Fabrication and characterization of nanoporous anodic alumina bilayers for biosensing applications

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Nanoporous anodic alumina (NAA) with pore diameters between 15 and 300 nm have shown promising results in areas such as optoelectronics [1] and materials science [2]. However, recently there has been an increasing interest in their possible application in biosciences, especially in label-free detection of biomolecules. To date, the studied approaches rely on self-ordered anodic alumina monolayers. These studies show promising results, but further investigation has been focused on surface modification and protein immobilization instead of structure modification. Here, we present our results in self-ordered nanoporous anodic alumina bilayers, focusing on fabrication, characterization and data processing for a further application as a biosensing platform.

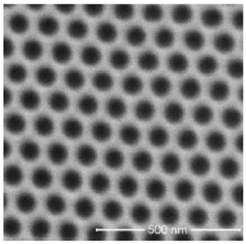

Figure 1: Top view of sample S2 showing highly ordered pores in a honeycomb-like manner.

Conventional two-step anodization [3] was performed on high-purity aluminium sheets (99.99% Ø20 mm 250 µm thick) purchased from Goodfellow Cambridge Ltd. Prior to anodization, a 4-min electropolishing pretreatment was performed in a mixture of ethanol (EtOH) and perchloric ($HClO_4$) acid 4:1 v/v at 20 V. Afterwards, the polished surface was anodized in oxalic acid ($H_2C_2O_4$ 0.3 M) at 40V and 4-6 ºC for 20 h in order to achieve self-ordering of pores. The grown aluminium oxide was then selectively dissolved in a mixture of phosphoric (H_3PO_4 6%wt.) and chromic acid (H_2CrO_7 1.8 %wt.) at 70 ºC for at least 3 h. A second anodization was performed under the same conditions but adjusted to obtain 1, 2, 3 and 4 µm respectively. Subsequently, pores were enlarged through wet chemical etching with phosphoric acid (5 %wt.) for 15 min. Finally, a third anodization took place under the same conditions in order to obtain a less porous 4-µm-thick second alumina layer. Fig.1 shows a top view of the samples.

Name	Layer 1 (µm)	Porosity 1 (%)	Layer 2 (µm)	Porosity 2 (%)
S1	1	50	4	10
S2	2			
S3	3			
S4	4			

Table 1: Sample structure characteristics.

Reflectance spectra were recorded for all samples in the 350-600 nm range using a PE Lambda 950 UV-Vis-NIR spectrometer at normal incidence (Fig.2). In order to establish the effective optical thickness (EOT) of each layer, fast Fourier transform (FFT) analysis was performed following a procedure described elsewhere [4].

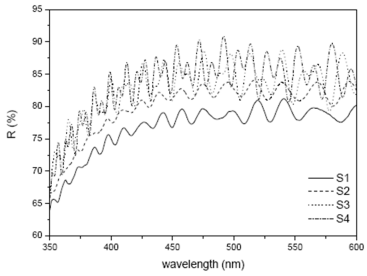

Figure 2: Reflectance spectra of NAA bilayers in the 350-600 nm range. The oscillations present in the spectra are not due to a single Fabry-Pérot effect, but to the combination of the intereference fringes of both layers.

According to literature regarding bilayers on porous silicon (PSi), three peaks should appear in the FFT graph, two of them referring to the first and second layers, and the last, to a combination of both [4]. However, the results obtained show just two peaks which refer to the second layer and the combination of layers (Fig.3). This may be a result of the overall shape of the NAA reflectance spectra (i.e. without the oscillations due to a Fabry-Pérot effect), which can mask low-frequency oscillations. Nevertheless, in-depth study must be undertaken to verify this theory.

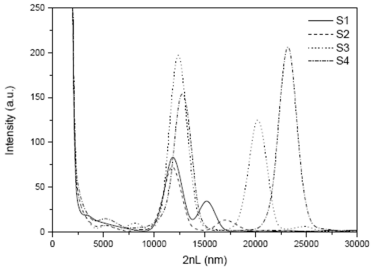

Figure 3: FFT plot of the reflectance spectra from Fig.2 of the NAA bilayers listed in Table 1. The peaks' position correspond to the EOT (i.e. 2nL=EOT) of the layer.

We have presented an easy approach for the fabrication of alumina bilayers with potential application in optical detection of biomolecules. FFT allows us to have a more robust and automated way of measuring the EOT. In addition, the FFT plot gives information in both axis. Peak position the EOT of the layer, while peak intensity is related with the refractive index contrast between two consecutive layers. Therefore, bilayers show promising results as they provide more information than monolayers thanks to their multiple FFT peaks which will be useful to follow functionalization and biomolecule immobilization. Finally, pore diameters can be tuned to promote or inhibit the entrance of certain macromolecules such as proteins and thanks to its funnel architecture give information of protein size.

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References

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