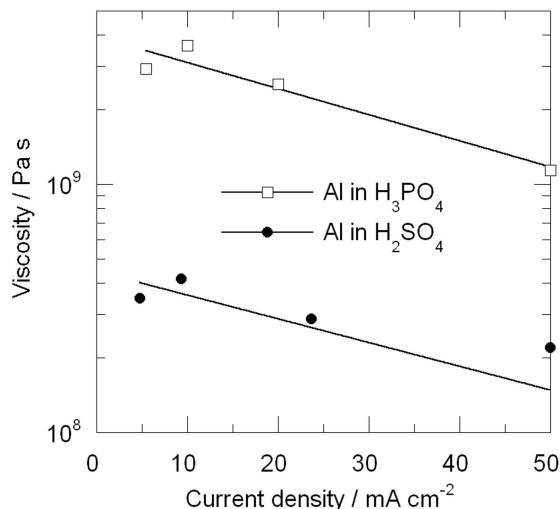


Figure 5.17: Viscosity of anodic alumina for Al anodizing in 1.0 mol l^{-1} H_2SO_4 and 0.4 mol l^{-1} H_3PO_4 , calculated from the measured average in-plane stress.

The viscosity of anodic alumina, calculated from Equations (5.11) and (5.12), is shown in Figure 5.17 as a function of the current density for Al anodizing in H_2SO_4 and H_3PO_4 . The calculated viscosity is of the order of 10^9 Pa s . The viscosity decreases with increasing current density, the fit in Figure 5.17 suggesting an exponential decrease. The oxide viscosity is an order of magnitude higher in phosphoric acid than in sulphuric acid.

As we have previously mentioned, stress gradients are needed for oxide flow to occur. Such stress gradients may originate from the gradients of the electric field in the oxide film, and the associated electrostatic stress gradients. Such stress gradients could explain qualitatively why oxide flow still occurs in some experimental conditions, although the measured average in-plane stress changes sign. Indeed, one could imagine that the in-plane stress gradients in the oxide layer do not change sign, although the average in-plane stress does. This situation is illustrated in Figure 5.18.

In that case, the stress gradients for oxide flow from the barrier layer

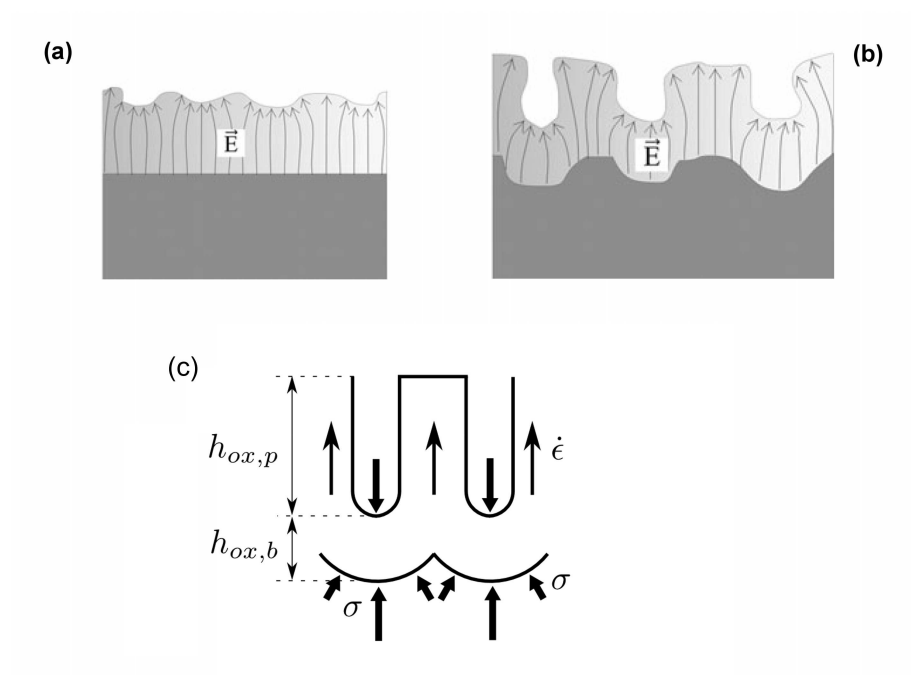


Figure 5.18: Schematic illustration of the porous anodic oxide film morphology with (a) and (b) non-uniform electric field, resulting in (c) non-uniform electrostatic stress in the barrier layer. Images (a) and (b) reproduced from reference 138.

5. Internal stress and porous anodic oxides

to the porous layer originate from the gradients of electrostatic stress in the oxide. The electrostatic stress σ^{ES} indeed depends on the electric field E in the anodic oxide, as quantified by Vanhumbecq and Proost, who obtained the following relationship for anodic oxide films:

$$\sigma^{ES} = -\frac{\nu_{ox}}{(1 - \nu_{ox})} \frac{\varepsilon_0}{2} [\varepsilon_r - (\alpha_1 + \alpha_2)] E^2 \quad (2.22)$$

where ν_{ox} is the Poisson ratio of the oxide, ε_0 is the vacuum permittivity, ε_r is the oxide relative permittivity and $\alpha_1 = -2/5(\varepsilon_r - 1)^2$ and $\alpha_2 = -1/3(\varepsilon_r - 1)(\varepsilon_r + 2) + 2/15(\varepsilon_r - 1)^2$ are electrostriction parameters [68]. The dependence of the electrostatic stress on the electric field for alumina ($\varepsilon_r = 8$), calculated using Equation (2.22), is shown in Figure 5.19. Typical electrostatic stresses in anodic alumina are of the order of -50 MPa. Using an electric field value of 0.9 V nm^{-1} for pure Al and Al(Si, Cu) anodized in sulfuric acid, and the measured electric field for Al anodized in phosphoric acid, allowed calculating the electrostatic stress in our anodic alumina films. Using the calculated electrostatic stress, the viscosity calculated from Equation (5.11) is represented in Figure 5.20 as a function of the current density. Since the electrostatic stress is compressive even when the average in-plane stress is tensile, viscosity values are also available for anodizing at low current densities, and Al(Si, Cu) anodizing. It can be seen that the average estimated viscosity calculated with the electrostatic stress is about the same order of magnitude than the viscosity calculated from the average in-plane stress. The same qualitative trends are observed whether the viscosity is calculated from the average in-plane stress or the electrostatic stress. Indeed, the viscosity decreases when the current density increases and the calculated viscosity for anodic alumina in sulfuric acid is lower than for anodic alumina in phosphoric acid. However, the viscosity decrease when the current density is increased from 1 mA cm^{-2} to 50 mA cm^{-2} is about one order of magnitude higher when the viscosity is calculated from the electrostatic stress rather than from the average in-plane stress. The dependence of the viscosity on the electrolyte used for anodizing could suggest that either the nature of incorporated electrolyte species or their distribution in the anodic aluminum oxide film either modifies the properties or the concentration gradients of defects through which oxide flow occurs. Similarly, the viscosity decrease when the current density increases suggests an increase of the gradient of defect concentration

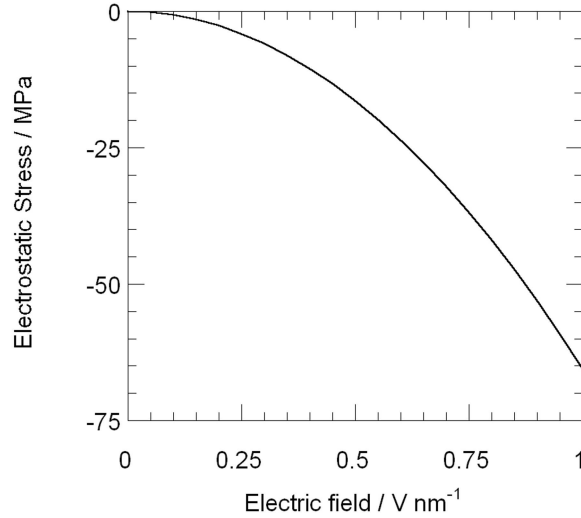


Figure 5.19: Electrostatic stress in anodic alumina as a function of the electric field.

through which oxide flow occurs. An increase of defect concentration, possibly accompanied by an increase in the defect concentration gradients, is consistent with the decrease of the oxide density when the current density increases [116, 117, 283]. This suggests that vacancies in anodic oxides play a key role for the flow.

As a final concluding remark, it should be pointed out that the internal stresses measured in our porous anodic aluminum oxides do not differ much from the internal stress in barrier anodic oxides. Indeed, internal stresses for pure Al anodizing in ammonium pentaborate range from 200 to -200 MPa when the current density increases from 0.5 to 50 mA cm^{-2} . This is illustrated in Figure 5.21, together with internal stress reported by Bradhurst and Leach for pure Al anodizing in ammonium borate [57]. Furthermore, internal stresses of the same order of magnitude were measured for anodizing of the Al(Si, Cu) alloy in either ammonium pentaborate or sulphuric acid at 5 mA cm^{-2} . The similar stress values and dependence on the current density suggest that stress generation mechanisms in porous and dense anodic oxide films are not fundamentally different. Although a logarithmic dependence of stress on

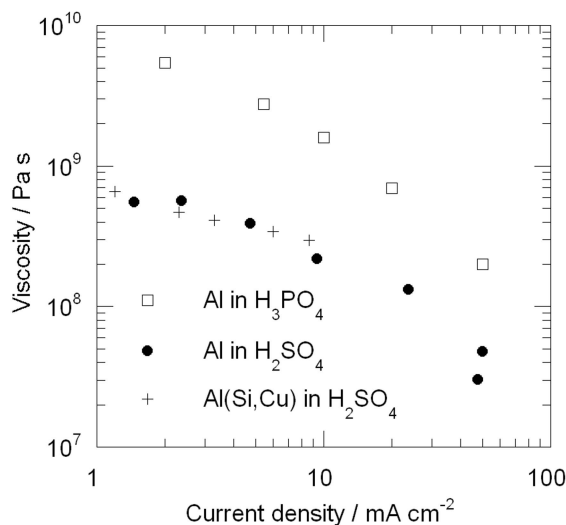


Figure 5.20: Viscosity of anodic alumina for Al anodizing in 1.0 mol l^{-1} H_2SO_4 and 0.4 mol l^{-1} H_3PO_4 and Al(Si,Cu) anodizing in 1.0 mol l^{-1} H_2SO_4 , calculated from the electrostatic stress in the barrier layer.

current density has been identified for all the anodizing conditions used in this work, it must be acknowledged that the origin of this dependence is still unclear.

5.4 Conclusions

In this chapter, the role of internal stress on pore initiation and pore growth was studied.

First, we showed that pore initiation could be detected *in situ* by monitoring the curvature evolution during aluminum anodizing. When porosity initiates, the oxide growth rate increases, which is consistent with pore growth by oxide flow.

