

New technology for metal nanorods formation

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ABSTRACT

The ongoing research on a new technology suitable for the large-scale fabrication of arrays of metallic nanorods suitable as nanoantenna dipole electromagnetic collectors is presented. The actual diameter and the height of the nanorods, centered approximately at the middle of the visible spectrum, have been settled as $D \sim 25\text{nm}$ and $H \sim 250\text{nm}$, respectively, in order to obtain a nanodipole antenna. The experimental work was carried on in two steps: first the synthesis of a template of anodic porous alumina by a two-step anodizing process of a 1100nm thick Al film, later the growing of the metallic nanorod inside the nanopores of the anodic template. It was used a new electroless metallic deposition method, based on a redox reaction of displacement realized by immersing the samples of nanoporous alumina into an acid solution made with cupric sulfate. Detailed scanning electron microscopy analysis of the samples structure is presented. SEM images show a copper nanorod with $H = 35\text{nm}$ and $D = 300\text{nm}$.

Keywords: metal nanorod, nanoporous alumina, anodization, displacement

1 INTRODUCTION

Many approaches have been used to successfully harvest energy from the sun and for conversion of solar energy into electricity, by means of photovoltaic (PV) cells is the most common approach. An alternative to photovoltaics is the optical rectenna, which is a combination of a rectifier and a receiving antenna. The initial concept of rectenna was demonstrated for microwave power transmission at Raytheon in the early 1960's. A rectifying antenna, or rectenna, was developed, consisting of a half wave dipole antenna with a balanced bridge or single semiconductor diode placed above a reflecting plane demonstrating conversion efficiency of 90.6% [1]. Nowadays, Novack et al. proposed a new and efficient approach for producing electricity from sun, using nanoantenna (nantenna) electromagnetic collectors with an efficiency approaching 84% [2]. The major technical challenge to be solved is the development of economical manufacturing methods for large-scale fabrication of nanoantenna-based solar collectors.

The main object of this work is to present the ongoing research on a new technology suitable for the large-scale fabrication of arrays of metallic nanorods suitable as nanoantenna dipole electromagnetic collectors. The actual diameter and the height of the nanorods, centered approximately at the middle of the visible spectrum, have been settled to have a nanodipole antenna with diameter $D \sim 25\text{nm}$ and height $H \sim 250\text{nm}$. Each nanorod has to be provided with rectilinear orientation, uniform distribution, has to be parallel to the other ones and perpendicular to a flat substrate. The experimental work was carried on in two steps: first step is the synthesis of a nanoporous alumina template, then metallic nanorods are grown inside the pores of the template.

The fabrication of anodized alumina template is promising since the processing time can be reduced by several orders of magnitude as compared with conventional lithographic methods and scanning probe methods. The principle is that, when aluminum is anodized in a suitable acidic electrolyte, under controlled conditions, it oxidizes to form an aluminum oxide (alumina) containing a two dimensional array of columnar hexagonal cells, each containing a nanopore normal to the substrate surface and provided with an almost round shaped section [3]. The nanopore base is separated from the non-converted underlying aluminum film from a thin and non-porous alumina layer, called the barrier layer. The pore diameter, the interpore spacing and the order degree of the structure as other geometrical parameters are controllable by the anodization conditions such as type of the electrolyte, concentration of the electrolyte, type of acid, anodization regimes (i.e. current or voltage), electrolyte temperature and duration of the electrochemical process [4][5]. In our research a huge number of nanopores, with a pore density of approximately 10^{10} pores/cm², were arranged in two-dimensional array by self-organization two-step anodic oxidation [6][7]. To obtain the metallic nanorods a new electroless metallic deposition method was used, based on a redox reaction of displacement realized by immersing the samples of nanoporous alumina into an acidic solution made with cupric sulfate [8]. Thus copper was deposited into nanopores. Detailed analysis of the alumina nanopores structure and that of the nanorods obtained, top and cross section, was conducted by Scanning Electron Microscopy (SEM).

2 FORMATION OF ORDERED NANOPORES ARRAY

Highly ordered nanoporous arrangement of the anodic alumina film was achieved by a two-step anodizing process of a flat and bright 1100 nm thick Al film (99,999% purity), deposited by magneto sputtering on a highly doped boron doped Si wafer (100) of $0.03\Omega\cdot\text{cm}$ resistivity. Next, a 340 nm aluminum layer was deposited on the backside of the wafers to form a good electrical contact. The pretreatment processes including annealing and electrochemical polishing of the aluminum were not necessary [9]. The ordered nanopore array was formed by stripping away the alumina layer obtained in the first anodization step and subsequently re-anodizing the remaining aluminum layer that was not converted during the previous step. Selective chemical etching of Al_2O_3 was carried out in a solution containing 3.5% vol H_3PO_4 , 2% vol CrO_3 , H_2O 94.5% vol for 3 min at a temperature of 328 K. The textured surface of the remaining aluminum, shown in figure 1, reflects the shape of the bottom of the nanopores of the removed alumina and makes easier pore nucleation during the second step. The anodization of both steps was conducted by applying a constant current density of $2\text{ mA}/\text{cm}^2$ in sulfuric acid electrolyte solution of 10 wt.% using a double-electrode temperature-controlled glass cell with graphite cathode.

