Simplified Method for 3D-structured Nanoporous Anodic Alumina with stop bands in the visible

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Abstract

Nanoporous anodic alumina (NAA) is a material obtained by the electrochemical etching of aluminum in acid electrolytes with great interest in nanotechnology [1,2]. Its mechanical and structural properties and cost-effectiveness make NAA a first-choice candidate for several applications, such as in Biosensing[3,4] or Energy Harvesting[5,6]. When produced in the adequate conditions NAA shows a porous structure with a self-assembled pore distribution, what confers NAA a structure close to a Photonic Crystal: it consists of a 2-D triangular lattice of cylindrical parallel pores in an aluminum oxide matrix. However, the periodicity is not perfect and natural self-assembled NAA shows symmetry breaking points that produce domains of random size (a few microns in characteristic length) and orientation. In this sense, we called such a structure quasi-random[7]. In this communication we show the development of a simplified method to modulate the pore geometry along its depth, and consequently to obtain a varying refractive index also in the direction parallel to the pores. With this, NAA-based distributed Bragg reflectors (DBR) can be fabricated. This modulation of the refractive index contrast along the length of the pores can be used to obtain photonic crystal properties for all propagation directions along the material.

The method is based in our previous work[8] which shows that when a wet etching is applied to NAA to enlarge the pore diameter, the pore widening rate depends on the voltage applied in the anodization process. This result is depicted in Fig. 1, where the evolution of the refractive index of single-layer NAA with the pore widening time is plotted. The straight lines are only included as a guide-to-the eye. This result shows that the refractive index for as-anodized samples is very similar if the applied voltage, but the refractive index contrast increases with the pore widening time.

This result enables the modulation of the pores by a slow variation of the anodization voltage as the one depicted in Fig. 2, followed by an additional pore widening step that contributes to the enhance these pore modulations. Figs. 2b,c show FESEM cross-sectional pictures of two samples produced with a cyclic voltage as shown in Fig. 2a. The cycles can be clearly distinguished, and their length can be controlled precisely by the amount of charge spent in the phase at which the voltage is maximum and constant. Even though the images in Fig. 2b,c correspond to as-anodized samples, a clear pore modulation can be observed with a conical shape (a) and the beginning of pore branchings (b), corresponding to the lowest voltage within a cycle.

Fig. 3 shows the evolution with the pore widening time of the transmittance spectra of NAA DBR in samples produced after 150 cycles. The first-order stop band shifts to lower wavelengths for increasing pore widening times and becomes deeper. The pore widening has also the effect of increasing the transmission losses for the shorter wavelengths. This stop band dependence can be related to the morphology of the pores. It has to be remarked that the stop bands in the visible range may have possible application in low-cost biosensors.

References

[1] Ingham, C. J., ter Maat, J., de Vos, W. M., Biotechnology Advances, **30** (2012) 1089.
[2] Lee, W., Schwirn, K., Steinhart, M., Pippel, E., Scholz, R., Gösele, U., Nature Nanotechnology, **3** (2008) 234.
[3] Nicolini, C.; Bragazzi, N.; Pechkova E., Advanced Drug Delivery Reviews, **64** (2012) 1522.
[4] de la Escosura-Muñiz, A and Merkoçi, A, ACS Nano, **6** (2012) 7556.
[5] Haberkorn, N; Lechmann, M.C.; Sohn, B. H.; Char, K; Gutmann, J. S.; Theato, P.; Macromolecular Rapid Communications, **30** (2009) 1146.
[6] Santos, A.; Formentín, P.; Pallarés, J.; Ferré-Borrull, J.; Marsal, L.F., Solar Energy Materials and Solar Cells, **94** (2010) 1247.
[7] Maksymov, I.; Ferré-Borrull, J.; Pallarès, J.; Marsal, L. F., Photonics and Nanostructures, Fundamentals and Applications, **10** (2012) 459.
[8] Rahman, M. M.; Garcia-Caurel, E.; Santos, A.; Marsal, L. F.; Pallarès, J.; Ferré-Borrull, J., Nanoscale Research Letters, **7** (2012) 474.

