Fabrication of free-standing porous silicon and alumina membrane, and measurement of the pore diameter using fluid flow under hydrostatic pressure.

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Research Area: Materials and Nanotechnology

INTRODUCTION:

The purpose of this study is to investigate the dependence of the geometrical characteristics of free-standing porous alumina and silicon membranes by fluid flow experiments. Porous materials are of scientific and technological importance due to the presence of controllable dimension voids at the nanometer scales. Research efforts in this field have been driven by the rapidly emerging applications such as biosensors, drug delivery, gas separation, energy storage and fuel cell technology. The research in this field offers exciting new opportunities for developing new strategies and techniques for the synthesis and applications of these materials.

EXPERIMENTAL PROCEDURE:

Porous Alumina (PA): Anodization of an aluminum foil is carried out in sulphuric acid 0.3M and oxalic acid 0.3M under applied voltages of 20V and 40V respectively in a two-step anodization process.
The process takes place into an electrochemical cell (fig. 1). Subsequently, the membranes' barrier layer is dissolved in a solution of phosphoric acid 5%wt. in the double tank cell (fig.2) in order to obtain a free-standing membrane.

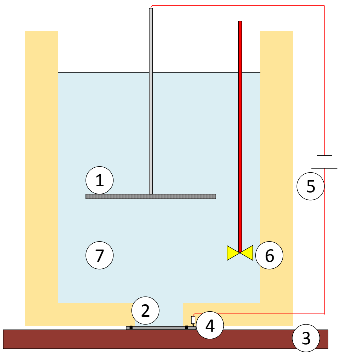

Figure 1: Electrochemical cell for PA anodization. (1) Ni cathode electrode, (2) aluminum foil, (3) Cu plate, (4) spring loaded electric contact, (5) Power supply, (6) stirrer, (7) electrolyte

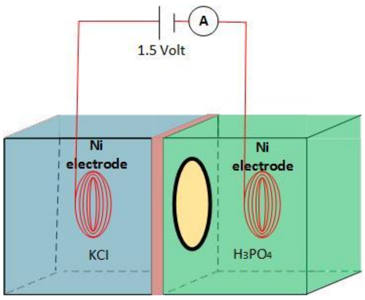

Figure 2: Double tank cell for PA barrier layer dissolution

Porous Silicon (PSi): Anodization of a silicon wafer is carried out in $HF:H_2O:CH_3CH_2OH$ (1:1:2) electrolyte solution. The procedure takes place inside a double tank electrochemical cell (fig.3). Electrical contact is achieved with an electrolytic backside contact.

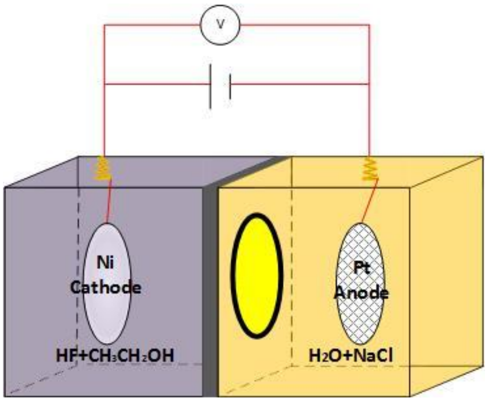

Figure 3: Double tank cell for PSi electrochemical etching.

The membrane thickness, pore density and pore diameter is measured with Scanning Electron Microscopy (SEM). A second method for the estimation of PA and PSi membranes pore diameter was by using them in a fluid flow experiment with toluene as flowing liquid (fig.4). The hydrostatic pressure difference imposed by the fluid column above the membrane is at the order of 10kPa and acts as the driving force for the flow establishment.

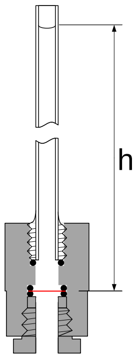

Figure 4: Experimental setup for the determination of the flow rate through the free-standing membranes.

RESULTS AND DISCUSSION:

Figure 5 shows the electrical current as a function of time during aluminum anodization in potentiostatic mode for constant applied voltage of 40 V. In this figure we can observe three characteristic stages of PA formation.

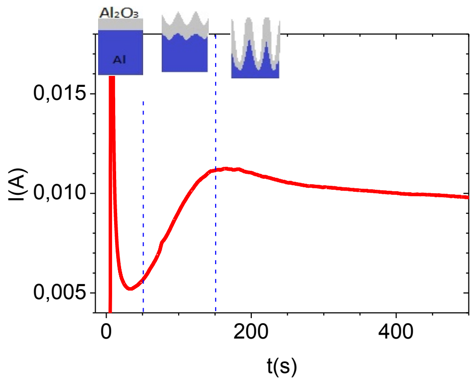

Figure 5 : Anodization current as a function of time for constant voltage of 40 V.