Second, energy-based perturbation criteria were examined to explain the appearance of porosity and the dependence of pore spacing on anodizing conditions. Internal stress data, measured *in situ* during galvanostatic aluminum anodizing, indicated that a strain-induced surface instability is unlikely to be the controlling factor for pore initiation and

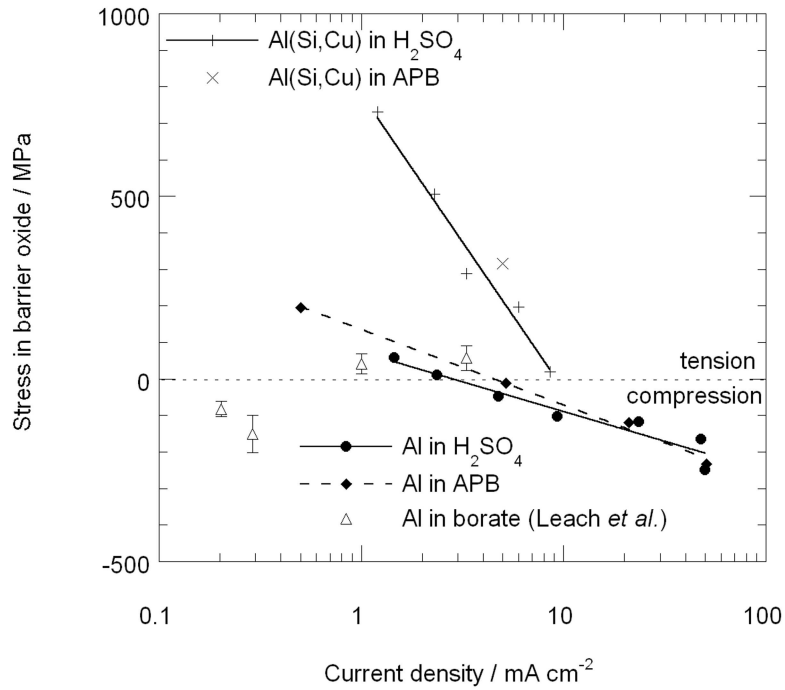


Figure 5.21: Dependence of stress during barrier layer growth stage on current density for pure Al anodizing in 1.0 mol l⁻¹ H₂SO₄, 0.01 mol l⁻¹ ammonium pentaborate (APB), or ammonium borate [57] and for Al(Si, Cu) anodizing in 1.0 mol l⁻¹ H₂SO₄ or 0.01 mol l⁻¹ APB.

pore spacing selection in anodic oxides. Instead, the observed pore spacing in anodic oxides of both aluminum and titanium, compiled for a wide range of galvanostatic and potentiostatic anodizing conditions, was found to be consistent with an electrostatic energy induced surface instability of the oxide/electrolyte interface. Anion ad- or absorption at this interface is a key factor for the pore spacing selection, through its influence on the surface energy.

Finally, the influence of stress on pore growth was studied. By combining internal stress and kinetic measurements for our porous anodic films, the viscosity of anodic alumina and its dependence on anodizing conditions could be evaluated. The viscosity of anodic alumina films grown in sulfuric acid was found to be lower than the one of films grown in phosphoric acid. The viscosity was also found to decrease when the current density increases. Such dependencies of the viscosity on experimental conditions are believed to be dependent on the concentration of vacancies in the anodic oxide.

The experiments described in this chapter were performed on anodic alumina, but because the growth mechanisms of porous anodic alumina and porous anodic oxides on other valve metals appear to be similar (see section 2.3), the generic conclusions presented here are believed to be generally applicable to porous anodic films on valve metals.

Chapter 6

Internal stress and the breakdown of anodic zirconia

As we have seen in section 2.4, two types of breakdown can take place during anodic oxide film growth. Type-I breakdown was associated with a decrease of the rate of voltage change and either holes or fissures in the anodic film (Fig. 2.25(b)). Type-II breakdown was associated with rapid fluctuations in the voltage-versus-time ($V-t$) curve and resulted in the arrest of the growth of the anodic oxide film (Fig. 2.25(a)).

Among the parameters that have been reported to affect anodic oxide film breakdown, internal stress is often cited [181], although a direct relationship between internal stress development and oxide breakdown in anodic oxide films has never been thoroughly established. Therefore, establishing a direct link between internal stress and breakdown would be of great value.

In this chapter, we demonstrate, by measuring the internal stress evolution in the oxide *in situ* during anodizing, that there is a direct relation between the internal stress level and the onset of type-I breakdown during the growth of anodic oxide films on zirconium in sulphuric acid. Based on electron diffractograms taken inside a transmission electron microscope (TEM) at different stages of anodizing, the origin of the breakdown could be related to stress-sensitive microstructural changes

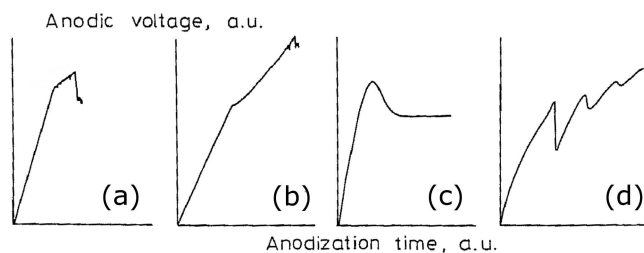


Figure 2.25: Schematic voltage evolution during galvanostatic anodizing of a valve metal in case of (a) type-II breakdown, or (b) type-I breakdown, followed by type-II breakdown. Not to be confused with (c) porous film formation nor (d) cyclic oxide growth / dissolution during silicon anodizing. Reproduced from reference 181.

occurring within the anodic zirconium oxide films. These changes are shown to result in an ionic efficiency decrease, which reduces the growth rate of the anodic zirconium oxide films.

Although we only studied the role of stress on type-I breakdown in this work, we believe that type-I breakdown may be a precursor for type-II breakdown. Indeed, as illustrated on Figure 2.25(a), the slope of the voltage evolution systematically decreases before the voltage fluctuations, which are indicative for type-II breakdown occur.

6.1 A new definition of breakdown

Before proceeding further, what the breakdown of anodic oxide films means must be precisely defined. Indeed, there has been much confusion in the literature about the breakdown of anodic oxide films, owing to the fact that the generic term “breakdown” has been used to describe different phenomena.

Some of the confusion seems to arise from the fact that “breakdown” has been used for a long time in different fields, namely the field of corrosion and solid-state physics. In the field of corrosion, the breakdown of a passive film relates to the loss of anti-corrosion properties of a passive film on a metal [284]. The breakdown of passive films may be caused by aggressive anions, such as Cl^- or F^- . This usually leads to pitting

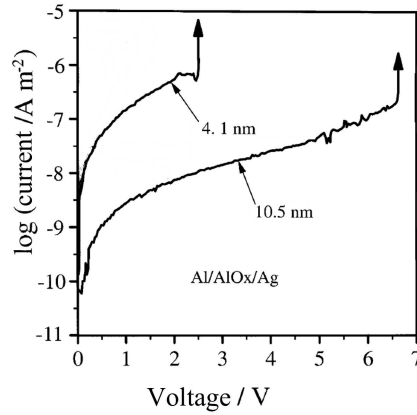


Figure 6.1: Current - voltage plot of a Al / anodic alumina / Ag structure, illustrating breakdown of dry anodic oxide films, which occurs at the voltage at which the current increases dramatically, indicated by the upper arrows. Reproduced from reference 287.

of the metal. This type of “breakdown” may be observed with anodic oxide films on aluminum that are cathodically biased [285], or during the growth of anodic films in fluoride-containing electrolytes [286]. This type of breakdown has not been studied in this work.

In the field of solid-state physics, “breakdown” refers to the sudden increase of the electronic current in an insulator or a semiconductor. In that case, a large current develops in the solid, eventually resulting in the loss of its dielectric properties. The latter type of breakdown has been observed on anodic oxide films used in dry solid state devices, such as metal/insulator/metal structures. This type of breakdown is illustrated in Figure 6.1, where the current vs. voltage plot of an Al / anodic Al_2O_3 / Ag multilayer structure is represented. The voltage at which breakdown occurs in such structures has been reported to be equal to the voltage at which the anodic oxide film was formed [287,288]. Thus, if one wants to increase the voltage that can be reached with such a dry structure prior to breakdown, one should increase the voltage up to which the anodic oxide film is grown, which is actually limited by type-II breakdown.

The latter type of breakdown is the one that has been studied in this thesis. It can be defined as the breakdown that practically limits the

thickness (or final formation voltage) of anodic films. This type of breakdown happens *during the growth* of anodic films. Within this definition, two types of breakdown have been identified in the anodizing literature. The first type of breakdown practically limits the film thickness because the number of defects in the film suddenly increases [73, 171, 172]. The anodic film can be further thickened, but due to the defects it will not be homogeneous anymore. We call it type-I breakdown in this work.

The second type of breakdown occurring during the growth of anodic oxide films limits the thickness of the anodic film [13, 84, 172–176]. Once such breakdown occurs, the thickness of the film does not increase anymore. We call it type-II breakdown in this work.

6.2 Experimental details

The zirconium films have been deposited by sputtering onto oxidized silicon wafers in two different batches, giving an average zirconium thickness of, respectively, 235 nm and 440 nm. The mean internal stress in the deposited zirconium metal was measured to be -80 MPa and -40 MPa for the 235 and 440 nm batch, respectively, by measuring the change in curvature resulting from complete Zr metal layer dissolution in a 10:45:45 mixture (volume ratio) of hydrofluoric acid:isopropyl alcohol:water. The average stress in the consumed metal was assumed constant, because the internal stress in sputtered zirconium has been reported, except for the very first thirty nanometers, to be essentially constant throughout its entire thickness [289]. No fundamental difference was observed in the anodizing behavior of the Zr coming from the different batches.

The thin film cantilevers were then anodized in 0.05 or 1.0 mol l^{-1} sulphuric acid (H_2SO_4) at room temperature. Anodizing was performed galvanostatically at current densities ranging from 0.6 to 250 mA cm^{-2} . The *in situ* stress measurements were only performed in the current density range of 0.6 to 21 mA cm^{-2} .

6.3 Influence of the breakdown on the voltage evolution

6.3.1 Experimental results

Figure 6.2 shows a typical evolution of both the cell voltage and the stress-thickness product as a function of anodizing time, as measured for a sample anodized at 9.4 mA cm^{-2} in $0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$. The cell voltage initially increased linearly with time, which is consistent with the growth of a dense barrier film. After passing through a local maximum, the rate of voltage change then decreased. This can be taken indicative for type-I breakdown to occur [171, 172].

Di Quarto *et al.* reported similar cell voltage evolutions during galvanostatic anodizing of zirconium in H_2SO_4 . The decrease of the rate of voltage change was attributed to the presence of cracks that covered the oxide surface [172].

A local cell voltage maximum was not observed for all experimental conditions, as illustrated on Figure 6.3. The reason for this, which has been further investigated, may be that the transition time between the first and second regime vary. As demonstrated in the case of an efficiency decrease during titanium anodizing, a local voltage maximum may show up in a more or less pronounced way, depending on the transition time from the high to the low efficiency regime and on the actual efficiency values before and after the transition [290].