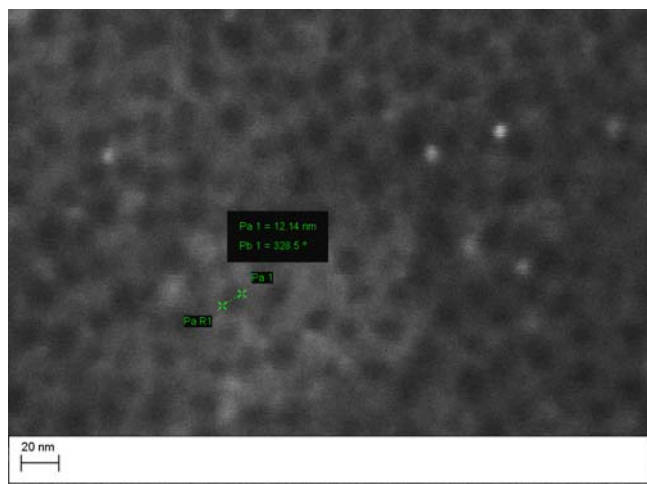


Figure 1. SEM image showing the indentation on the aluminum surface before the second step anodization.

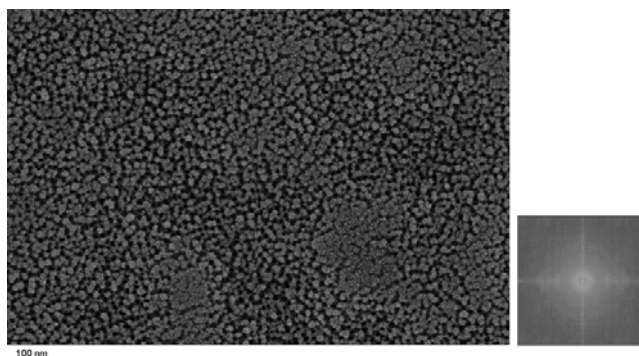


Figure 2. SEM image (left) of the alumina surface obtained after the two step anodization process at 297 K and its Fast Fourier Transform (right).

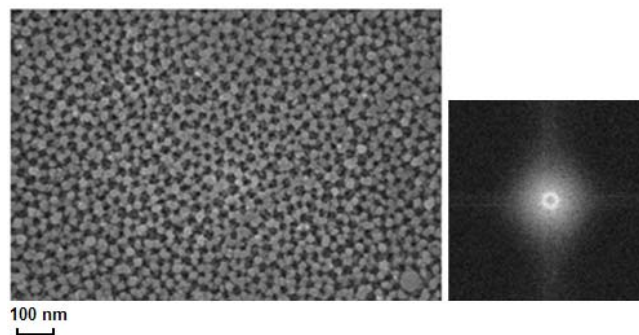


Figure 3. SEM image (left) of the alumina surface obtained after the two step anodization process at 275 K and its Fast Fourier Transform (right).

The second anodizing step was performed up to the complete anodization of the aluminum substrate leaving silicon at the base of the alumina nanopores. Silicon is necessary for the subsequent copper deposition process. The anodizations of both steps were conducted at two different temperatures: 297 K and 275 K. The anodization steps were done for 21 minutes for the first step and 4 minutes for the second step at 297 K and for 24 minutes for the first step and 4 minutes for the second step at 275 K. At the beginning of anodization a barrier layer forms on top of the aluminum film and, as anodization is continued, an array of nanopores develops on the barrier layer, whose diameters increase until reaching a final dimension determined by the anodization conditions. Once the final diameter is reached, the nanopore diameter does not increase any further, while the nanopore depth increases. The voltage-time characteristic shows a sharp rise in the voltage as the nanopores reach the silicon substrate. This sharp rise is due to oxidation of the silicon surface [10]. To settle the correct anodization times for the first and the second anodization steps it was necessary to previously determine the value of the volume expansion during nanoporous oxide formation. With the help of an optical profilometer (Fogale Zoomsurf 3D), it was measured a volume expansion of 1.4 for both anodizing conditions at different temperatures (i.e. at 297 K and 275 K). Furthermore, it was also determined the oxidation rates at

the two different temperatures: 44 nm/min at 297 K and 34 nm/min at 275 K.

