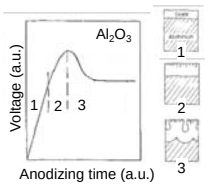
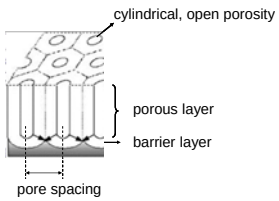
Does internal stress affect pore initiation in anodic oxides ?

Quentin Van Overmeere, Frédéric Blaffart and Joris Proost
Division of Materials and Process Engineering, Université catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

1. Introduction

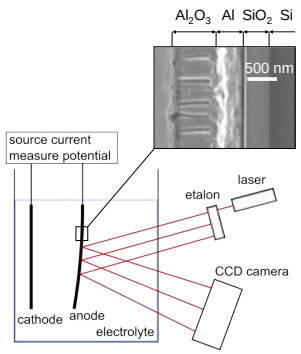
- Porous anodic aluminum oxide known for decades
- Recent synthesis of other porous anodic oxides: TiO_2 [1], ZrO_2, Nb_2O_5…
- Porous anodic oxides grow in 3 stages:
  1. Dense oxide growth (barrier layer)
  2. Initiation of pores (incipient pores)
  3. Steady-state pore growth (major pores)





What controls pore dimensions ?
Why do pores appear ?

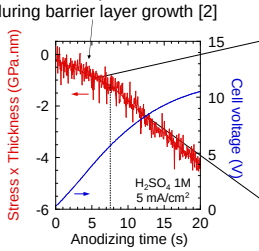
2. Experimental setup



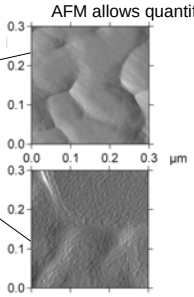
- Three electrolytes used:
  - 1.0 M H_2SO_4: 10 to 50 nm pores
  - 0.4 M H_3PO_4: 200 to 350 nm pores
  - 0.01 M ammonium pentaborate (APB): no pores
- Current densities from 0.5 to 50 mA/cm²
- Electron-beam evaporated Al
- Substrates: double-side polished Si, 400 nm thermal SiO_2 to insulate Si from Al
- Oxide thickness = (AR) x Cell voltage
  - H_2SO_4 / H_3PO_4 : AR = 1.0 nm/V
  - APB : AR = 1.4 nm/V
- Pore spacings measured by:
  - AFM on top surface (incipient pores)
  - SEM on cross-sections (major pores)

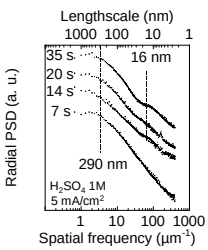
3. *In situ* detection of porosity initiation

Constant compressive stress during barrier layer growth [2]

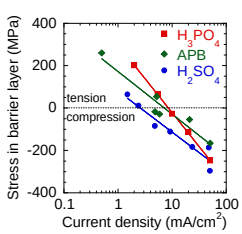


AFM allows quantifying pore spacings

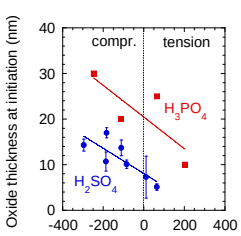




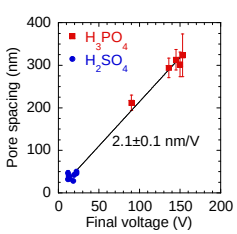
4. Influence of internal stress on pore initiation

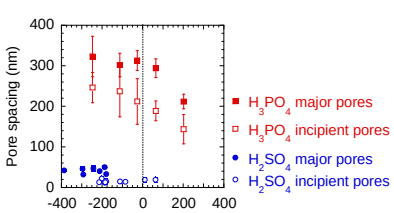


- Stress in barrier layer proportional to logarithm of current density.
- Low current density: tensile stress
  high current density: compressive stress.
- Influence of current density more pronounced than electrolyte chemistry.
- Similar stress dependence on current density in APB and H_2SO_4.



- The more tensile the stresses, the thinner the barrier oxide upon pore initiation.
- Thickness at pore initiation larger in H_3PO_4 than in H_2SO_4.

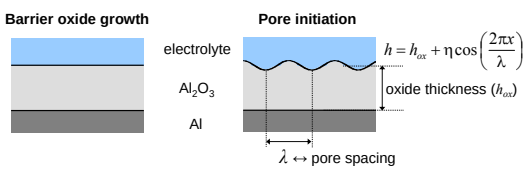




- Larger pore spacing in H_3PO_4 than in H_2SO_4.
- In H_3PO_4, pore spacing decreases the more tensile the stress.
- In H_2SO_4, no clear tendency observed.

5. Surface instability and pore initiation

- In some systems, undulation of an initially flat surface is energetically favorable.
- Undulations increase the surface energy → flat surface preferred.
- Undulations may decrease strain / electrostatic energy → undulating surface preferred.



- A critical λ exists above which an undulating surface is stable [3,4,5]:

Strain energy

Young modulus

$$\lambda_c = \frac{\pi M \gamma}{\sigma^2}$$

Surface energy

internal stress

Electrostatic energy

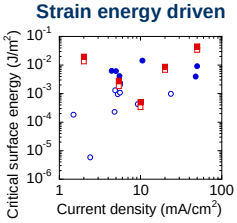
$$\lambda_c = \sqrt{\frac{4\pi^2 h_{ox}^2 \gamma}{\varepsilon_0 \varepsilon E^2}}$$

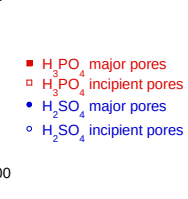
oxide permittivity

electric field

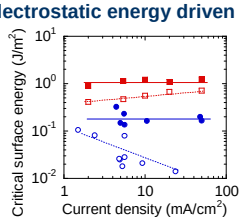
- We calculate a critical surface energy value, below which the pores with measured pore spacing are energetically stable.

Strain energy driven





Electrostatic energy driven



- If electrostatic energy-driven pore initiation, calculated critical surface energies are in the range of literature values for Al_2O_3 (1.5 to 0.034 J/m²) [6,7].
- Adsorption of anions expected to modify the surface energy.

6. Conclusions

- No experimental evidence for Asaro-Tiller type effect of internal stress on pore initiation in anodic alumina.
- Electrostatic energy driven pore initiation more likely.

References

[1] A. Ghicov, H. Tsuchiya, J. M. Macak, P. Schmuki, *Electrochem. Commun.* **7**, 505 (2005).
[2] Q. Van Overmeere, B. Nysten, J. Proost, *Appl. Phys. Lett.* **94**, 074103 (2009).
[3] R.J. Asaro, W. A. Tiller, *Metall. Trans.* **3**, 1789 (1972).
[4] J.-H. Kim, J. J. Vlassak, *Int. J. Solids Struct.* **44**, 7924 (2007).
[5] V. Gill, P. R. Guduru, B. W. Sheldon, *Int. J. Solids Struct.* **45**, 943 (2008).
[6] M. L. Guzmán-Castillo, X. Bokhimi *et al.*, *J. Non-Cryst. Solids* 329, 53 (2003).
[7] S. Liu, J. Luo, G. Li, C. Zhang, X. Lu, *Appl. Surf. Sci.* **254**, 7137 (2008).

Acknowledgements

QVO acknowledges the support of the Belgian National Science Foundation (FRIA).