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Introduction to the special issue on 'Nanostructures by Valve Metal Anodization'

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With this special issue of *JMSN* we are pleased to present significant contributions to a fascinating topic in the field of *materials nanostructing*, which is the anodization of valve metals. By this treatment *porous oxides* of controlled geometry can be grown on the respective metal surfaces. To date, aluminum (*Al*) has been used most often, as confirmed in this special issue where nine out of ten contributions deals with its anodization. However, applications of other valve metals are also emerging [1], mainly titanium (*Ti*), as attested by the present contribution of Uttiya et al. These porous oxides can be used by themselves, e.g. as surfaces of biomedical implants in contact with *living cells and tissues* [2-4], possibly loaded with functional agents for *drug delivery* [5-7], or as *templates* for the fabrication or nanostructures of different materials [8]. For example, metal *nanowires* may be grown in the pores and then set free by template etching [9,10]. Alternatively, the porous oxide nanostructure may be used as a *bed coated* with a material becoming an *in situ positive replica,* as is the case for gold deposited on substrates used for surface enhanced Raman scattering (*SERS*) [11,12]. Still other applications can be found in *catalysis* [13], *sensors* [14-16] and *photonic devices* [17,18].

In this special issue we had ten contributions from nine different groups (professor Shingubara's group presenting two works, Wang et al 'a' and 'b'), forming an interesting collection of disparate applications.

A general contribution came from Dr. *J. Runge*, whose goal is '*making anodizing an engineering process … that enables tuning the structure … to fulfill design and application requirements*'. She presented a nice overview of the theory, merging the analysis of anodization common in the academia with the corrosion point-of-view of the industrial environment. She introduced the Tafel equation and the concept of chemical potential, as well as a view of APA cell nucleation based on flakes of oxides. The comprehensive picture given by Dr. Runge may help to understand metallurgical issues [19] and side effects emerging during APA fabrication from Al alloys [20], which in the future could foster the use of recycled Al from e.g. beverage cans or food packaging.

The use of APA as a template for fabrication of nanowires is represented by the papers of Aisu et al and Wang et al 'a'. In the former $BaTiO_3$ *nanowires* were made in the APA pores. First barium acetate and tetraisopropyl-orthotitanate were used as Ba and Ti sources, loaded by vacuum-assisted means into the 200 nm diameter pores. Calcination followed at 700 °C for 2 h, and then NaOH etching of the APA at 40 °C during 72 h. Bundles of nanowires with length in excess of 40 μm were obtained. The nanowires were characterized in morphology, composition and microstructure by XRD and SEM plus EDS. Additionally, in view of future use in sensors, actuators and capacitors, the nanowires have been dispersed onto a silicon substrate and their dielectric constant has been measured by *impedance measurements* in a frequency range of 0.1-4000 kHz.

In Wang et al 'a' APA was also used as a template, for the complex fabrication of Cu_2ZnSnS_4 *nanowires* by electroplating. Thin APA from a sputtered Al layer (~700 nm) on molybdenum-coated silicon was first fabricated. The pores used were 70 nm in diameter (0.3 M oxalic acid at 40 V). After electroplating CuZn/CuSn, sulphurization was carried out at 600 °C for 10 min in CS_2+Ar atmosphere. Here the nanowires were not detached from the substrate after template removal, but remained attached to the molibdenum-coated silicon as an array to be used for *solar cells*. The resulting nanowire arrays were characterized by XRD and cross section SEM and TEM for the morphology.

The application of APA in optical devices based on luminescence has involved two different papers. Stepniowski et al presented *incorporation* into APA *of complex ions* of chelated vanadyl citrate. Two-step anodization was carried out in a mixture of sulphuric (2%wt) and citric (0.08 M) acids with addition of 0.04 M V_2O_5. The process was optimized by testing combinations of temperatures and voltages in the ranges of 0-15 °C and 13-23 V, respectively. Optical absorption in the Vis-NIR range was used to identify the presence of the doping ions in solution, while SEM was used to check the APA morphology. Despite the small pore size (~30 nm) successful loading was obtained. PL intensity maps at different excitation emission wavelengths combinations were used to quantify the amount doping ions present in the pores. Time decay study of the respective *fluorescence* was also done, showing long lifetimes (~45 ns) of the fluorescent anions, thanks to their complex structure.

On the other hand, Larosa et al loaded the APA with fluorophore indole molecule *cyanine Cy3*. This dye was stabilized in aqueous solution in a buffer phosphate at pH 7.3, at a concentration of 50 mm, and drop-casted onto APA. On excitation by a mercury lamp at ~530 nm wavelength, *fluorescence* emission was observed at ~593 nm in real time by a sensitive CCD photo camera coupled with the optical microscope. From the fluorescence maps frequency histograms were obtained, before and after a rinsing treatment that showed possible reuse of the substrates, for potential application in biomedical assays [21]. In particular, the authors observed by AFM the occurrence of APA pores in excess of 1 μm, even if anodization was carried out under standard conditions (0.5 M oxalic acid, 5-20 °C, 50 V). This ultra large pores were ascribed by the authors to their *annealing* treatment preliminary to the anodization.