In figures 2 and 3 are presented SEM (Scanning Electron Microscopy) top view photographs of anodized sample at the two different temperatures of 297 K and 275 K and their FFT (Fast Fourier Transform) images. When the process is performed at 297 K there is no order in the array of the alumina nanopores and FFT image shows a very cloudy ring. It is clearly shown that spatial order of nanopores improved with the decreasing of temperature. Figure 4 shows the cross-section SEM image of the samples processed at 275 K.

The features of the anodically formed structure at 275 K are: uniform regular distribution of nanopores diameter (i.e. 14 nm); arrangement of vertically directed nanopores (height 210 nm) at almost identical distance from each other; ability to control the order degree and the geometrical parameters of the nanopores by changing temperature of anodizing and an high reproducibility of the ordered film structure.

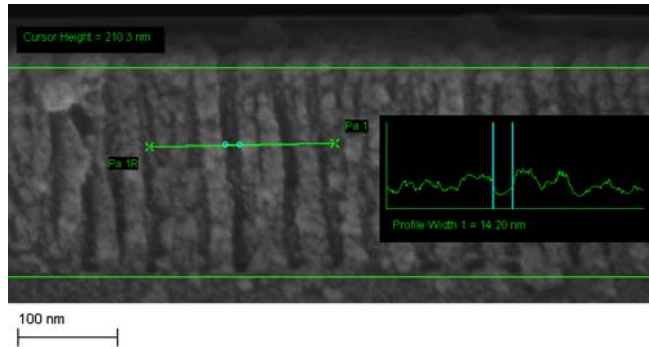
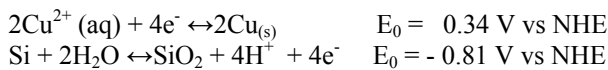


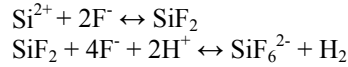
Figure 4. SEM image of the nanopores alumina cross-section obtained at 275 K. The figure shows height of 210nm and nanopore diameter of 14nm.

3 FABRICATION OF NANORODS ARRAY BY GALVANIC DISPLACEMENT

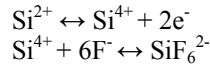
To obtain the copper nanorods a new electroless metallic deposition method was used. The method is based on a redox reaction of displacement realized by immersing the samples of nanoporous alumina obtained at 275 K into a solution made with cupric sulfate CuSO_4 , hydrofluoric acid HF, isopropyl alcohol (IPA) and deionized water (DI). Cu^{2+} ions are reduced and deposited on the Si substrate with electrons provided by oxidation and dissolution of Si [11], following the chemical reactions:



HF must be added to dissolve oxidized Si and expose additional Si to continue the galvanic displacement, following the reactions:



or



The displacement reaction occurs spontaneously because the deposited metal (Cu) is nobler than both the substrate and hydrogen. IPA was added for a better wetting of the samples. This part of the experimental work was aimed to discover the proper duration of the immersion of the samples in the chemical bath and the proper quantities of the components of the bath necessary to provide a selective deposition of Cu: the Al_2O_3 mask has not to be dissolved from the fluoride species.

The best result has been achieved, after many trials, by an immersion time of 20 sec into a solution containing 205 ml DI, 20 ml IPA, 2 ml HF, 0.1 g CuSO_4 , that was the most concentrated solution in CuSO_4 used. By this way the metal deposition enlarged the diameters, from 14 nm to 35 nm, of the alumina nanopores without dissolving totally the alumina structure. The cross-sectional SEM images show a copper nanorods with height (figure 5.a) and diameter (figure 5.b) dimensions that are approximately 300 nm and 35 nm, respectively. The copper nanorods are the bright white areas, as EDS analysis confirmed.

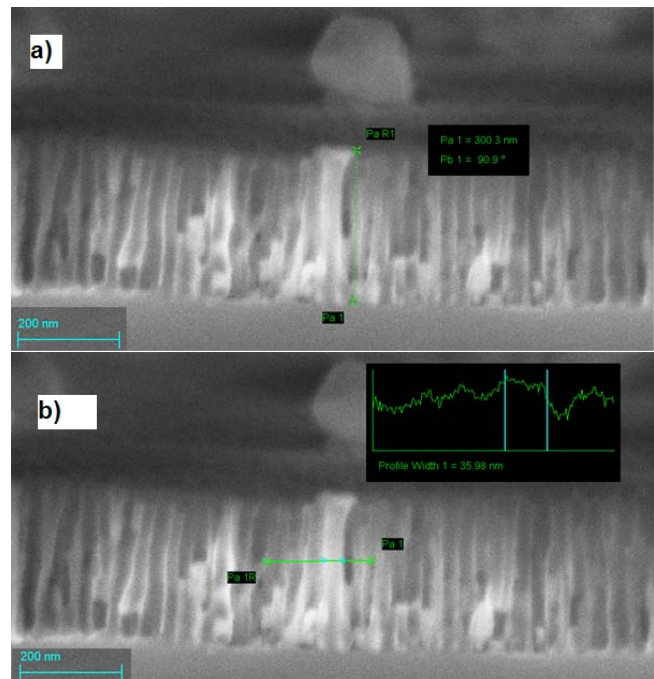


Figure 5. Cross-sectional SEM image of the sample obtained by immersing the alumina template for 20 sec into a solution containing 205 ml DI, 20 ml IPA, 2 ml HF, 0.1 g CuSO_4 . The image shows a copper nanorod with height (a) and diameter (b) dimensions that are around 35 nm and 300 nm.

