Nanoporous anodic alumina produced with variable voltages

Mohammad Mahbubur Rahman, Gerard Macias Sotuela, Maria Alba, Lluís F. Marsal, Josep Pallarès and Josep Ferré-Borrull*

Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, Universitat Rovira i Virgili, Tarragona, Spain

josep.ferre@urv.cat

Nanoporous anodic alumina (NAA) is a very interesting material in nanotechnology due to its selfassembled nanoscale-ranged porous structure. In the adequate fabrication conditions the interpore distance is of the order of the wavelength of visible light [1,2]. We have recently demonstrated that this fact in combination with the quasi-ordered structure of the pores makes it possible the existence of stop bands inside the material[3,4]. Recently, three-dimensional structuring of NAA has been introduced, where attention was paid on the fabrication of Bragg mirrors based on NAA having cyclic porosity with the depth by applying a cyclic voltage with carefully chosen voltage profiles[5,6]. However, the control over the optical properties of the layers obtained on every cycle is not studied in depth. If the 2D inplane confinement properties cited above can be combined with confinement in the direction parallel with the pores by means of a cavity surrounded by Bragg mirrors, 3D confinement of light could be achieved.

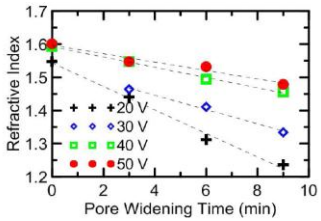

Figure 1: Effective refractive index of the NAA layer for the wavelength λ=750nm as a function of the pore widening time, for NAA made under different anodization voltages.

In this communication we report on the efforts being carried out at our group to achieve this 3D confinement. With our approach, it is possible to obtain photonic stop bands for light propagating along the direction of the pores by an in-depth structuring of NAA. In contrast with previous works of other authors, besides applying a periodic voltage to obtain a Bragg structure, we introduce a subsequent pore widening step which increases the refractive index contrast between the different layers, what permits to improve the optical performance of the structure.

In order to obtain the maximum refractive index contrast between the different layers in the NAA we have investigated the dependence of the pore widening rate of single-layer NAA with the voltage applied to obtain them. Figure (1) shows the effective refractive index of the porous NAA estimated from ellipsometric measurements of single-layer structures as a function of the pore widening time. The structures were fabricated by anodization in 0.3M oxalic acid at 4°C and at applied voltages of 20 V, 30V, 40V and 50 V, at which 2D self-assembly of the pores takes place. It can be seen that the refractive index is very similar for all voltages and for the as-produced layers, while the refractive index decreases and the differences between voltages increase with increasing pore widening time. This indicates that if a cyclic voltage is applied in the fabrication of NAA, layers with different porosity can be obtained, and that this differences in porosity can be enlarged with a subsequent pore widening step.

Figure 2a) shows the first three anodization voltage cycles and the corresponding current transient for an in-depth structured NAA. After the first anodization at 40 V and removal of the alumina layer to obtain the self-ordering of the pores, a second anodization starts at 20 V and it lasts until a charge of 2 C has flowed through the system. In this way, a self-ordered layer of vertical pores is obtained. After this, a voltage cycle is applied for 150 times. Each cycle consists of i) a linear ramp from 20 V to 50 V, at a rate of 0.5 V/, ii) an interval

of constant voltage at 50V that lasts until a charge of 2C has flowed through the system, and iii) a subsequent ramp from 50 V to 20 V at 0.1V/s. Whit this cyclic voltage we aim at obtaining alternating layers with different porous structure. After this process, a subsequent pore widening step is applied. This pore widening step provides an increase in refractive index contrast that improves the optical properties of the cyclic-layered structure.

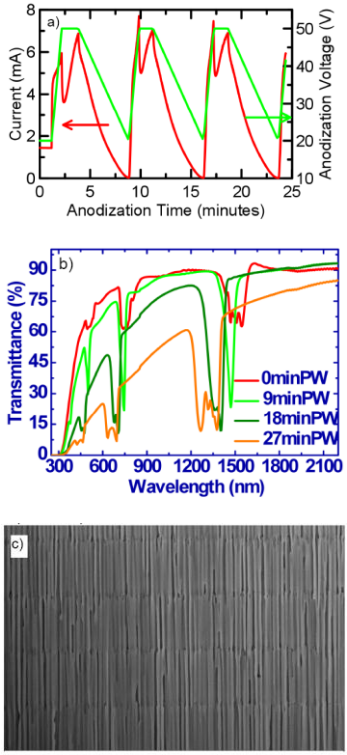

Figure 2: a) First three cycles of periodic anodization voltage used to produce an in-depth structured NAA with DBR structure and the corresponding current. b) reflectance spectra of the as-produced indepth structured NAA and for the same structure after different pore widening times as indicated in the graph. c) FE-SEM cross-section picture of four cycles of the sample.

Figure 2b) depicts the reflectance spectra of the NAA structure obtained with this cyclic voltage for the as-produced structure and for the same structure after different steps of pore widening with a solution of 5%wt H_3PO_4. The spectrum of the as-produced sample shows a decrease in transmittance in three intervals centred approximately at 1500 nm, 750 nm and 375 nm. This is clearly related to the existence of a Bragg mirror structure. The successive pore widening steps produce an increase in the depth of the transmittance stop bands as well as in their width, together with a decrease in the centre wavelength. This is a clear consequence of the increase of refractive index contrast between layers. Finally, in figure 2c) a FE-SEM picture of a cross section of the sample is depicted, showing the layered structure.

This in-depth nanostructuring of NAA with a fairly good control over the optical properties of the constitutive layer opens the possibility of building new devices based on 3D optical confinement in such structures.

This work was supported by the Spanish Ministry of Science under the projects TEC2009-09551, TEC2012-34397, HOPE CSD2007-00007 (Consolider-Ingenio 2010).

References

[1] A. P. Li, F. Müller, A. Birner, K. Nielsch, and U. Gösele, J. Appl. Phys. 84 (1998) 6023.
[2] L. Vojkuvka, L. F. Marsal, J. Ferre-Borrull, P. Formentin, and J. Pallares, Superlattices Microstruct. 44 (2008) 577.
[3] I. Maksymov, J. Ferré-Borrull, J. Pallarès, L. F. Marsal, Photonics and Nanostructures - Fundamentals and Application, http://dx.doi.org/10.1016/j.photonics.2012.02.003
[4] Mohammad Mahbubur Rahman, Josep Ferré-Borrull, Josep Pallarès, Lluis F. Marsal, Phys. Status Solidi C 8 (2011) 1066–1070.
[5] Dusan Losic, Mickael Lillo, and Dusan Losic Jr, Small 5 (2009) 1392–1397.
[6] Yan Su, Guang Tao Fei, Yao Zhang, Peng Yan, Hui Li, Guo Liang Shang, Li De Zhang, Materials Letters 65 (2011) 2693–2695.