In the experiments where the change of slope was more gradual and no local voltage maximum was observed, the moment of breakdown was arbitrarily defined as the time when the cell voltage derivative was halfway between its two steady-state values, as illustrated on Figure 6.3.

The voltage derivative with respect to the charge passed per unit area $q = j t$, before and after breakdown is represented in Figure 6.4 as a function of the current density j . Clearly, the voltage derivative decreases after breakdown. The mean ratio of the derivative before and after breakdown for all samples is equal to 1.8 ± 0.4 . To first elucidate the origin of the change of slope of the cell voltage evolution, the explicit expression for the voltage derivative, with respect to q is considered, using Equation (2.21):

$$\frac{dV}{dq} = \eta_i \eta_a \frac{M_{ox}}{\rho_{ox} z F} \frac{1}{(AR)} = \eta_i \eta_a \frac{M_{ox}}{\rho_{ox} z F} \frac{1}{\beta} \ln \left(\frac{\eta_i j}{j_0} \right) \quad (6.1)$$

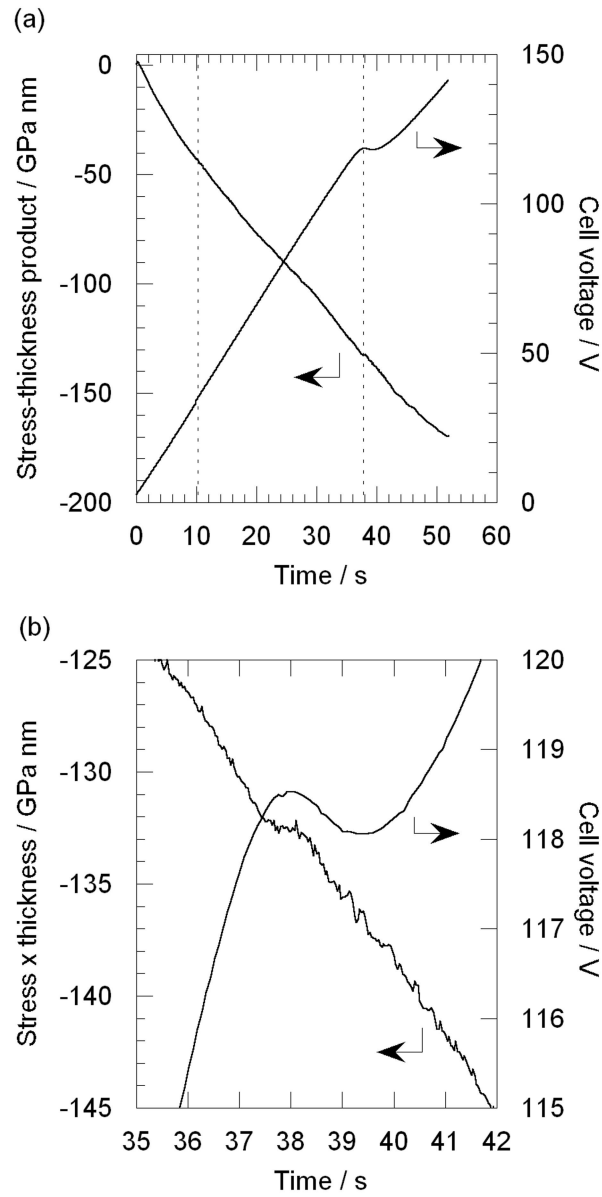


Figure 6.2: Time evolution of the cell voltage and stress-thickness product for a sample anodized at 9.4 mA cm^{-2} in $0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$. (a) global view of the curve and (b) zoom on the local cell voltage maximum.

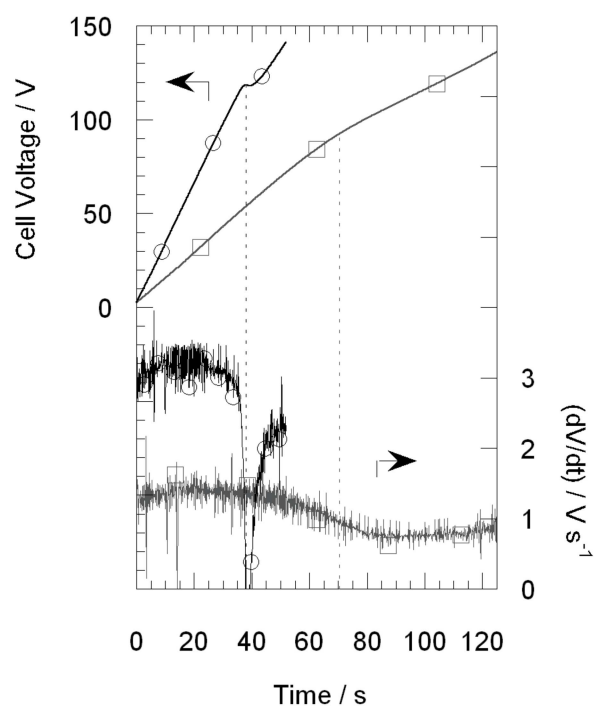


Figure 6.3: Time evolution of the cell voltage and its time derivative for samples anodized in $0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ at, respectively, 9.4 mA cm^{-2} (open circles) and 4.6 mA cm^{-2} (open squares).

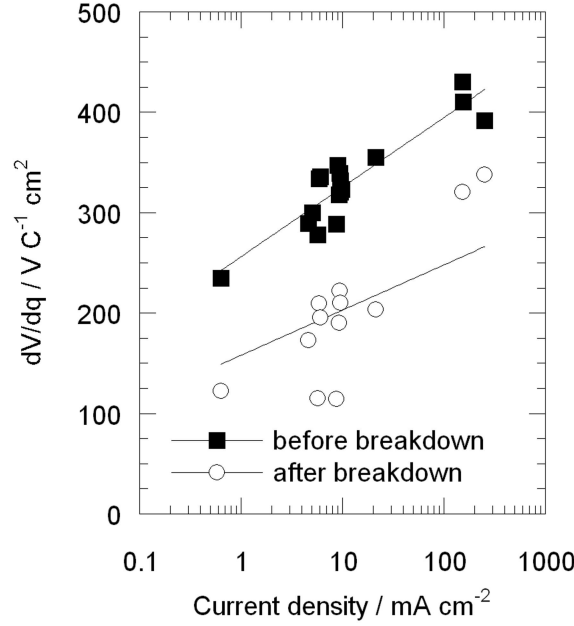


Figure 6.4: Derivative of the cell voltage with respect to charge per unit area before and after breakdown as a function of the current density for Zr anodizing in H_2SO_4 .

with M_{ox} , the molecular weight of the oxide, ρ_{ox} , its density, z its valence, (AR) the anodizing ratio, j_0 and β the high-field rate constants, and η_i and η_a , the ionic and anodizing efficiencies, respectively ¹. From Equation (6.1), a decrease of dV/dt , or equivalently, dV/dq can thus be due to either an ionic or anodizing efficiency decrease, an increase of the density of the oxide formed, or an increase of the anodizing ratio.

Note that these four parameters are not independent of one another, since a change of the oxide density, which would modify the ionic conductivity of the oxide through a change of the charge hopping distance, would then also modify the anodizing ratio. Similarly, a change of ionic efficiency would also modify the anodizing ratio by decreasing the ionic

¹As we have seen in section 2.2.2, the ionic efficiency indicates the amount of current used to oxidize the metal, while the anodizing efficiency indicates the amount of current effectively used to form the oxide film.

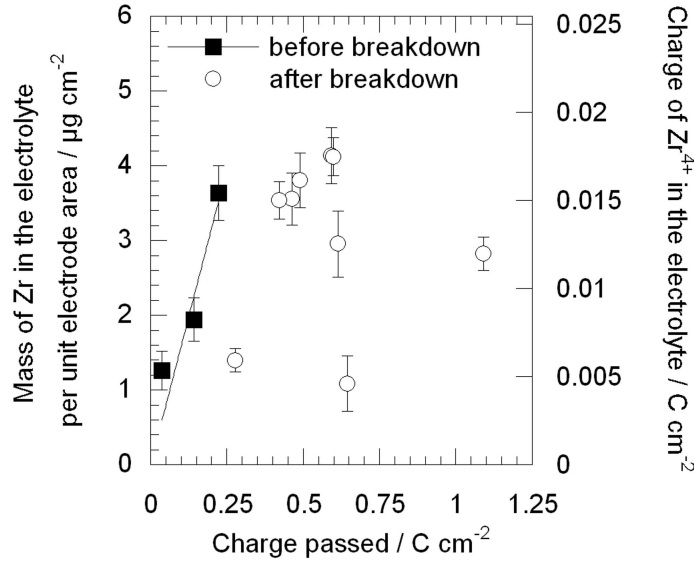


Figure 6.5: Mass loss of Zr per unit electrode area and corresponding charge measured by ICP-OES in the electrolyte as a function of the charge consumed.

current density.

A decrease of anodizing efficiency was first considered. As we have seen in section 2.2.2, a decrease of anodizing efficiency is either due to an increase of the rate of direct ejection of Zr in the electrolyte, or to an increase of the oxide dissolution rate. Therefore, the Zr content in the electrolyte after anodizing was measured by ICP-OES.

It can be seen from Figure 6.5 that the amount of Zr in the electrolyte after anodizing did not increase after breakdown, so that the dV/dt decrease cannot be attributed to an increased Zr loss in the electrolyte. In fact, from Fig. 6.5, it rather seems that the amount of Zr lost per unit charge decreased after breakdown occurred. This can be taken indicative as such for a decrease in ionic efficiency occurring after breakdown, as the rate of direct Zr^{4+} ions ejection in the electrolyte can be expected to decrease with decreasing ionic current density. Indeed, it can easily be shown that the rate of Zr mass loss per charge consumed is linked to

the anodizing efficiency by:

$$\frac{dm_{\text{Zr}}}{dq} = (1 - \eta_a)\eta_i \frac{M_{\text{Zr}}}{zF} \quad (6.2)$$

Equation (6.2) further indicates that a change of the oxide density alone can not explain both the decrease of the rate of voltage change and the decrease of the rate of Zr loss in the electrolyte.

To further test the assumption of an ionic efficiency decrease, cross-sections of samples anodized for different times were observed by scanning electron microscopy. Due to the uncertainty on the location of the oxide/metal interface, particularly at low oxide thicknesses, it is the change of the total thickness of both the metal and oxide layer that has been measured. This change Δh_{tot} is shown in Figure 6.6 as a function of charge for all the anodized samples. A decrease in the slope of the Δh_{tot} vs. charge curve is observed after breakdown occurred, the ratio between the two slopes being 1.9 ± 0.6 .

