

Structural engineering of micro- and nanoporous silicon and nanoporous alumina for biosensing applications

L. F. Marsal¹, A. Santos², P. Formentin¹, L. Hernández¹, G. Macias¹, M. Alba¹, J. Pallares¹ and J. Ferré-Borrull¹

¹Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, Universitat Rovira i Virgili, Avda. Països Catalans 26, 43007 Tarragona, Spain

²School of Chemical Engineering, The University of Adelaide, Engineering North Building, 5005 Adelaide, Australia

lluis.marsal@urv.cat

In the last years, a new generation of optical biosensors based on micro- and nanoporous silicon and nanoporous alumina structures has been proposed with promising results. These porous materials are produced by electrochemical anodization of silicon or aluminium in different acid electrolytes and their pore morphology can be effectively modified by adjusting the anodizing conditions such as the acid electrolyte, temperature, voltage or time. For example, many innovative pore architectures such as funnel-like [1], modulated, serrated-like, hierarchical, three-dimensional, tip-like, etc. have emerged from different electrochemical approaches [2-6].

These pore structures also have an exclusive set of optical properties (e.g. photoluminescence, transmittance, reflectance, absorbance and so on) and their performance has been successfully tested in such optical devices as microcavities, filters, resonators or waveguides. Notice that, anodization is based on a cost-effective technology and is fully compatible with current semiconductor processing technologies.

Furthermore, the surface chemistry of these porous materials can be modified at will. Therefore, the functionality of nanoporous silicon and alumina can be tuned for different chemical and biological environments. Their particular surface structure can be easily modified and used as a label-free enzymatic or immunosensors. All this brings an opportunity to design and fabricate nanoporous materials with special features for multiple biotechnological purposes (e.g. cell culture, molecular separation-adsorption, drug delivery, optical sensors and so forth).

Herein, we report on the experimental procedures and results of fabrication, characterization and optimization of new structures based on nanoporous anodic alumina and micro-nanoporous silicon obtained by different anodization strategies. The fabricated structures were characterized by different structural and optical methods such as scanning electron microscopy (SEM), Atomic Force Microscopy (AFM), confocal microscopy, photoluminescence (PL), UV-Vis-NIR spectroscopy, spectroscopic ellisometry, etc.

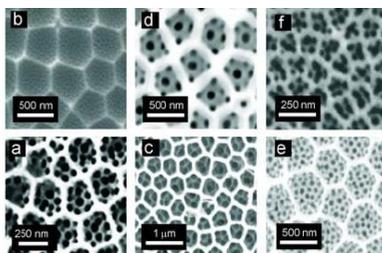


Figure 1: SEM top view images of the different types of HNAATs fabricated by the asymmetric two-step anodization process.

Figure 1 shows a set of SEM images of the fabricated hybrid nanoporous anodic alumina (HNAA). An asymmetric two-step anodization process makes it possible to fabricate HNAAs with a wide range of geometric characteristics such as interconcavity and interpore distance and concavity and pore diameter. These structures can be useful for molecule separation or drug delivery purposes. Figure 2a shows an example of nanoporous anodic alumina (NAA) used in a PL characterization. Figure 2b shows photoluminescence spectra as a function of the porosity (i.e. time of pore widening, T_{pw}) for a pore

length of 6.8 μm . As can be seen, the PL oscillations can be adjusted by changing the porosity (i.e. pore diameter) [7,8]. Consequently, the combination of nanoporous anodic alumina with PL spectroscopy allows us to generate multiple photonic barcodes, which can be used as an objective biosensing system for detecting and quantifying substances infiltrated within the nanopores. Finally, macroporous silicon produced by electrochemical etching of silicon has been proved to be a promising material in a broad range of applications due to its versatility and remarkable characteristics (e.g. well-controlled geometry, biocompatibility, etc.). One example is the fabrication of silicon dioxide (SiO_2) micropillars, which can be obtained from the oxidation of macroporous silicon templates and subsequent etching steps. The geometry and uniformity can be accurately controlled by the etching conditions. Figure 3 shows two examples of high-aspect ratio random and ordered silicon dioxide micropillars.

Several bioapplications can be proposed for macroporous silicon based structures, such as microneedles from drug delivery [9] or SiO_2 pillars for DNA separation [10].

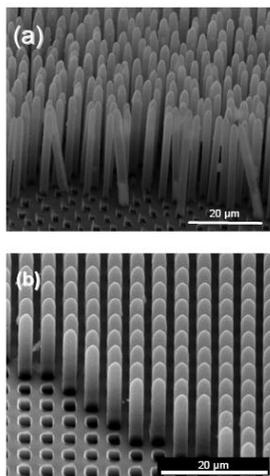


Figure 3: ESEM micrographs of (a) random and (b) ordered SiO_2 micropillars based on macroporous silicon.

References

- [1] A. Santos, P. Formentín, J. Pallarès, J. Ferré-Borrull, L. F. Marsal, *Journal of Electroanalytical Chemistry*, 655 (2011) 73.
- [2] W. Lee, R. Ji, U. Gösele, K. Nielsch, *Nature Materials*, 5 (2006) 741.
- [3] W. Lee, K. Nielsch, U. Gösele, *Nanotechnology*, 18 (2007) 475713.
- [4] D. Losic, D. Jr. Losic, *Langmuir*, 25 (2009) 5426.
- [5] K. Pitzschel, J. M. Montero-Moreno, J. Escrig, O. Albrecht, K. Nielsch, J. Bachmann, *ACS Nano*, 3 (2009) 3463.
- [6] K. Schwirn, W. Lee, R. Hillebrand, M. Steinhart, K. Nielsch, U. Gösele, *ACS Nano*, 2 (2008) 302.
- [7] A. Santos, V. S. Balderrama, M. Alba, P. Formentín, J. Ferré-Borrull, J. Pallarès, L. F. Marsal, *Advanced Materials*, 24 (2012) 1050.
- [8] A. Santos, G. Macías, J. Ferré-Borrull, J. Pallarès, L. F. Marsal, *ACS Applied Materials & Interfaces*, 4 (2012) 3584.
- [9] A. Rodríguez, D. Molinero, E. Valera, T. Trifonov, L.F. Marsal, J. Pallarès, R. Alcubilla, *Sensors and Actuators B*, 109 (2005) 135.
- [10] S. Izuo, H. Ohji, P. French, K. Tsutsumi, M. Kimata, *Sens. Mater.*, 14 (2002) 239.

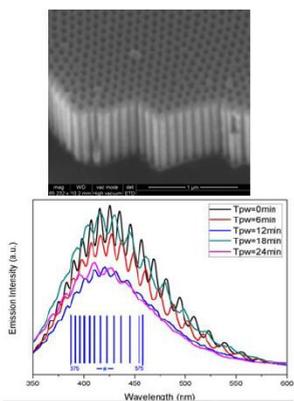


Figure 2: a) Top and cross section view of nanoporous alumina sample with a pore length of 6.8 μm and 40 nm pore diameter. b) PL spectrums for different porosities of nanoporous alumina: 11% ($T_{pw}=0$ min), 16% ($T_{pw}=6$ min), 22% ($T_{pw}=12$ min), 34% ($T_{pw}=18$ min) and 40% ($T_{pw}=24$ min).