

Nanoporous Anodic Alumina

Hydrophobically Modified Porous Anodic Alumina Membranes

**Nikolaos Spiliopoulos, Alexandros A. Vradis
Chris Toprakcioglu and Dimitris L. Anastassopoulos**

Department of Physics, University of Patras, Greece 26504

4/11/2016

Dept. of Physics

1

Nanoporous Anodic Alumina

Brief Historical Review

Protection of Aluminum and its alloys, over 100 years

Masuda & Fukuda, Closely Packed Hexagonal Array, 1995

Versatile Template for Nanopatterning, Today

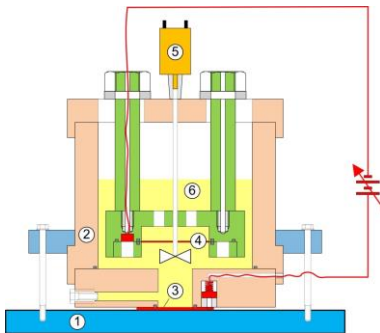
4/11/2016

Dept. of Physics

2

Nanoporous Anodic Alumina

Experimental Set up



1. Cooling Stage (Peltier)
2. Teflon Cell
3. Aluminum Foil (Anode)
4. Platinum mesh (Cathode)
5. Stirrer
6. Electrolyte



Photograph of experimental set up
in the Solid State Lab of U. of Patras

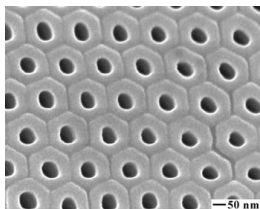
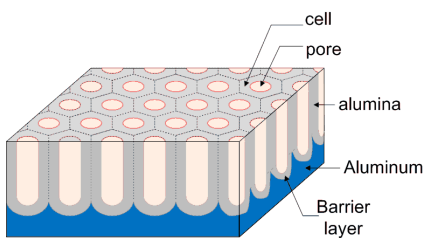
4/11/2016

Dept. of Physics

3

Nanoporous Anodic Alumina

Ordered Structure



Masuda, H. & Fukuda, K.
Science **268**, 1466 (1995)

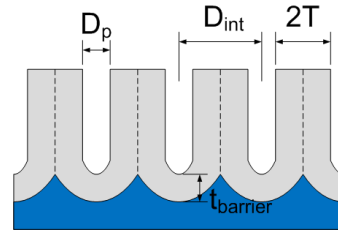
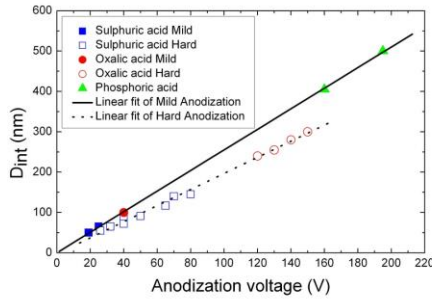
Lee et al, *Nature Materials*, **5**,
741 (2006)

4/11/2016

Dept. of Physics

4

Nanoporous Anodic Alumina

Interpore Distance, D_{int} ,
and Pore Diameter, D_p 

$$D_{\text{int}} = k_1 V \quad K_1 = 2.5 \text{ nm/V}$$

$$D_p = k_2 V \quad K_2 = 1.0 \text{ nm/V}$$

4/11/2016

Dept. of Physics

5

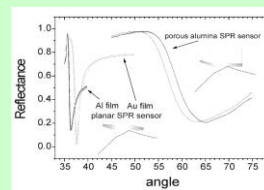
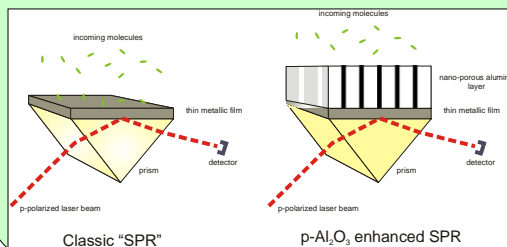
Nanoporous Anodic Alumina

Experiment
University of PatrasJOURNAL OF APPLIED PHYSICS **103**, 094521 (2008)

Nanoporous alumina enhanced surface plasmon resonance sensors

Alexandros G. Koutsoubas, Nikolaos Spiliopoulos, Dimitris Anastassopoulos,
Alexandros A. Vradis,^a and George D. Pifitis
Department of Physics, University of Patras, GR 26 500, Greece

(Received 13 September 2007; accepted 15 March 2008; published online 13 May 2008)



4/11/2016

Dept. of Physics

6

Nanoporous Anodic Alumina

Experiment

University of Patras

Adsorption of Block Copolymers in Nanoporous Alumina

SOTIRIA KARAGIOVANAKI,¹ ALEXANDROS KOUTSIUBAS,¹ NIKOLAOS SPILIOPOULOS,¹ DIMITRIS L. ANASTASSOPOULOS,¹
 ALEXANDROS A. VRADIS,¹ CHRIS TOPRAKCIOGLU,¹ ANGELIKI ELINA SIOKOU²