This slope change can be rationalized by considering an explicit expression for $d\Delta h_{\text{tot}}/dq$, based on the evolution of both the oxide (h_{ox}) and metal (h_{Zr}) thickness with the consumed charge per unit surface q , Equations (2.18) and (2.20):

$$\frac{dh_{\text{ox}}}{dq} = \eta_i \eta_a \frac{M_{\text{ox}}}{\rho_{\text{ox}} z F} \quad (6.3)$$

$$\frac{dh_{\text{Zr}}}{dq} = -\eta_i \frac{M_{\text{Zr}}}{\rho_{\text{Zr}} z F} \quad (6.4)$$

Combining these equations then results in:

$$\frac{d\Delta h_{\text{tot}}}{dq} = \frac{\eta_i}{zF} \left(\eta_a \frac{M_{\text{ox}}}{\rho_{\text{ox}}} - \frac{M_{\text{Zr}}}{\rho_{\text{Zr}}} \right) \quad (6.5)$$

Similarly to the decrease of the slope of the V - t curve, the decrease in slope of Δh_{tot} vs. q after breakdown can be attributed to either a decrease in the ionic or anodizing efficiency, or to an increase of the density of the oxide formed.

From the chemical measurements, a decrease of η_a has been excluded. Furthermore, the density difference between the three ZrO_2 polymorphs²

²monoclinic ZrO_2 : $\rho_{\text{ox}} = 5.7 \text{ g cm}^{-3}$, tetragonal ZrO_2 : $\rho_{\text{ox}} = 6.0 \text{ g cm}^{-3}$ and cubic ZrO_2 : $\rho_{\text{ox}} = 6.1 \text{ g cm}^{-3}$

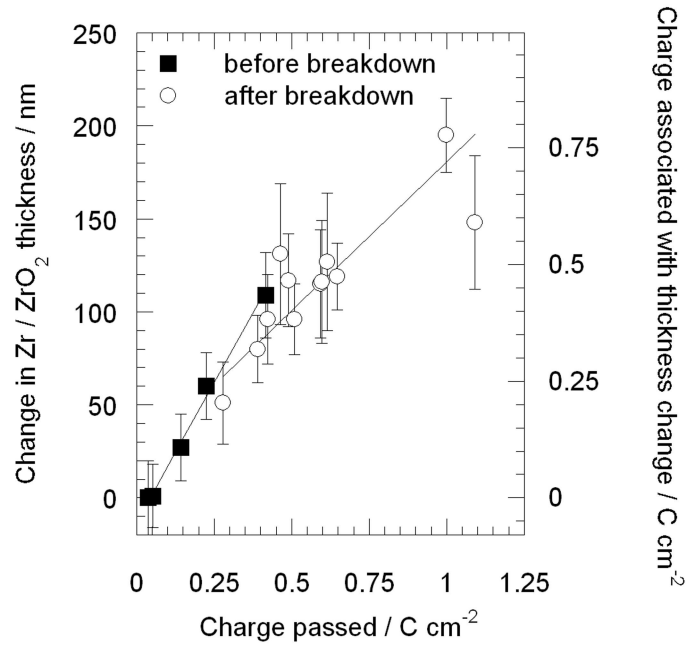


Figure 6.6: Change of total zirconium and zirconium oxide film thickness and corresponding charge per unit area as a function of the charge per unit area passed during anodizing. The charge was calculated assuming an anodizing efficiency of 1 and an oxide density of 5.0 g cm^{-3} .

is not large enough for the density alone to modify dV/dq and $d\Delta h_{tot}/dq$ by the amount observed. Therefore, only a decrease of ionic efficiency will be considered in the following.

6.3.2 Ionic conduction parameters

Combining Equations (6.2) and (6.5) allows calculating the ionic and anodizing efficiencies prior to breakdown from a linear fit of the data in Figure 6.5 and 6.6. The growth of monoclinic zirconia ($\rho_{ox} = 5.7 \text{ g cm}^{-3}$) was assumed prior to breakdown, as found by electron diffraction of the oxide films (cfr. section 6.4). Furthermore, it was assumed that $z = 4$, $M_{ox} = 123 \text{ g mol}^{-1}$ and $\rho_{Zr} = 6.1 \text{ g cm}^{-3}$.

Before breakdown, the ionic efficiency $\eta_i = 1.4 \pm 0.1$. The unrealistic high value of efficiency may be due to an overestimation of the density of our anodic films, since using a value for $\rho_{ox} = 5.0 \text{ g cm}^{-3}$ leads to efficiency values of $\eta_i = 1.0 \pm 0.1$ and $\eta_a = 0.93 \pm 0.1$. The density difference between our anodic zirconia films, and the one of relatively pure, defect-free zirconia may be ascribed to a higher number of defects, such as vacancies in the anodic films [291].

Using these efficiency and density values, the high-field rate constants β and j_0 can be calculated from Equation (6.1) and a linear fit of the data of Figure 6.4, prior breakdown. Values of $\beta = 19.6 \pm 2.2 \text{ nm V}^{-1}$ and $j_0 = (2.06 \pm 2.57) \times 10^{-4} \text{ mA cm}^{-2}$ were obtained. While our β value is of the same order of magnitude than literature values for bulk zirconium anodizing, our j_0 value is several orders of magnitude higher. From section 2.2.2, this could be due to a higher concentration of charge carriers in our anodic films. As charge transport in anodic zirconia presumably occurs along the zirconia grain boundaries [28], the small zirconia grain size anticipated from our small sputtered Zr grain size could make up for a higher concentration of grain boundaries, hence charge carriers, relative to the charge carrier concentration in coarser grained zirconia.

Nevertheless, these j_0 and β -values were used to calculate the anodizing ratio as a function of the ionic current density. A good agreement was obtained with one of the anodizing ratios calculated from literature values for β and j_0 , as can be seen in Figure 6.7. Our result also compares well with the reported value of 2 nm V^{-1} , for zirconia films obtained by anodizing sputtered Zr thin film substrates at 5 mA cm^{-2} [35].

Further assuming that only η_i changes after breakdown allows calcu-

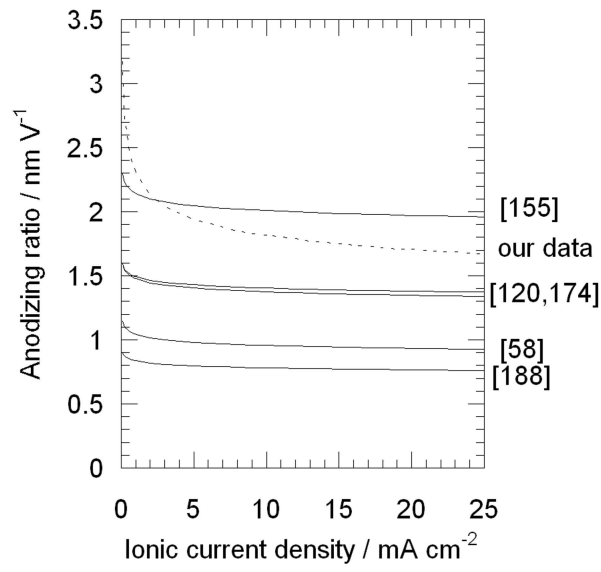


Figure 6.7: Dependence of the anodizing ratio on ionic current density, calculated from the high-field rate constants compiled for anodic zirconia in reference 20, and those calculated for our samples. Bracketed numbers refer to references in [20].

lating a mean ionic efficiency $\eta_i = 0.65 \pm 0.04$ from a linear fit of the post-breakdown data in Figure 6.4. It seems, however, from the scattering of values around the linear fit that the ionic efficiency after breakdown was different for some experiments (see Figure 6.4). The ionic efficiency decrease is probably caused by oxygen evolution.

6.3.3 Simulation of the voltage evolution

To obtain further insight into the transition mechanisms from a high to low efficiency, the voltage evolution was calculated assuming a progressive transition from the high to the low ionic efficiency described by the function:

$$\eta(t) = \eta_2 + \frac{(\eta_1 - \eta_2)}{\exp((t - t_m)/\alpha) + 1} \quad (6.6)$$

with η_1 and η_2 the ionic efficiencies before and after breakdown, respectively, t_m the time at which the efficiency is halfway between η_1 and η_2 , and α is a parameter representing the time needed for the transition to occur [290].

Using Equation (6.6) with the integrated form of Equation (6.1) yields the following expression for the voltage evolution:

$$V(t) = \frac{1}{(AR(t))} \left(\frac{M_{ox} j \eta_a}{\rho_{ox} z F} \int_0^t \eta(t) dt + h_0 \right) \quad (6.7)$$

where h_0 is the thickness of a possible native oxide layer on the anode surface. The anodizing ratio is then deduced from the calculated ionic efficiency (Eq. (6.6)) and the high-field rate constants obtained previously:

$$AR(t) = \frac{\beta}{\ln(\eta(t)) + \ln(j) - \ln(j_0)} \quad (6.8)$$

Four parameters ($\eta_1 \approx 1$, η_2 , t_m and α) can be adjusted in order for the calculated voltage evolution to fit the measured values. As seen in Figure 6.8, the calculated voltage evolution reproduced quite well the experimentally recorded voltage evolution for the two representative experiments of Figure 6.3. However, the agreement is less convincing in the case where a local voltage maximum was observed. The inability to exactly simulate the experiments where a local voltage maximum is present may be due to the fact that the transition from the high to the low efficiency is not described well by Equation (6.6), in the case of Zr

anodizing, compared to Ti-anodizing. The experiments where the voltage goes through a local maximum are probably characterized by a smaller transition time from the high to the low efficiency regime. However, the presence or absence of a local voltage maximum could not be linked in a systematic way to the current density, electrolyte concentration, or batch of deposited Zr.

6.4 Influence of breakdown on the microstructure

To further investigate the origin of the ionic efficiency decrease, samples anodized for different times were examined by TEM. Indeed, microstructural changes in anodic oxides have been associated to oxygen evolution [39]. A bright-field image and corresponding electron diffraction pattern typical of samples for which anodizing was ceased before breakdown occurred, are shown in Figure 6.9(a), together with the corresponding radial distribution of the diffracted intensity. Similarly, a plane-view TEM image and corresponding electron diffraction pattern representative of samples for which breakdown occurred are shown in Figure 6.9(b).

It can be seen that the relative intensity of the peaks at $0.33 \text{ \AA}^{-1}$ and $0.66 \text{ \AA}^{-1}$ increased after breakdown. This increase is due to an increase of, respectively, the (101) and (202) tetragonal ZrO_2 content, or the (111) and (222) cubic zirconia content in our oxide films. Other peaks, marked by the vertical dashed lines in Figure 6.9, indicate that the oxide film is still composed of monoclinic zirconia, whether breakdown had occurred or not.

From the bright-field images, the zirconia crystals can be estimated to be about 30 nm to 40 nm in size, although smaller crystals may be present as well. It can also be noted that the obtained diffraction patterns are characteristic for a well-textured oxide [292]. Indeed, the circles of the diffraction patterns in Figure 6.9 broke up into multiple arcs when the relative orientation between the electron beam and the texture axis varied. Unfortunately, the texture of the oxide films limited the number of peaks available for structure identification, so that it was not possible to discriminate between tetragonal and cubic zirconium oxide.