During the first step a layer of dense aluminum oxide is created and therefore the current is decreased. In the next step the creation of the first pores starts and an increase in the current is observed. The current reaches a steady state value in the third step indicating the development of the pores with a steady growing rate.

Figure 6 presents the anodizing voltage as a function of time during silicon anodization in galvanostatic mode under constant current density of 30 mA/cm^2.

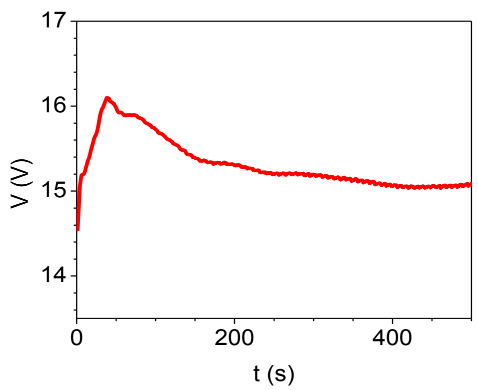

Figure 6. Anodization voltage as a function of time for constant current density of 30mA/cm^2

During first seconds of the process the voltage is increasing until the pore creation is initiated. The peak in voltage corresponds to the pore opening.

Fluid Flow experiment: Poiseuille's law gives the flow rate of a fluid through a cylindrical channel due to a pressure difference by:

$$Q = \frac{\pi R^4}{8\eta l} \Delta P \qquad (1)$$

where ΔP is the pressure difference, R the radius of the tube, η the dynamic viscosity of the solvent and l the tube length.

From a macroscopic point of view, the rate of flow can be described as the volume of solvent passing through the glass tube in a period of time:

$$Q = \frac{dV}{dt} = \frac{S_t dh}{dt} \qquad (2)$$

where S_t is the surface area of the glass tube, dh/dt the rate of change in the height level of the solvent. By rearranging equations (2) and (3) one can obtain:

$$B = \frac{NR^4 \rho g}{2\eta l D_t^2} \qquad (3)$$

where B is the slope of the graph plot $-\ln(h/h_0)$ vs t.

In figure 7 we observe the results of PA fluid flow experiment.

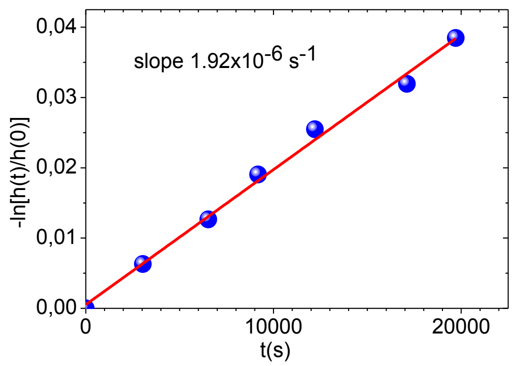

Figure 7: Height level of fluid as a function of time.

The porous alumina membrane can be considered as a porous medium with a number of parallel cylindrical nanotubes penetrating throughout its whole thickness. Meanwhile, PSi membranes don't always provide symmetrical and cylindrical pores so Darcy's Law must be used to determine the flow rate of a liquid through the branches:

$$Q = -\frac{\kappa A \Delta P}{\eta l}$$

where κ is the permeability of the medium, A the cross sectional area to flow, ΔP the pressure difference, η the viscosity of the fluid and l the tube length.

Then the membranes are analyzed by SEM (fig. 8,9,10) in order to check the agreement with the fluid flow experiment results.

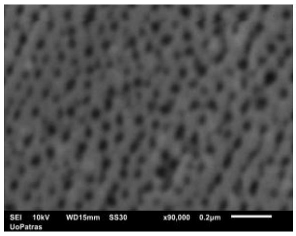

Figure 8: Top View of PA

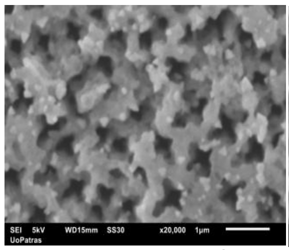

Figure 9:Top view of PSi

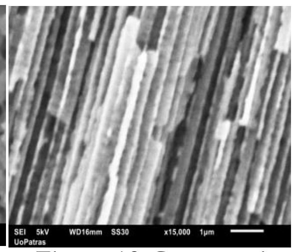

Figure 10:Cross section view of Psi

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