¹Department of Physics, University of Patras, Patras 26500, Greece

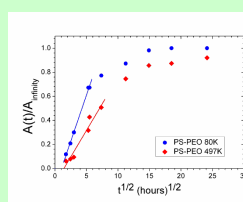
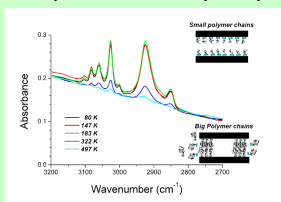
²Foundation for Research and Technology, Institute of Chemical Engineering and High Temperature Chemical Processes (FORTH/ICE-HT), Hellas, Stadiou Str., Platani, P.O. Box 1414, GR-26504 Patras, Greece

Received 20 October 2009; revised 23 December 2009; accepted 29 December 2009

DOI: 10.1002/polb.21972

Published online in Wiley InterScience (www.interscience.wiley.com).

J Polym Sci Part B: Polym Phys 48: 1676–1682, 2010



4/11/2016

Dept. of Physics

7

Nanoporous Anodic Alumina

Simulation

University of Patras

THE JOURNAL OF CHEMICAL PHYSICS 131, 044901 (2009)

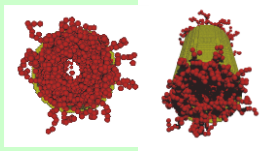
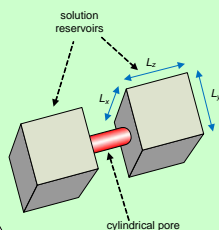
Formation of polymer brushes inside cylindrical pores: A computer simulation study

Alexandros G. Koutsioubas,^{a)} Nikolaos Spiliopoulos, Dimitris L. Anastassopoulos,
 Alexandros A. Vradis^{b)} and Chris Toprakcioglu

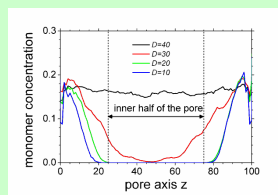
Department of Physics, University of Patras, Patras 26500, Greece

(Received 2 April 2009; accepted 24 June 2009; published online 22 July 2009)

BFMC Simulation of brush self assembly



Snapshot at equilibrium




4/11/2016

Dept. of Physics

8

Nanoporous Anodic Alumina

Free Standing Membrane Fabrication



The diagram shows a cross-section of a substrate (Al) before and after the first anodization. Before anodization, it's a solid purple block. After anodization, a porous layer of Al_2O_3 (grey) has formed on top, with air (white) filling the pores. The top surface is irregular and jagged.

1st Anodization

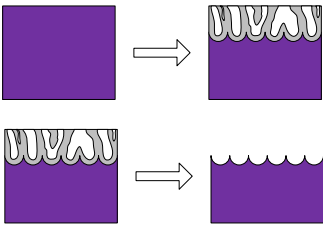
Legend:

- Al
- Al_2O_3
- air

4/11/2016 Dept. of Physics 9

Nanoporous Anodic Alumina

Free Standing Membrane Fabrication



The diagram shows a cross-section of the substrate after the first anodization and after oxide removal. Before removal, the top surface is jagged. After removal, the top surface is smooth and flat, while the porous Al_2O_3 layer remains below.

1st Anodization

Oxide Removal

Legend:

- Al
- Al_2O_3
- air

4/11/2016 Dept. of Physics 10

Nanoporous Anodic Alumina

Free Standing Membrane Fabrication

The diagram illustrates the first three steps of free standing membrane fabrication:

- 1st Anodization:** A flat aluminum (Al) substrate is anodized to form a porous alumina (Al₂O₃) layer on top.
- Oxide Removal:** The porous alumina layer is removed, leaving a flat Al substrate with a rough surface.
- 2nd Anodization:** The Al substrate is anodized again to form a second porous alumina layer.

Legend:

- Al (Purple)
- Al₂O₃ (Grey)
- air (White)

4/11/2016 Dept. of Physics 11

Nanoporous Anodic Alumina

Free Standing Membrane Fabrication

The diagram illustrates the final step of free standing membrane fabrication:

- Al Removal:** The aluminum substrate is removed from the porous alumina layer, resulting in a free-standing porous alumina membrane.

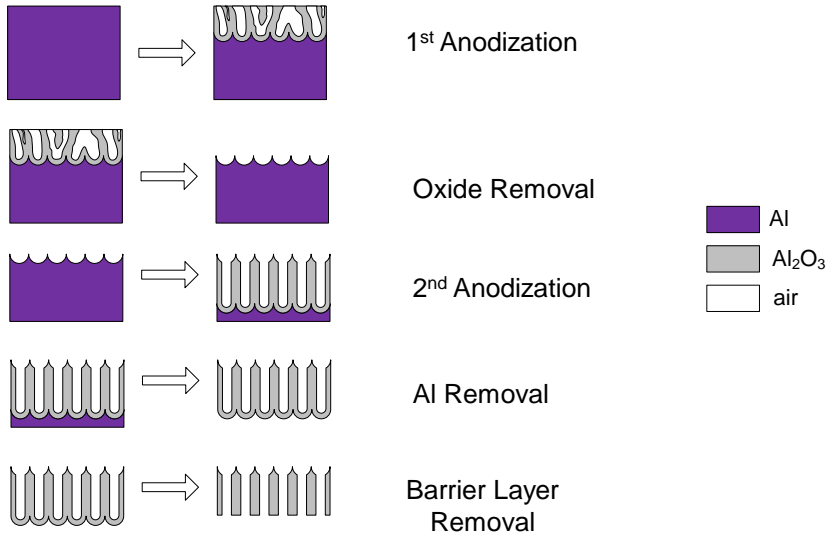
Legend:

- Al (Purple)
- Al₂O₃ (Grey)
- air (White)

4/11/2016 Dept. of Physics 12

Nanoporous Anodic Alumina

Free Standing Membrane Fabrication

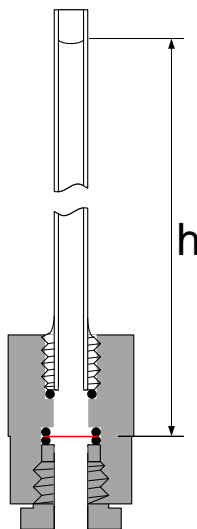


4/11/2016

Dept. of Physics

13

Nanoporous Anodic Alumina



Poiseuille's law

$$Q = \frac{\pi R^4}{8\eta l} \Delta P$$

$$Q = \frac{N\pi R^4}{8\eta l} \Delta P = \frac{N\pi R^4}{8\eta l} \rho g h$$

$$Q = \frac{dV}{dt} = \frac{S_t dh}{dt}$$

$$\frac{dh}{h} = \frac{nNR^4 \rho g}{2\eta l D_t^2} dt$$

$$-\ln \frac{h}{h_0} = \frac{NR^4 \rho g}{2\eta l D_t^2} t = Bt$$

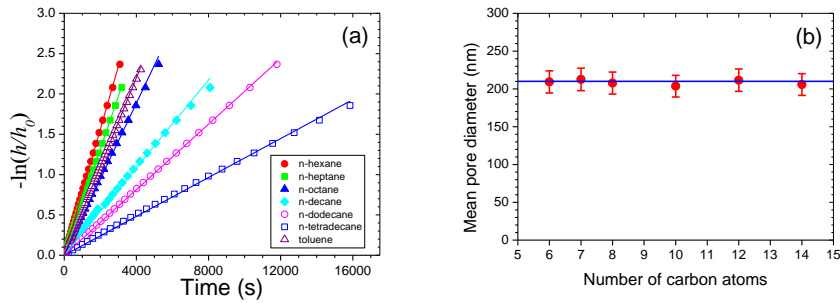
Schematic view of the experimental set-up consisting of a Teflon cell and a scaled glass tube, for the determination of the flow rate through nanoporous alumina membrane.

4/11/2016

Dept. of Physics

14

Nanoporous Anodic Alumina



$$-\ln \frac{h}{h_0} = \frac{NR^4 \rho g}{2\eta l D_t^2} t = Bt$$

(a) Plot of $-\ln(h/h_0)$ vs. time diagram for various solvents through bare porous alumina membrane.

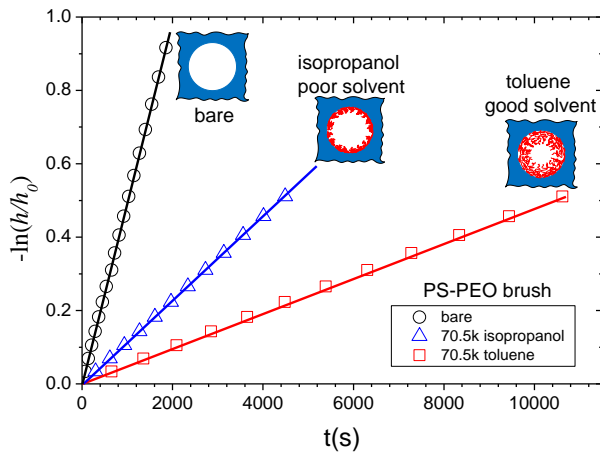
(b) Pore diameter determination for the various slopes, B of diagram (a)

4/11/2016

Dept. of Physics

15

Nanoporous Anodic Alumina



Plot of $-\ln(h/h_0)$ vs. time diagram for the flow of toluene through bare porous alumina membrane (black,) and for flow of isopropanol (blue) and toluene (red) through porous alumina membrane in which the polymer brush of PS-PEO with molecular weight 70.5k has been formed.

4/11/2016

Dept. of Physics

16

Conclusions

- Porous Anodic Alumina: A versatile template for nanofabrication.
- Controlled porous diameter and interpore distance
- Can be Functionalized or Modified

Thanks

- Prof. A. Katsaounis for inviting
- D. Anastassopoulos, A. Vradis,
C. Toprakcioglu: Co-workers