As we have shown, the observed decrease of dV/dt and of the rate

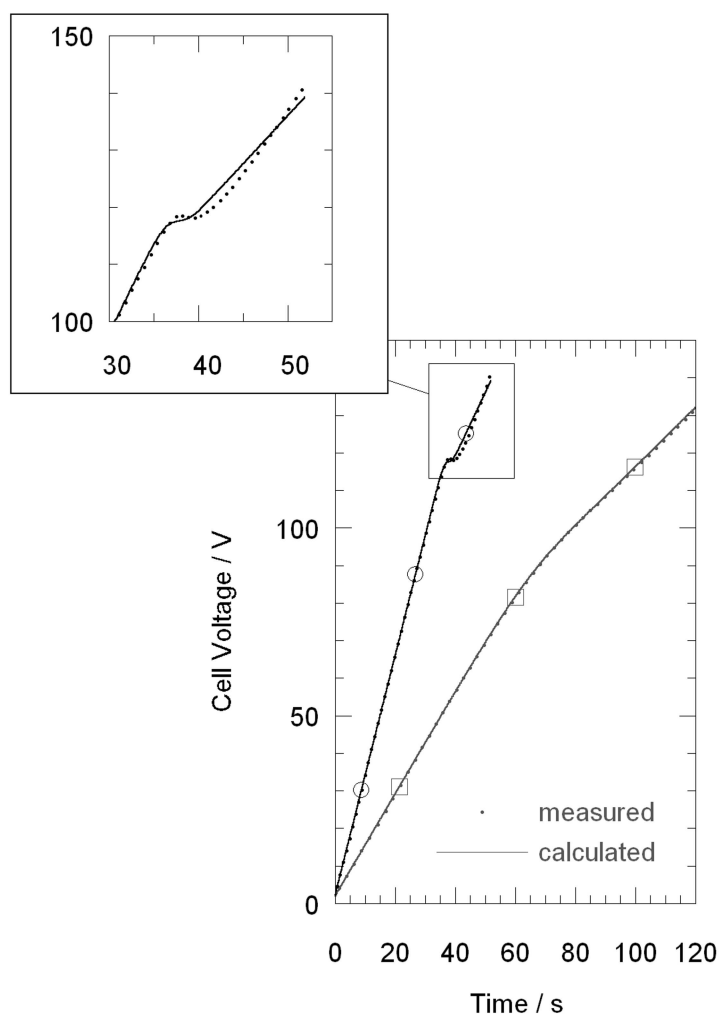


Figure 6.8: Simulated and measured time evolution of the cell voltage for samples anodized in $0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ at, respectively, 9.4 mA cm^{-2} (open circles) and 4.6 mA cm^{-2} (open squares).

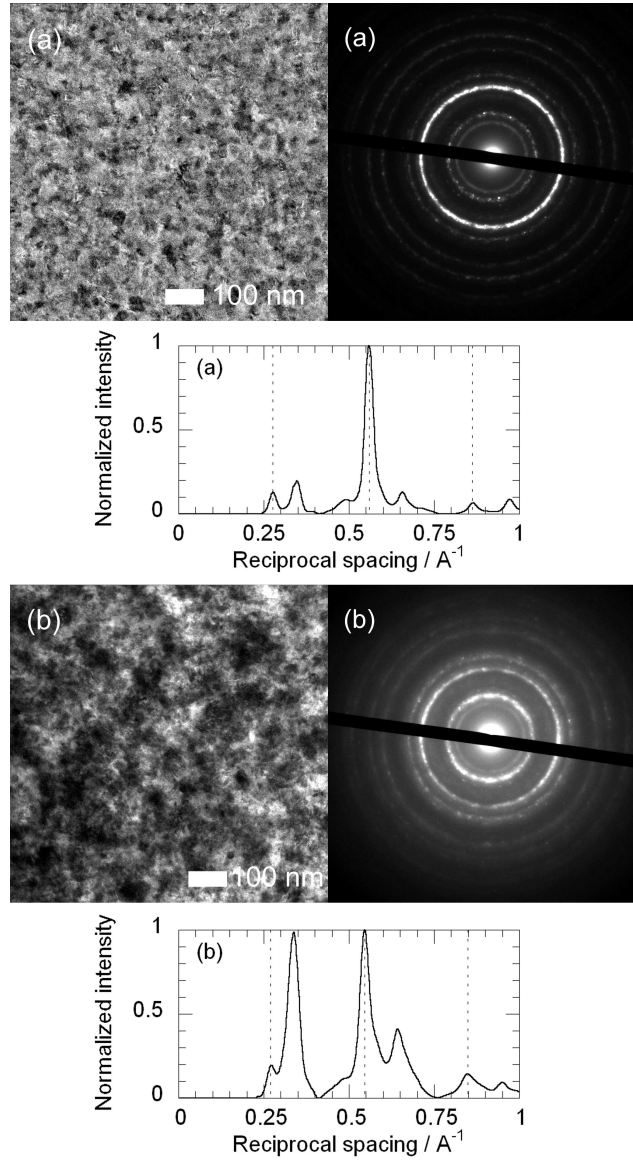


Figure 6.9: Bright-field TEM images, electron diffraction patterns and corresponding radial intensity distribution of oxide films grown in $0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ at 9.4 mA cm^{-2} to a voltage of (a) 50 V and (b) 140 V, i.e. before and after breakdown occurred (cfr. Fig. 6.2). Dashed vertical lines identify diffraction peaks from monoclinic zirconia.

of thickness change after breakdown can be attributed to a decrease of ionic efficiency. Ionic efficiency decrease during zirconium anodizing has been reported by investigators who observed oxygen evolution [13, 293]. Oxygen evolution is often related to the structure of the anodic oxide. During the growth of amorphous films, crystallization may trigger oxygen evolution by an associated increase of the electric field in the crystalline region [73].

However, our zirconium oxide films are already crystalline before the oxygen evolution reaction occurs, as was shown in Figure 6.9(a). Nonetheless, it has been suggested before [39] that cubic zirconia crystallites allow for oxygen evolution, while monoclinic zirconia does not, on the basis of the possibly higher electronic conductivity of cubic zirconia. At this time, only the bandgap value of monoclinic anodic ZrO_2 grown on sputter deposited Zr thin films has been documented, with a measured value of $4.80 \pm 0.05 \text{ eV}$ [294]. Unfortunately, there is currently no conclusive evidence in the anodizing literature on possible differences between the bandgap values of the different zirconia polymorphs, so that it cannot be excluded that all bandgap values are very similar [295, 296].

The higher electronic conductivity of our anodic oxide films after breakdown would then arise from a change in the type or amount of electronic defects, like oxygen interstitials or vacancies, which would be induced in turn by the microstructural changes associated with breakdown.

In-plane scanning electron microscopy revealed that the morphology of the zirconium oxide had changed after breakdown. Figure 6.10 shows that before the breakdown (b), the oxide surface is similar to that of the zirconium substrate (a), reproducing the roughness of the deposited-Zr grains, which are about 30 nm in diameter. After breakdown (c), the surface shows larger features of about 100 to 200 nm in diameter, and the surface roughness increases. Thus, in the case of our sputtered zirconium thin films, although we did observe a dV/dt decrease as Di Quarto *et al.* did [172], we did not observe any cracks on the oxide surface when anodizing into the second, lower efficiency regime after breakdown.

This can be related to the fact that our films probably have very different mechanical properties than those from Di Quarto *et al.*, which were grown on bulk zirconium, with for an instance a very different grain size. Indeed, once cubic or tetragonal zirconia crystallites appear and

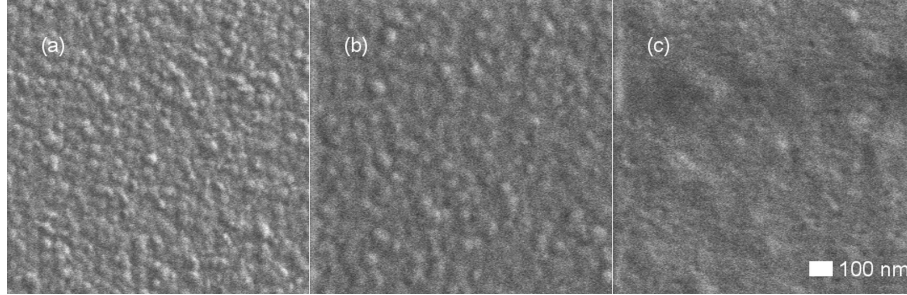


Figure 6.10: Scanning electron micrographs of (a) as-deposited zirconium, and of oxide films grown in $0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ at 9.4 mA/cm^2 up to (b) 50 V, i.e. before breakdown, and (c) 140 V, i.e. after breakdown.

grow in a matrix of monoclinic ZrO_2 , it can be expected that the internal stress in the oxide will not be homogeneously distributed around these second phase inclusions. As a result, the film morphology may change, for instance by cracking at locations where the tensile stress is high, or by a roughness increase where the compressive stress is high.

Depending on the size of the non-monoclinic crystallites and the grain size of the remaining monoclinic matrix, the internal stress distribution and hence the mechanical strength of the films will be different. This may be a qualitative explanation for the roughness increase after breakdown of our own oxide surface, grown on nanocrystalline zirconium, while Di Quarto *et al.* observed cracks after breakdown on anodized bulk zirconium for which the grains were several microns in size. Indeed, the grain size of our anodic zirconia films (30 to 40 nm from Figure 6.9) is of the same order of magnitude than the grain size of the as-deposited Zr films (Fig. 6.10 (a)).

6.5 The role of the internal stress on the breakdown

As to the stress-thickness product evolution, Figure 6.11(a) combines the data of Figure 6.2 by representing the stress-thickness product as a function of cell voltage, while Figure 6.11(b) represents the stress-thickness product as a function of the oxide thickness, the latter being calculated from the variable anodizing ratio of Figure 6.7.

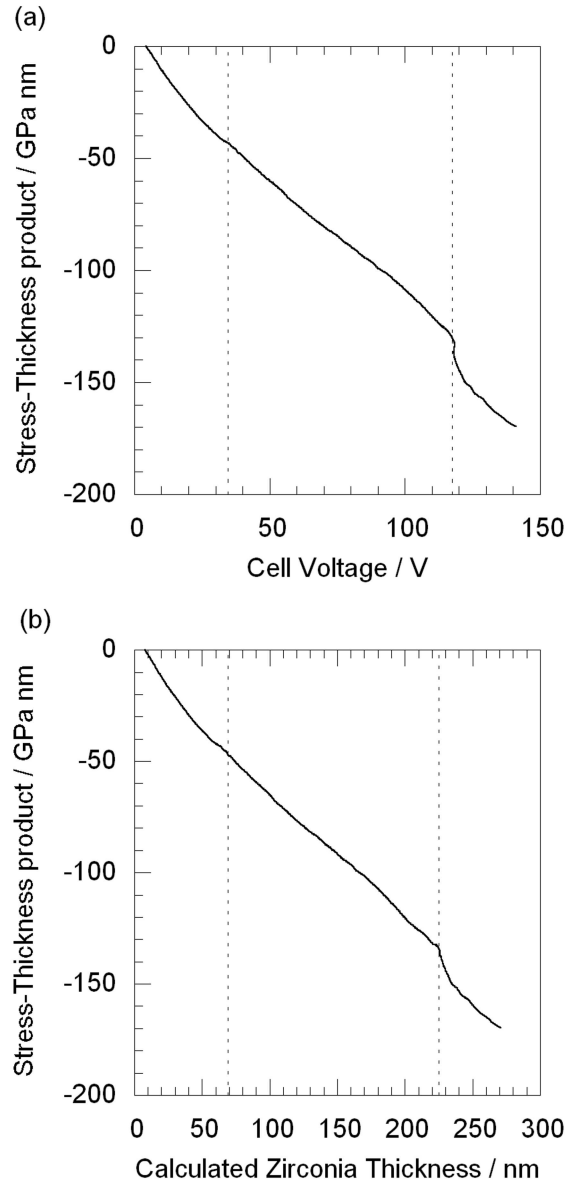


Figure 6.11: Stress-thickness product versus (a) voltage curve as obtained by combining the data from Figure 6.2 (b) anodic film thickness as obtained by the variable anodizing ratio in Equation (6.8).