Bocchetta et al described the fabrication of large area (up to 50 cm^2) APA layers. In this case the APA was still a traditional *self-supporting membrane*, yet comparatively thin (down to 10 μm). The authors presented interesting technological solutions, allowing simultaneous anodization at 150 V in 0.3 M of two substrates in the same electrochemical cell, and removal of the remaining Al and barrier layer at an inner area of the sample, leaving an holding frame around it. Characterization was made by SEM and Hg-porosity measurements, identifying pore sizes of 200 nm and densities of 10^{12} cm^{-2}, with specific surface area above 30 m^2/g. Preliminary results on the way to use of these membranes – after functionalization with CsH_2PO_4 and CSNST proton conductors – for H_2/O_2 *fuel cells* are also presented, in comparison to commercial APA membranes.

Three articles are focused on the fabrication of APA in itself. Wang et al 'b' demonstrated the fabrication of ordered arrays of thin APA (starting Al thickness 500 nm) with *inter pore spacing smaller than* that of *nano-pits* previously made by ion beam milling through an electron-beam lithography fabricated mask. This is a type of intelligent pre-patterning, which uses the forced relationships among the ordered APA pores to push the limit of resolution in APA nano-structuring. 60 nm pore spacing was reached, when starting from a triangular array of pits with 100 nm spacing, according to the geometrical constraint ratio of 1/√3. This method can be defined as '*guided*' self-organization. The resulting morphology was checked by both AFM and SEM, with additional analysis of FFT cross sections as well known in the literature [22,23].

Ottone et al also worked on thin APA, investigating the *effects* on the resulting pattern quality of the starting *Al* film *thickness and roughness*, in the ranges of 100-800 nm and 2-15 nm root mean square; respectively, the latter as resulting from 10x10 μm^2 AFM scans. The substrate was in this case *ITO-coated glass* with Al sputtered on top. SEM imaging was the means for evaluation of the thickness from APA cross-sections. The best anodization conditions turned out to be either 0.3 M oxalic acid at 40 V or 0.02 M phosphoric acid at 60 V, at temperature of 0-5 °C. An interesting observation was that the resulting APA pattern is *affected by* the *Al grains* in the thin film, with pores following the grain *edges*. Furthermore, below 300 nm in thickness phosphoric acid seems to work better, whereas *oxalic acid* gives rise to *delamination* issues.

In the work by Mukhurov et al, the electrolytes used for anodization were oxalic acid and a mixture of oxalic-phosphoric acid (0.33 and 0.5 M, respectively). The authors addressed the issue of fast APA growth by *hard anodization* at high voltage and high current density in – at least partly - galvanostatic mode as typical of the industry, while *still forming ordered* pores *pattern. Non standard* conditions were used, such as *electropolishing* in a mixture of phosphoric and acetic acid at 75-80 °C, and second *anodization* carried out *first* in *galvanostatic* mode with ramp, *then* in *potentiostatic* mode. With high voltage of 140 V in oxalic acid, still ordered APA domains were obtained, as shown by SEM images, with cell and pore sizes in the range of 225-320 nm and 50-70 nm, respectively. Different from Larosa et al, these authors found no effect of Al annealing prior to anodization, up to 500 °C treatment for 30 min.

Finally, the only work dealing with anodization of a valve metal different from Al was that of Uttiya et al, who treated Ti. After mechanical polishing with sandpaper, 99.7% purity-*1 mm thick Ti* was anodized in *1 M sulphuric and 1.5 M phosphoric acid* for 1 min only, at potentials ranging from 50 to 150 V. The SEM and AFM morphological analysis indicates that, within this potential range, *oxidation in sulphuric* acid produces *better* developed mesoporous oxide layers. XPS analysis and Raman spectroscopy showed that oxide layers grown in sulphuric acid present a better defined Ti oxidation state and anatase phase content, with the additional presence of *phosphate inclusions*, potentially interesting for biomedical applications.

The works presented here are by far not exhaustive of all the potential that porous anodic oxides have in modern nanotechnology. Still, they represent one more window open on the field, which we hope will help interested readers to expand their background and positively contaminate with different disciplines. We are grateful to the authors who submitted their papers for this issue, and worked pro-actively with us during manuscript revisions. Additionally, I am personally grateful to Dr. Francis Barin, the Associate Managing Editor, for his patience and constant help throughout all the *JMSN Special Issue* processing.

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