

RF GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY FOR THE ANALYSIS OF ARRAYS OF Ni NANOWIRES IN NANOPOROUS ALUMINA AND TITANIA MEMBRANES

V. M. Prida^(1,2), *D. Navas*⁽²⁾, *K. R. Pirola*⁽²⁾, *M. Hernandez-Velez*^(2,3) y, *A. Menéndez*⁽⁴⁾, *N. Bordel*⁽¹⁾, *R. Pereiro*⁽⁴⁾, *A. Sanz-Medel*⁽⁴⁾, *B. Hernando*⁽¹⁾ y *M. Vázquez*⁽²⁾

¹*Dpto. Física, Universidad Oviedo, Calvo Sotelo s/n, 33007-Oviedo, Spain*

²*Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049 – Madrid, Spain*

³*Dpto. Física Aplicada, C-XII, Universidad Autónoma Madrid, Cantoblanco 28049 - Madrid, Spain*

⁴*Dpto. Química Física y Analítica, Facultad de Química, Julián Clavería 8, 33006-Oviedo, Spain*

vmpp@uniovi.es

During the last decade, a great variety of nanostructures (nanotubes, nanofibers or nanowires) based on metals, carbons, polymers or semiconductors, have been synthesized following different synthesis procedures by using nanoporous anodic alumina membranes (AAM) as templates [1]. The principal reason for using templates of nanoporous AAM as precursor patterns lies on the possibility to obtain, under certain experimental conditions, periodic self-organized and highly ordered hexagonally dense packed nanoporous arrays [2]. This fact allows optimizing the performance of the devices so obtained [3]. On the other hand, the fabrication of self-ordered nanotubular titanium dioxide has a great interest for its technological application as a versatile material in photocatalyst, photovoltaic materials, gas sensor, biocompatible materials for bone implants, or spacer materials for magnetic spin valves, among others [4].

The characterization and chemical analysis of such membranes is of great importance to determine their quality. X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS) [5,6] are the more common techniques used for this kind of samples. Besides, Glow discharge (GD) spectrometry is being established nowadays as an important technique for the direct analysis of solid samples both, homogeneous solids and coatings (as thin as a few nanometers). Radiofrequency (rf) GDs coupled to optical emission spectrometry (OES) have proven a great capability for the direct analysis of either conducting or insulating materials (7). Preliminary studies have shown that rf-GD-OES could offer interesting information (depth profiling chemical concentration analysis) in very thin nanoporous films [8], as compared with other characterization techniques, e.g. XPS or RBS.

In this communication it has been investigated the potential of the rf-GD-OES (JY 5000 rf) to perform a comparative study of the depth profiling analysis in self-ordered anodic alumina and titania nanoporous/nanotubes, grown by using a potentiostatic electrochemical anodization procedure [2, 4]. Results show that this technique proves to be adequate for such a challenging new application. It has been obtained lengths about 5 μm or more for the hexagonally self ordered nanoporous (Al_2O_3) investigated (for the two steps AAM anodized in oxalic acid), with an average inner pore diameter of 35 nm and 105 nm interspacing. Besides, the analysis of the self aligned titania nanotubes (TiO_2) (grown by a single anodization process in a mixture of $\text{HF}+\text{H}_2\text{SO}_4$ acidic electrolyte) and with an average inner pore diameter of 100 nm and 40 nm wall thickness, was done and showed to be about 300 nm in length.

For both membranes, the empty nanoporous/nanotubes were filled with Ni by electrodeposition. The direct analysis by rf-GD-OES reveals that this technique is able to control the quality of this electrochemical deposition and, therefore, the characteristics of the Ni nanowires formed (see Figure 1). Finally, the rf-GD-OES experimental results were

correlated with the characterization of these samples obtained by RBS and scanning electron microscopy (SEM) techniques (Figure 2).

References:

- [1] T.M. Whitney, J.S. Jiang, P.C. Searson and C.L. Chien, *Science* 261, 1316 (1993).
- [2] H. Masuda and K. Fukuda, *Science* 268, 1466 (1995).
- [3] D. Routkevitch, A.A. Tager, J. Haruyama, D. AlMawlawi, M. Moskovits and J. M. Xu, *IEEE Trans. Electron Dev.* 43, 1646 (1996); M.T. Bohr, *IEEE Trans. Nanotech.* 1, 56 (2002).
- [4] G.K. Mor, K. Shankar, M. Paulose, O.K. Varghese and C.A. Grimes, *NanoLett.* 1, 191 (2005).
- [5] R. Beranek, H. Hildebrand and P. Schmuki, *Electrochem. Sol.-State Lett.* 6, B12 (2003).
- [6] M. Hernández-Vélez, K.R. Pirota, F. Paszti, D. Navas, A. Climent and M. Vázquez, *Appl. Phys. A*, (in press, 2005).
- [7] J. Pisonero, J.M. Costa, R. Pereiro, N. Bordel and A. Sanz-Medel, *Analytical and Bioanalytical Chemistry*, 379, 17 (2004).
- [8] K. Shimizu, H. Habazaki, P. Skeldon and G.E. Thompson, *Surf. Interface Anal.* 35, 564 (2003).

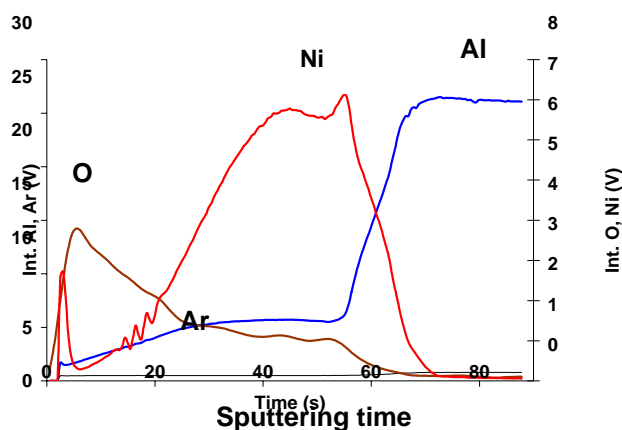


Figure 1: Rf-GD-OES depth profile analysis of a nanoporous alumina membrane filled with Ni by electrodeposition.

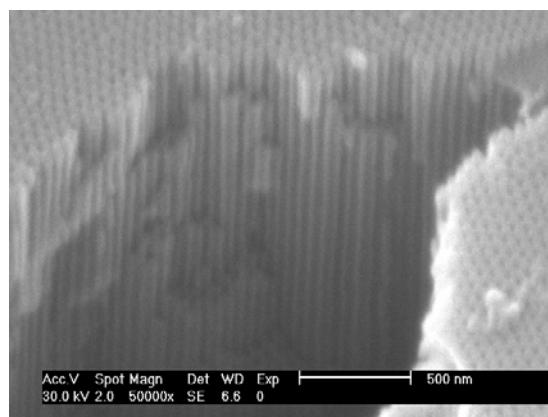


Figure 2: Field emission-SEM image (cross sectional view), of a nanoporous alumina membrane obtained by anodization process