Based on the changing slope of the stress-thickness product vs. thickness curve, three regimes have been identified by vertically dashed lines in Figure 6.11: the first one ranging up to about 35 V, the second one extending to the local voltage maximum, and the third one characteristic for the post-breakdown region. Note that for the first stress-thickness product transition occurring at 35 V (i.e. at about 10 s in Figure 6.2), no associated slope change in the cell voltage evolution is observed. As outlined previously, a negative, constant slope of the stress-thickness product vs. thickness curve is indicative for a constant incremental compressive internal stress σ_{ox} .

A marked influence of the incremental internal stress in the second regime (i.e. the one immediately preceding breakdown) on the charge at which breakdown occurred was observed. This is illustrated on Figure 6.12, on which the charge at breakdown was also transformed into the equivalent oxide thickness at breakdown, based on Equation (2.17). In Figure 6.12, variations in the magnitude of the internal stress have been induced by varying the current density, the sulphuric acid concentration, and the batch of deposited Zr metal. It is clearly seen that the more compressive the internal stress in the second regime, the smaller the charge at which breakdown occurred.

Regarding the effect of current density on the internal stress evolution, Figure 6.13 shows that increasing the current density decreased the magnitude of the incremental stress. This behavior is in qualitative agreement with results reported by Archibald and Leach [58]. While changing the electrolyte concentration between 0.05 and 1 mol l⁻¹ did not have any effect on the values reported in Figure 6.13, a large variation in the magnitude of the internal stress evolution was found when anodizing Zr films coming from different deposition batches. The reason for this is unclear, but confirms the well-documented importance of zirconium surface preparation on the subsequent anodizing process [35, 294].

It can be noted that although Figure 6.13 shows, for reasons of clarity, only the data corresponding to the second stress-thickness product regime (i.e. the one immediately preceding breakdown), the same behavior has been observed for the first regime, for which internal stress values are simply increased in the compressive direction by a factor 1.13 ± 0.03 with respect to the ones reported in Figure 6.13. At this moment, we are still unable to explain the existence of two distinct internal stress regimes before breakdown occurs. We already pointed out before that

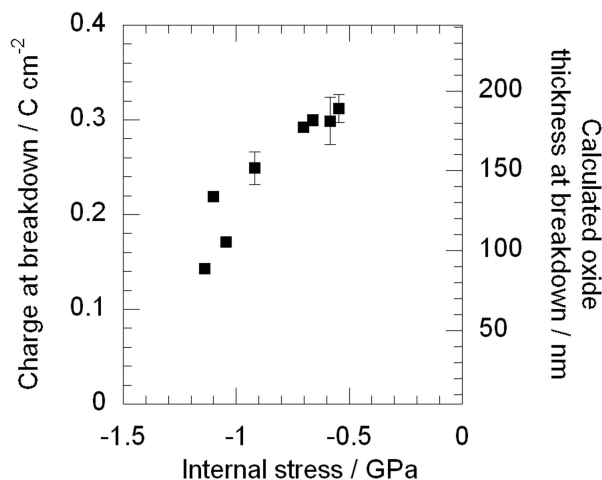


Figure 6.12: Charge and corresponding oxide thickness at breakdown versus incremental internal stress in the second regime (i.e. the regime immediately preceding breakdown, cfr. Fig. 6.11).

no change in the cell voltage evolution was observed at the first stress-thickness product transition (occurring after 10s in Figure 6.2). Moreover, electron diffractograms taken before and after this transition did not indicate any change in crystalline structure of the oxide film, as illustrated on Figure 6.14.

The question still remains how internal stress is related to the increase of the cubic or tetragonal phase content in the anodic films, relative to the monoclinic one. At atmospheric pressure, pure zirconia has three phases. At room temperature, the monoclinic phase, which also has the lowest density, is thermodynamically the more stable one in bulk zirconia, while cubic and tetragonal zirconia are stabilized only at higher temperatures.

However, the presence of impurities or a decrease in the size of the oxide crystals allows metastable cubic and tetragonal zirconia to exist at room temperature [297–299]. Compressive stresses in the order of 2 GPa have also been reported to stabilize tetragonal zirconia at temperatures down to 350 °C, while high-pressure X-ray diffraction experiments in-

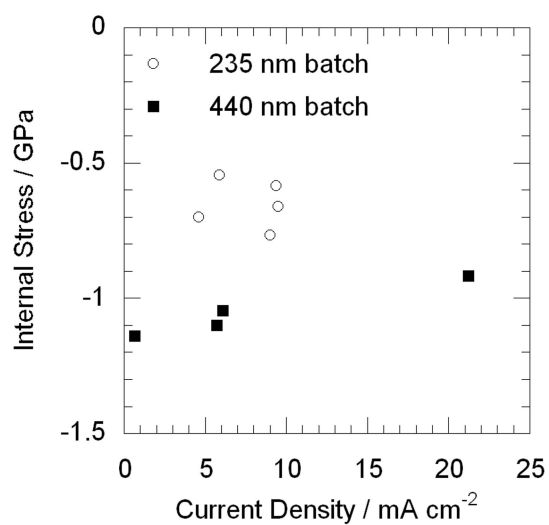


Figure 6.13: Instantaneous internal stress during the second regime as a function of current density for anodizing in $0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$.

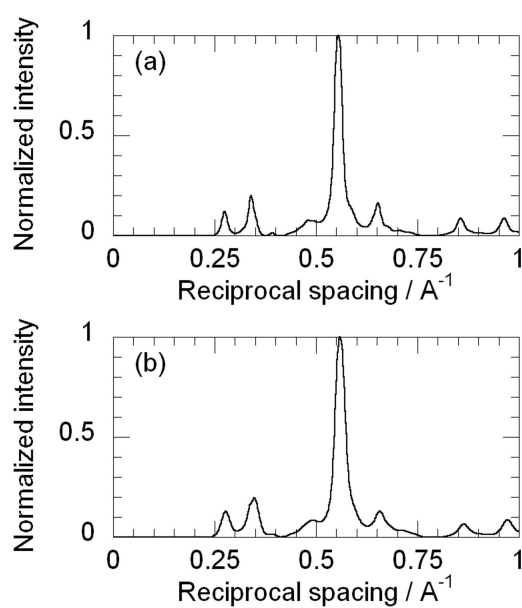


Figure 6.14: Radial intensity distribution of electron diffraction patterns of oxide films grown in $0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ to a voltage of (a) 18 V and (b) 50 V, i.e. before and after the first stress transition (cfr. Fig. 6.11).

indicated that at room temperature, nanocrystalline tetragonal zirconia evolved to cubic zirconia at 8 GPa [300]. Therefore, in our zirconium anodic oxide films, the small size of the zirconia crystals (resulting from the small Zr grain size), the presence of impurities in the oxide film (caused by anion incorporation), and the high compressive internal stresses may all contribute to the presence at room temperature of the cubic or tetragonal phases.

The increase of the thickness at which monoclinic zirconia transforms into the cubic or tetragonal phase with a decrease of the compressive internal stress may be rationalized by considering the change in free energy associated with the monoclinic-to-tetragonal or monoclinic-to-cubic phase transition ΔG :

$$\Delta G = V \Delta G_{chem} + V \Delta G_{dil} + A \Delta \gamma - W_a \quad (6.9)$$

where ΔG_{chem} , ΔG_{dil} and $\Delta \gamma$ are the change in chemical free energy, the change in strain energy density generated by the volume expansion associated with the transformation and the surface energy change, respectively. V is the sum of the volume of the crystals undergoing the phase transformation and A is the sum of their surface. W_a is the work done by the extrinsic factors such as the internal stress in the oxide film and the electric field [301].

The strain energy density generated by the volume expansion is equal to:

$$\Delta G_{dil} = \int_0^{\epsilon_{tr}} \sigma d\epsilon = \frac{1}{2} M_{ox} \epsilon_{tr}^2 \quad (6.10)$$

where M_{ox} is the bulk modulus of the oxide and ϵ_{tr} is the strain associated with the phase transformation, which is approximately equal to:

$$\epsilon^{tr} \approx \frac{1}{3} \frac{\Delta V}{V} = \frac{1}{3} \frac{\rho_{t/c}^{-1} - \rho_m^{-1}}{\rho_m^{-1}} \approx -0.02 \quad (6.11)$$

where ΔV is the change in volume of the crystal, and ρ_m and $\rho_{t/c}$ are the density of the monoclinic and tetragonal/cubic polymorph, respectively.

The work provided by the internal biaxial stress σ in the oxide is equal to:

$$W_{a, stress} = V_{film} \frac{\sigma^2}{Y_{ox}} = A_{film} h_{ox} \frac{\sigma^2}{Y_{ox}} \quad (6.12)$$

6. Internal stress and the breakdown of anodic zirconia

where V_{film} , A_{film} and h_{ox} are respectively the volume of the film, its area and thickness and Y_{ox} is the biaxial modulus of the oxide [239].

The work provided by the electric field in the oxide is equal to:

$$W_{a,elec} = V_{film} \frac{1}{2} \varepsilon_0 \varepsilon_{r,ox} E^2 = A_{film} h_{ox} \frac{1}{2} \varepsilon_0 \varepsilon_{r,ox} E^2 \quad (6.13)$$

where ε_0 , $\varepsilon_{r,ox}$ and E are the vacuum permittivity, relative oxide permittivity and electric field in the oxide.