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Figures

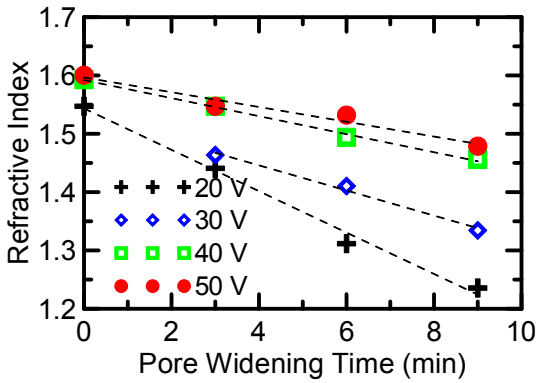

Figure 1. Refractive index of NAA single layers produced with different anodization voltages as a function of the pore widening time.

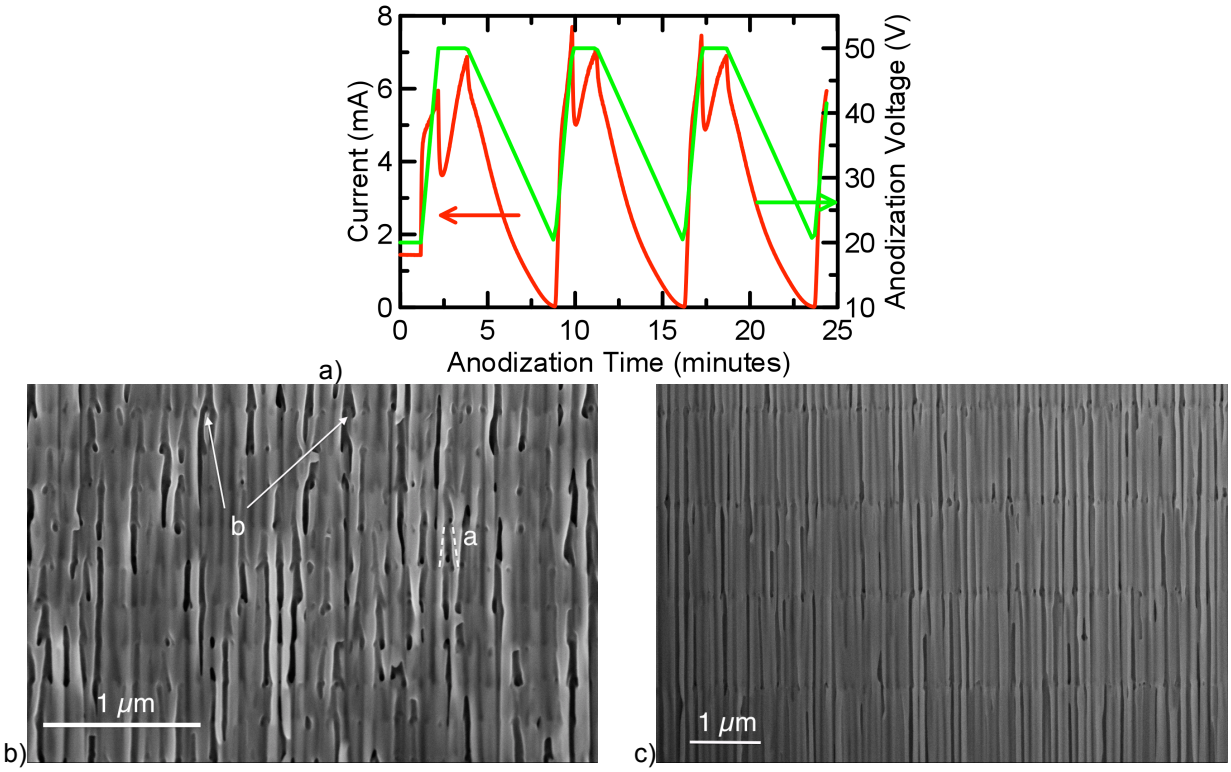

Figure 2. a) Applied voltage-time and registered current time curves for the first three cycles used to obtain NAA-based DBRs. b) and c) FE-SEM cross-sectional pictures of two different samples obtained with a different amount of charge spent in the constant 50V phase of each cycle.

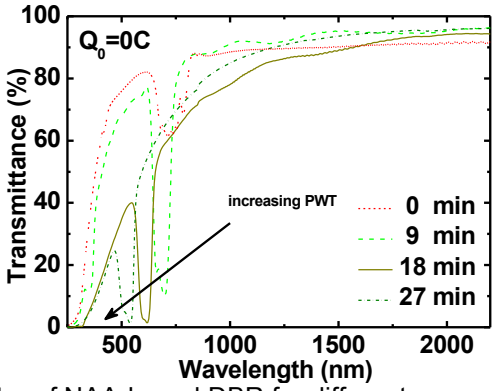

Figure 3. Transmittance spectra of NAA-based DBR for different pore widening times.