

### 3D nanostructuring of nanoporous anodic alumina for photonic applications

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#### Abstract

The nanoporous anodic alumina (NAA) has attracted significant attention due to its self-assembled, densely packed and nanoscale-ranged porous structure. In the adequate fabrication conditions the two-dimensional pore pattern shows a characteristic interpore distance which can be of the order of the wavelength of visible light [1, 2], what makes it possible to control light inside the material. The low absorption coefficient, excellent thermal stability, the wide electronic band gap (7–9.5 eV) and easy handling of the NAA has made it a potential candidate for two-dimensional photonic crystal (2D PC) in the visible and infrared range [3]. Furthermore, quasi-random nanostructures based on NAA have been demonstrated to show photonic stop bands for all in-plane propagation directions [4, 5]. If this in-plane 2D photonic stop band could be combined with vertical optical confinement provided by a periodic change of refractive index in the direction parallel to the pores, then 3D confinement of light could be achieved. The ability of the porous materials to confine light in a small volume make them good candidate for sensing, LED light extraction, laser light generation. Recently, three-dimensional structuring or multilayer (in-depth) structures or Bragg's stakes of NAA have 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[6, 7]. However, the control over the optical properties of the layers obtained on every cycle is not studied in depth.

In this communication we will present a different approach to obtaining photonic stop bands for light propagating along the direction of the pores by an in-depth structuring of NAA. As in previous works, we apply a periodic voltage although 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 fabricate in-depth structured NAA with significant optical properties, it is necessary to have different layers with the highest possible refractive index contrast. However, it is known that in the self-ordering regime of pore growth, porosity depends weakly on the applied voltage [8, 9]. Thus, if a periodic voltage is applied to obtain in-depth structured NAA, the different layers will have a small refractive index contrast. Although porosity of as-anodized layers is very similar for all anodization voltages, interpore distance, and consequently pore diameter, depend on the applied voltage. This difference in pore diameter induces a difference in the etching rate in the pore widening step, which results in an increase of the refractive index contrast. 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.

With this result in mind, it is possible to modulate the thickness and refractive index only by changing the anodization voltage, whereas the acid electrolyte or concentration and anodizing temperature are kept constant. Figure (2a) shows the first five 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, 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 a linear ramp from 20 V to 50 V, at a rate of 0.5 V/s and a subsequent ramp from 50 V to 20 V at 0.1V/s. The current transients shows that with the continuous change in the anodizing voltage induces a change in etching current in which modulates the size of the pores within the cycles.

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 9 minutes of pore widening with a solution of 5%wt H<sub>3</sub>PO<sub>4</sub>. The spectrum of the as-produced sample shows an unstable behaviour around 682 nm. However, the spectrum of the same sample after pore widening shows a stop band: a range of

wavelengths (725nm to 639nm) where reflectance is increased with respect the surrounding values in the spectrum. The onset of the stop band is a consequence of the increase in refractive index contrast for the different voltages applied. Further studies are required to calibrate the position of the stop band and its width with the applied voltages and charges.

## References

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## Figures

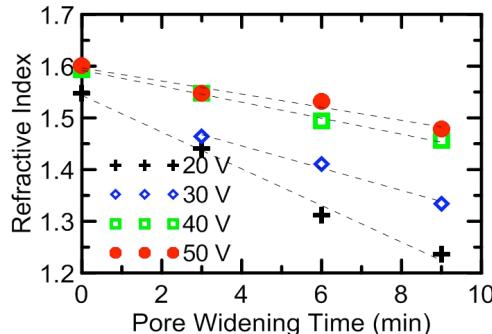


Figure 1: effective refractive index of the NAA layer for the wavelength  $\lambda=750\text{nm}$  as a function of the pore widening time, for NAA made under different anodization voltages.

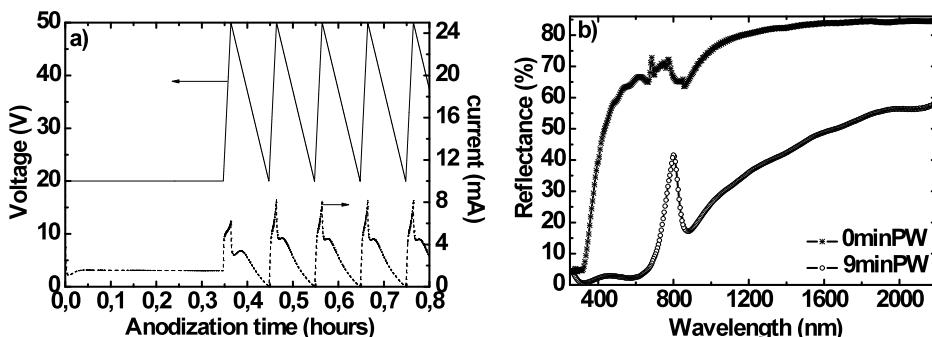


Fig 2: a) first five cycles of periodic anodization voltage used to produce an in-depth structured NAA with DBR structure and the corresponding current, b) reflectance spectra of the as-produced in-depth structured NAA and for the same structure after 9 minutes of pore widening.