For the phase transformation to occur, ΔG must be negative. Combining Equations (6.9)–(6.13) yields:

$$\Delta G = V \Delta G_{chem} + 2 \times 10^{-4} M_{ox} V + A \Delta \gamma - A_{film} h_{ox} \left(\frac{\sigma^2}{Y_{ox}} + \frac{1}{2} \varepsilon_0 \varepsilon_{r,ox} E^2 \right) \quad (6.14)$$

The critical anodic oxide film thickness $h_{ox,c}$ for the phase transformation to be thermodynamically favorable can thus be obtained by equating Equation (6.14) to zero. This yields:

$$h_{ox,c} = \frac{V(\Delta G_{chem} + 2 \times 10^{-4} M_{ox}) + A \Delta \gamma}{A_{film} \left(\frac{\sigma^2}{Y_{ox}} + \frac{1}{2} \varepsilon_0 \varepsilon_{r,ox} E^2 \right)} \quad (6.15)$$

In Figure 6.15, the anodic zirconium oxide film thickness at breakdown $h_{ox,bd}$, calculated from the charge passed, versus the incremental internal stress σ is represented, together with a fit of the relevant parameters in Equation (6.15):

$$h_{ox,bd} = \frac{A}{\sigma^2 + B} \quad (6.16)$$

Thus, the thermodynamics of phase transformation provide a rigorous framework to explain why the oxide thickness at breakdown decreases when the magnitude of the internal stress in the oxide increases.

Another point supporting the idea of a stress-driven phase transformation is that if the cubic or tetragonal phase content appears out of a phase transformation of monoclinic material, internal compressive stresses will favor such a transformation as it allows the oxide to densify. If the oxide film densifies during breakdown as a result of the relatively large compressive stresses, the incremental stress should become less compressive in the post-breakdown regime. Such a stress relaxation is

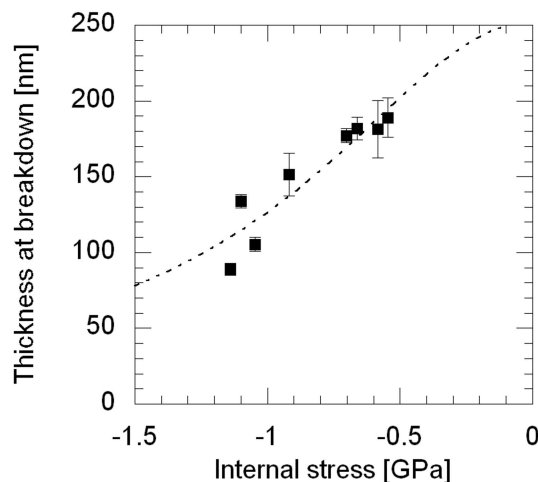


Figure 6.15: Calculated oxide thickness at breakdown versus incremental internal stress in the oxide layer.

confirmed by comparing our stress data directly after and before breakdown, as shown in Figure 6.16.

Moreover, after breakdown occurred, an increase of the incremental internal stress occurs. The existence of an additional compressive internal stress component after breakdown could be associated with the oxygen evolution reaction occurring within the anodic oxide film rather than at its surface, similarly as observed in the case of Ti-anodizing [63, 73].

Finally, a last point worth noting concerns the amount of charge passed when oxide breakdown occurs. It has been a long-standing open question whether the presence of breakdown is related to a fixed quantity of electricity having passed through an anodic oxide (i.e. a fixed number of Coulombs) [186], or if the role of charge is rather indirect, representing for instance a critical oxide thickness [184]. Our own data seem to indicate that, at least in the case of type-I breakdown of anodic zirconia, it is not the mere number of coulombs itself that causes breakdown, as for the same amount of charge passed, experimental anodizing conditions exist in which breakdown has both been observed or not: the two linear regimes in Fig. 6.6 overlap in terms of charge.

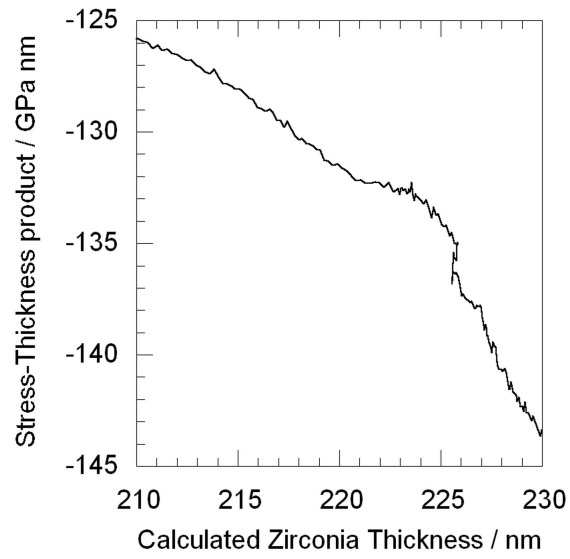


Figure 6.16: Stress-thickness product for the sample of Fig. 6.2 versus anodic film thickness calculated from the variable anodizing ratio in Eq. (6.8).

6.6 Conclusions

In this chapter, type-I breakdown during galvanostatic anodizing of sputtered zirconium thin films in sulfuric acid was studied. The breakdown was identified from a significant decrease of the rate of voltage change, which was occasionally preceded by a local cell voltage maximum. This decrease was attributed to a decrease in ionic efficiency, caused by oxygen evolution on, or within the oxide.

Based on electron diffraction studies inside a TEM, the increase in the electronic conductivity of the oxide films that allows such oxygen evolution to occur was suggested to be the result of an increase of either the cubic or tetragonal phase content of the oxide, relative to the monoclinic one. The latter increase was in turn shown to be driven by elastic energy, as the oxide thickness at which breakdown occurred was found to decrease with increasing values of the internal compressive stress directly preceding breakdown.

Chapter 7

Conclusions and perspectives

In this work, the role of internal stress on pore development and breakdown in anodic oxide films was investigated. The original approach that was followed consisted in measuring the internal stress *in situ* during anodizing, characterizing in detail the different growth stages, i.e. dense barrier film growth, pore initiation and growth, and breakdown, as well as the morphology of the anodic oxide films. The role of internal stress was elucidated by correlating quantitatively the internal stress magnitude during the different growth stages and the morphology of the anodic oxide films.

We first demonstrated in chapter 4 the applicability of the multiple beam optical sensor to measure internal stress *in situ* during anodizing. The requirements of the experimental setup, in order for Stoney equation to be applicable were examined. The influence of various complicating factors for *in situ* stress measurements during thin film anodizing, compared to vacuum thin film deposition, were then studied. One of these complicating factors is that the internal stress in the metallic film being anodized has to be accounted for to accurately measure the internal stress in the anodic oxide film. In this work, the internal stress in the metallic films was measured by monitoring the curvature change resulting from the chemical dissolution of the metallic films.

A simplified calibration equation was derived to calculate the cur-

7. Conclusions and perspectives

vature of a sample in a liquid from the mean differential spacing, the variable actually measured by the multiple beam optical sensor. We have shown that the simplified calibration equation can be used with confidence if the setup geometry is characterized by a small clamp-to-laser beam distance, a quasi-normal angle of incidence of the laser beam on the substrate, a short optical path in the liquid, and a large sample-to-detector distance. Future internal stress measurements using a MOS should use such an optimized geometry, or account for large systematic errors that the geometry may induce.

Various sources of optical perturbations limiting the attainable measurement resolution in liquids were also identified. Such perturbations considerably limit the curvature resolution, and potentially impede experiments. Future curvature measurement setup designs should attempt to reduce the occurrence of such perturbations.

Chapter 5 and 6 presented the results of our *in situ* internal stress measurements during anodizing. The role of internal stress on pore development in anodic alumina was investigated in chapter 5. Pore development occurs in two stages: pore initiation, and pore growth.

We first showed that porosity initiation could be precisely detected *in situ* during aluminum anodizing in sulfuric acid by monitoring the internal stress-induced curvature of the substrate. Upon porosity initiation, the rate of curvature change increases. The latter increase in the rate of curvature change provides new experimental evidence for pore growth by viscous flow of oxide, rather than by field-assisted dissolution. Secondly, the factors affecting porosity initiation were investigated by performing a stability analysis of the oxide / electrolyte interface, from an energetics point of view. The contributions of strain, electrostatic, and surface energies as driving forces for destabilizing or stabilizing surface perturbations were considered. Internal stress and morphological data obtained for aluminum anodizing in phosphoric acid indicated that the possibility of a strain energy-induced surface instability is unlikely. The measured pore spacing, electric field and barrier oxide thickness obtained on our anodic alumina films indicated instead that the electrostatic energy is the main driving force for pore initiation, as well as the factor controlling the pore spacing. Further evidence for an electrostatic energy-induced surface instability was obtained by compiling data from the literature for nanoporous anodic alumina and nanotubular anodic titania. The com-

peting effect of electrostatic and surface energy are therefore believed to be the controlling factor for porosity initiation as well as the factor controlling the pore spacing in anodic oxides. The fundamental parameters which control the pore spacing are the surface energy of the oxide / electrolyte interface, the oxide permittivity, and the electric field in the barrier layer. Anion ad- or ab-sorption is a key process, because it modifies the surface energy of the oxide / electrolyte interface.

Finally, internal stress and kinetic data for the pore growth stage during aluminum anodizing allowed us to estimate, for the first time, the viscosity of anodic alumina at room temperature and in the presence of large ionic currents. The viscosity was shown to be strongly dependent on the current density and on the electrolyte used for anodizing. This dependence was attributed to the influence of the anodizing parameters on the properties and concentration of vacancies in the anodic oxide.

Future work should, on the one hand, try to reconcile the electric field and surface energy-induced instability of the oxide / electrolyte interface with the stress-driven pore growth. A detailed stability analysis taking into account the interplay between surface energy, electric field, stress and mass transport would allow a more detailed prediction of the porous anodic oxide geometry to be made. On the other hand, future experiments should try to elucidate how these fundamental variables (electrical properties of the oxide, stress and mass transport) vary during the transition from the barrier layer growth stage to the porous layer growth stage. The use of *in situ* measurement techniques such as *in situ* optical emission spectrometry and the electrochemical quartz crystal microbalance could allow to improve the knowledge of the kinetics of oxide film growth during the transition between barrier layer growth and porous layer growth. A better knowledge of the kinetics of oxide film growth would also improve the spatial resolution of the *in situ* internal stress measurements, since the accuracy on the stress depends on the accuracy on the oxide thickness. Information on the existing stress gradients through the oxide thickness will also be gained. Such stress gradients play a key role for viscous flow of oxide during the growth of porous anodic oxides.

The role of internal stress on type-I breakdown during the growth of anodic zirconia films in sulfuric acid was discussed in chapter 6. The breakdown was attributed to a decrease in ionic efficiency, caused by

7. Conclusions and perspectives

oxygen evolution. The increase of electronic conductivity of the oxide films that allows oxygen evolution to occur was suggested to be the result of an increase of either the cubic or tetragonal phase content of the oxide, relative to the monoclinic one. The latter increase was in turn shown to be driven by elastic energy, as the oxide thickness at which breakdown occurred was found to decrease with increasing values of the internal compressive stress directly preceding breakdown. Internal stress therefore plays a key role for the type-I breakdown of anodic zirconia. By decreasing the internal stress in anodic oxides, it is believed that the onset of type-I breakdown could be delayed. Increasing the current density was shown to decrease the internal stress in anodic zirconia. A much more pronounced unelucidated dependence of internal stress on the batch of deposited zirconium was however observed.