4 CONCLUDING REMARKS

We attempted to obtain self-organization of a two-dimensional array of nanopores into alumina by a two-step anodic oxidation of an high-purity aluminum sheet. Both steps were performed by applying galvanostatic conditions, i.e. constant current density of 2 mA/cm² in sulfuric acid electrolyte solution of 10 wt.%. The second anodizing step was performed up to the complete anodization of the aluminum substrate leaving silicon at the base of the alumina nanopores. We did not observe a high order degree of pores in the samples anodized at 297 K, while we could observe an high order degree of nanopores with 14 nm diameter when processing at 275 K. The method presented allows to fabricate a template of nanoporous alumina in which nanopores are rectilinear, normal to the substrate, having each one the same required dimensions with uniform distribution and high reproducibility.

The alumina template obtained at 275 K was used as a mask for the copper electroless chemical deposition made by immersing the template into a solution of cupric sulfate. The conditions selected for the deposition process allowed the Al₂O₃ mask to not be dissolved from the fluoride atoms and permitted to observe copper nanorods formation with height of 300 nm and a diameter of 35 nm. To obtain a better uniformity in the copper deposition some trials may be done, for example it is possible and worthy to increase the IPA content of the solution to increase the wetting action of the solution into the very narrow nanopores, or increase the duration of the immersion period of the sample into the solution or enrich the solution with chemical additives to facilitate the redox chemical reactions on the silicon surface. In future, to investigate the cross-section of the copper deposited sample it will be used FIB (Focus Ion Beam) technology in order to obtain a much better controlled cut avoiding the copper nanorods to jump out due to the strong mechanical vibration caused by the usual mechanical cleavage made with silicon carbide knife.

REFERENCES

- [1] W. C. Brown, "The history of power transmission by radio waves," *IEEE Trans. Microwave Theory Tech.*, vol. MTT-32, pp. 1230–1242, Sept. 1984.
- [2] D. K. Kotter and S. D. Novack, W. D. Slafer, P. J. Pinhero, "Theory and Manufacturing Processes of Solar Nanoantenna Electromagnetic Collectors", *J. Sol. Energy Eng. -- February 2010 – Volume 132, Issue 1, 011014 (9 pages)* doi:10.1115/1.4000577.
- [3] O. Jessensky, Müller, Gösele "Self-organized formation of hexagonal pore arrays in anodic alumina" *Applied Physics Letters* Vol.72, Number 10, 1998.
- [4] Sulka, Parkola Temperature influence on well-ordered nanopore structures grown by anodization of aluminum in sulphuric acid *Electrochimica Acta* 52 (2007)1880-1888.

- [5] AlmasiKashi, Ramazani The effect of temperature and concentration on self-organized pore formation in anodic alumina *J.Phys. D : Appl. Phys.* 38 (2005) 2396-2399.
- [6] Masuda, Hasegawa Self-Ordering of Cell Arrangement of Anodic Porous Alumina Formed in Sulfuric Acid Solution *J. Electrochem. Soc.*, Vol.144, No. 5, May 1997.
- [7] ShosoShingubara, Osamu Okino, Sayama, Sakaue, Takahagi Ordered Two-Dimensional Nanowire Array Formation Using Self-Organized Nanoholes of Anodically Oxidized Aluminum, *J.Appl.Phys.* Vol 36 v(1997) pp.7791-7795, Part.1 No. 12B.
- [8] Calvin P.daRosa, RoyaMaboudian, Enrique Iglesia Copper deposition onto Silicon by Galvanic Displacement: Effect of Silicon Dissolution Rate *Journal of Electrochemical Society*, 155(6)E70-E78 (2008).
- [9] Montero-Moreno, M. Sarret, C. Müller Influence of the aluminum surface on the final results of a two-step anodizing *Science Direct, Surface and Coatings Technology* 201 (2007) 6352-6357.
- [10] Biswajit Das Investigation of Nanoporous Thin-Film Alumina Templates *Journal of the Electrochemical Society*, 151 (6) D-46-D50 (2004).
- [11] Calvin P.daRosa, Enrique Iglesia, Roya Maboudian Dynamics of Copper Deposition onto Silicon by Galvanostatic Displacement *Journal of Electrochemical Society*, 155(3) D244-D250 (2008).