The role of internal stress on type-II breakdown, and the precise relationship between type-I and type-II breakdown should be investigated in future work. A preliminary result obtained in the course of this thesis revealed that instabilities in the stress-thickness evolution occur during type-II breakdown of zirconia in sulfuric acid. *In situ* internal stress measurements during type-II breakdown of anodic oxide films could therefore prove to be a valuable complementary diagnostic tool to classical chronopotentiometry. Although this work was restricted to the breakdown occurring during the growth of anodic oxide films, whether the breakdown mechanisms of passivation films in general, such as the mechanisms of pitting, are related to the breakdown mechanisms studied here also remains to be determined.

In this work, new data for the dependence of the internal stress in anodic oxide films on the anodizing conditions was also provided. For anodic alumina, the internal stress was always proportional to the logarithm of the current density. Similar proportionality coefficients were found for anodic oxide films formed in different electrolytes. The substrate composition did however have a much more important effect. Regarding the unexplained dependence of internal stress in anodic oxide films on the anodizing conditions, future work should quantify the contributions of intrinsic and extrinsic stresses to the total internal stress magnitude. Quantifying the magnitude of intrinsic growth stresses would allow a better understanding of the microstructural mechanisms responsible for stress generation in anodic oxide films, and of the dependence

of internal stress on experimental conditions.

Some of the results of this work are also relevant for engineering applications. For instance, the ability to tailor the internal stress in the anodic oxide by modifying not only the anodizing conditions, but also the aluminum alloy composition, would allow producing films with virtually zero internal stress. This should be of interest to the anodizing industry where internal stresses are generally considered as a “bad” physical quantity, to be minimized. It can also be expected that engineering the substrate composition of alloys in general could also modify the internal stress in either the native oxide or passivation layer in order to further improve the corrosion resistance of these alloys.

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List of Figures

2.1	Architectural applications of porous anodic alumina	19
2.2	Self-organized nanoporous alumina	20
2.3	Cyclic high-temperature corrosion of zirconium	21
2.4	Potential-pH diagrams of Al, Zr and Ti in water.	24
2.5	Activation energy for charge carrier hopping	25
2.6	Comparison of electric field in anodic oxide films and the oxygen density of the oxide	26
2.7	Potential profile in the metal/anodic oxide/electrolyte sys- tem	27
2.8	Elementary reactions in growing anodic alumina films . . .	29
2.9	Dependence of the cation transport number on the current density in anodic oxide films	33
2.10	Dependence of the cation transport number on its ionic radius	34
2.11	Distribution of phosphate in anodic alumina forms formed in a aqueous phosphate electrolyte	36
2.12	Anodic alumina films contamination in various electrolytes.	37
2.13	Relative migration rate of anionic species in anodic alumina	38
2.14	Illustration of tungsten enrichment and incorporation dur- ing anodizing of a dilute Al-W alloy	45
2.15	Illustration of a porous anodic alumina film	48
2.16	The four stages of porous anodizing	49
2.17	TEM of phosphate-contaminated barrier layer in porous anodic alumina	52
2.18	Dependence of the cell diameter on the anodizing voltage	56
2.19	Dependence of the cell diameter on the anodizing voltage for ordered anodic alumina	60

LIST OF FIGURES

2.20	Nanotubular anodic titania	62
2.21	TEM of the different stages of pore nucleation during electropolished aluminum anodizing	64
2.22	Tungsten tracer profile evolution during aluminum anodizing in phosphoric acid	70
2.23	Expected behavior of a tungsten tracer for pore formation by either field-assisted dissolution or viscous flow of oxide	71
2.24	Predicted current lines, potential, dimensionless stress and oxide velocity for viscous flow driven oxide transport	72
2.25	Cell voltage evolutions corresponding to breakdown, pore formation and Si anodic oxidation	75
2.26	Sequence of events leading to type-II breakdown	76
2.27	Morphology of partially crystallized anodic tantalum	78
2.28	Bandgap values of different oxides	79
2.29	Dependence of type-II breakdown voltage on electrolyte resistivity	84
2.30	Dependence of type-II breakdown voltage on the anion concentration and the electrolyte pH	86
2.31	Voltage evolution for subsequent anodizing / breakdown in electrolytes of different concentrations	87
2.32	Simulated and measured voltage evolution during tantalum anodizing in the presence of an avalanche electronic current	92
3.1	Illustration of the wafer preparation procedure	98
3.2	Illustration of the preparation of the electrical contact	99
3.3	Illustration of the wafer preparation using a lift-off process	100
3.4	Illustration of the sample clamping in resin	102
3.5	Illustration of the sample placement in the electrochemical cell	103
3.6	Schematic representation of the curvature measurement setup	105
4.1	Stress-thickness product evolution during sputtered aluminum film dissolution	114

LIST OF FIGURES

4.2	Evolution of the product of stress and thickness change of the oxide for aluminum anodizing in ammonium pentaborate without and with taking the internal stress in the metal into account	116
4.3	Illustration of the setup geometry for a flat sample in air .	119
4.4	Illustration of the setup geometry for a curved sample in air	120
4.5	Relative error when using a simplified relationship for the curvature in air	122
4.6	Biaxial curvature change upon removal of the electric field in anodic zirconium oxide	125
4.7	Illustration of the setup geometry for a flat sample in a liquid	126
4.8	Illustration of the setup geometry for a curved sample in a liquid	128
4.9	Relative error when using a simplified relationship for the curvature in water	130
4.10	Definition of the cell window misalignment angle	131
4.11	Error on calculated curvature when the cell window is misaligned	133
4.12	Curvature baseline recording	134
4.13	Influence of convection effects on the differential spacings .	136
4.14	Influence of a particle on the differential spacings	137
5.1	Curvature and cell voltage evolution for Al anodizing . . .	142
5.2	AFM images of Al samples anodized before and after porosity initiation	145
5.3	Radial power spectral density of Al samples anodized before and after porosity initiation	146
5.4	Scanning electron micrographs of an Al sample anodized in sulfuric acid	147
5.6	Similarities between a parallel plate capacitor and an anodic oxide film	151
5.7	Cross-sectional scanning electron micrographs of porous anodic alumina	152
5.8	Barrier layer thickness and pore spacing vs. current density	153
5.9	Steady-state voltage and electric field vs. current density .	153
5.10	Stress vs. current density for Al anodizing in H_3PO_4 . . .	154

LIST OF FIGURES

5.11	Stress-thickness product and cell voltage evolution for Al anodizing in H_3PO_4	155
5.12	Electrostatic energy-induced surface instability in anodic alumina and anodic titania	156
5.13	Velocity resulting from oxide viscous flow	160
5.14	Schematic illustration of the porous anodic oxide film morphology	161
5.15	Stress vs. current density for Al anodizing in H_2SO_4 and H_3PO_4 and for Al(Si, Cu) anodizing in H_2SO_4	162
5.16	Porous layer growth rate for Al anodizing in H_2SO_4 and H_3PO_4 and Al(Si, Cu) anodizing in H_2SO_4	163
5.17	Viscosity of anodic alumina calculated from the average in-plane stress	164
5.18	Schematic illustration of the porous anodic oxide film morphology with non-uniform electric field	165
5.19	Electrostatic stress vs. electric field in anodic alumina . .	167
5.20	Viscosity of anodic alumina calculated from the electrostatic stress	168
5.21	Stress vs. current density for Al and Al(Si, Cu) anodizing in sulfuric acid or borate-containing electrolytes	169
2.25	Cell voltage evolutions corresponding to breakdown, pore formation and Si anodic oxidation	172
6.1	Current vs. voltage for dry anodic oxide film breakdown .	173
6.2	Evolution of stress-thickness product and cell voltage during Zr anodizing in H_2SO_4	176
6.3	Cell voltage and time derivative evolution for Zr anodizing in H_2SO_4	177
6.4	Derivative of cell voltage before and after breakdown vs. current density for Zr anodizing in H_2SO_4	178
6.5	Mass loss of Zr in the electrolyte vs. the charge consumed	179
6.6	Total film thickness change as a function of the charge consumed	181
6.7	Anodizing ratio vs. current density for Zr anodizing . . .	183
6.8	Simulated and measured cell voltage evolution	186
6.9	Transmission electron micrographs and diffractograms before and after breakdown	187

LIST OF FIGURES

6.10	Scanning electron micrographs of Zr surface before and after anodizing and breakdown	189
6.11	Stress-thickness product vs. voltage and vs. film thickness	190
6.12	Charge and oxide thickness at breakdown vs. internal stress	192
6.13	Dependence of internal stress on current density for Zr anodizing	193
6.14	Transmission electron diffractograms before and after first transition in the rate of curvature change	194
6.15	Oxide thickness at breakdown versus incremental internal stress in the oxide layer	197
6.16	Stress-thickness product vs. oxide thickness at breakdown	198

List of Tables

2.1	Standard free energy of formation of the oxide of valve metals	23
2.2	Range of anodizing ratios reported for various anodic oxides	30
2.3	Range of internal stress reported by different research groups	40
2.4	Measured and calculated electrostatic stress in barrier an- odic oxide films	43
2.5	Internal stress sign during the barrier and porous layer growth stages of anodic alumina	54
3.1	Summary of the metallic films used in this thesis	97

The role of internal stress on the growth and breakdown of barrier and porous anodic oxide films

Anodic oxidation, or anodizing, can be defined as the electrochemically-controlled growth of an oxide film on a metal. Owing to its simplicity, anodizing is used extensively in a wide range of applications. These include providing corrosion protection and an aesthetic finish to metallic surfaces, manufacturing nanoporous templates, and producing a dielectric medium in electrolytic capacitors. In all these cases, process instabilities which terminate the growth of a dense anodic oxide film, like breakdown and pore initiation, are of key importance. Internal stresses have often been suggested to be a key factor controlling these instabilities in anodic oxide films. However, no direct quantitative correlation between internal stress and either pore development or breakdown of anodic oxide films has ever been established.

In this thesis, we measured the internal stress in anodic oxides in situ during their growth. By systematically varying the electrochemical growth conditions, and thereby the magnitude of the internal stress, we were able to unravel its influence on the development of porosity in anodic alumina films, and on the breakdown of anodic zirconia films. In the case of anodic alumina, energy-based stability analyses revealed that the internal stress is unlikely to be the controlling factor for pore initiation and pore spacing selection. Instead, these processes were found to be rather governed by an electrostatic energy induced surface instability. On the other hand, experimental evidence was provided that, contrary to pore initiation, pore growth in anodic alumina can be considered to be a stress-assisted viscous flow process. In this respect, our internal stress data allowed to quantify the viscosity of anodic alumina at room temperature in the presence of large ionic currents. Finally, internal stress was identified as a key factor as well for initiating breakdown in anodic zirconia films. The microstructural origin of the breakdown in that case was identified as a phase transformation allowing the zirconia to densify, the compressive internal stress in the growing anodic oxide film being the driving force for such a transformation.