

# Electrochemical and Electroless Deposition of Metal in Anodic Aluminium Oxide Nanoporous Template

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**Abstract** – In the present work, the techniques for chemical and electrochemical metal deposition in and on the dielectric layer of anodic aluminium oxide lied on aluminium substrate are described. The possibilities for obtaining the parallel three-ply structures Al/Al<sub>2</sub>O<sub>3</sub>/Me with dielectric core and anisotropic conductivity by growth of nanowires in the pores of Al/Al<sub>2</sub>O<sub>3</sub>+Me/Me oxide are shown. The obtained structures can be used as parts of different electronic devices such as conductive images on dielectric substrate or solderless interconnectors.

**Keywords** – Anodic Aluminium Oxide, Nanowires, Electrochemical deposition, Chemical deposition

## I. INTRODUCTION

The anodic aluminium oxide is wide used for obtaining of different structures and devices for electronics [1]. The continuous interest in this material is due to its physical and electrical properties as well as its high ordered nanoporous structure. The electrochemically obtained cellular structure is suitable for fill with different substances for receiving nanowires, nanotubes and nanorods. An orderly and uniformly sized nanowire array is extraordinarily useful, as it can act as both a functional and a structural component in a device. Metallic nanowire arrays with different aspect ratios offer many modern applications as nanoscale electronic components [2], optoelectronic devices [3], nanosensors [4], and high-density magnetic memories [5].

Many different methods used for fabrication of metallic nanowires with a high aspect ratio have been reported in the literature. These strategies include vacuum evaporation, magnetron sputtering, electroless deposition, electroplating, and chemical vapour deposition. Among them, electrochemical and electroless deposition of metallic materials into the pores of anodic aluminum oxide membranes seems to be ones of the simplest, flexible and inexpensive approaches.

During the last ten years the AAO template is wide used for electrochemical growth of 1D nanowires. However in this case the expensive and complicated technologies are used. The lasts include the obtaining of free membrane from anodic aluminium oxide with removed barrier layer at first, which subsequently have to be one side covered with noble metal by PVD for initial cathode surface [6].

The present work examines the possible ways for obtaining different parallel three-ply structures as Al/Al<sub>2</sub>O<sub>3</sub>+Me/Me with anisotropic conductivity by electrochemical growth of nanowires inside the pores of oxide or Al/Al<sub>2</sub>O<sub>3</sub>/Me with dielectric core by electroless

deposition.

## II. MATERIALS AND EQUIPMENT

The aluminium oxide used as matrix for metal deposition is obtained by anodizing of aluminium foil (thickness 0,1 mm and 99 % purity) during eight hours in 0,3M solution of oxalic acid at 40V and temperature 15 °C. The anodizing was made using the computer controlled laboratory power supply Voltcraft DPS-4005PFC in thermostatic cell with 200 mL volume and stainless steel counter electrode. The growth rate of anodic aluminium oxide in these conditions is 0.1 µm/min with average pores diameter 30 nm.

For receive the defined topological image on the surface, a solid negative photo resist was used. Thus prepared surfaces are catalyzed by palladium or re-anodized for thinning of barrier layer.

For microscopic observations the optical metallographic microscope Optika XDS-3MET with camera for take capture of examined image (maximum magnification of 500x), was used. The determination of aluminium oxide thickness, as well as the evaluation of pores filling degree was made by observation of cross-section of specimens.

## III. FABRICATION PROCESS AND RESULTS

This study exploits the nanostructured anodic aluminium oxide to realise two different designs: (A) composite Al<sub>2</sub>O<sub>3</sub>+Cu with an anisotropic conductivity and (B) the three-plate parallel structure Al/Al<sub>2</sub>O<sub>3</sub>/Me. On figure 1 the two technological plans of their obtaining are presented.

### A. Electrodeposition of metal inside the nanopores

Before the electrochemical metal deposition it is necessary to ensure an electrical contact of the aluminium substrate with the electrolyte. It is well known that the thickness of the barrier layer, as the pores diameter decrease in proportion to applied voltage [7]. During step reduction of voltage  $\sqrt{n}$ -times each pore divides in  $n$  narrowly ones. This is commonly used by some authors to receive metallic nanowires with dendriform hierarchical structure [8, 9] and thinning or even removing of barrier layer in order to make electrochemical metal deposition inside pores [9]. However at lightly decreasing of voltage there are not conditions for formation of new pores (big number with small diameter). At this kind of voltage decreasing, the rate of chemical dissolution is higher as compared to the rate of electrochemical oxide formation. As a result the barrier layer goes thinner. In this investigation the barrier layer thinning and ensuring of electrical contact between aluminium and electrolyte is realized by secondary

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anodizing processes with lightly decreasing of voltage from 40 V to 10 mV for about 50 minutes. The achieved thinning of barrier layer is sufficient to make possible the electrochemical DC metal deposition in the bottom of pores.

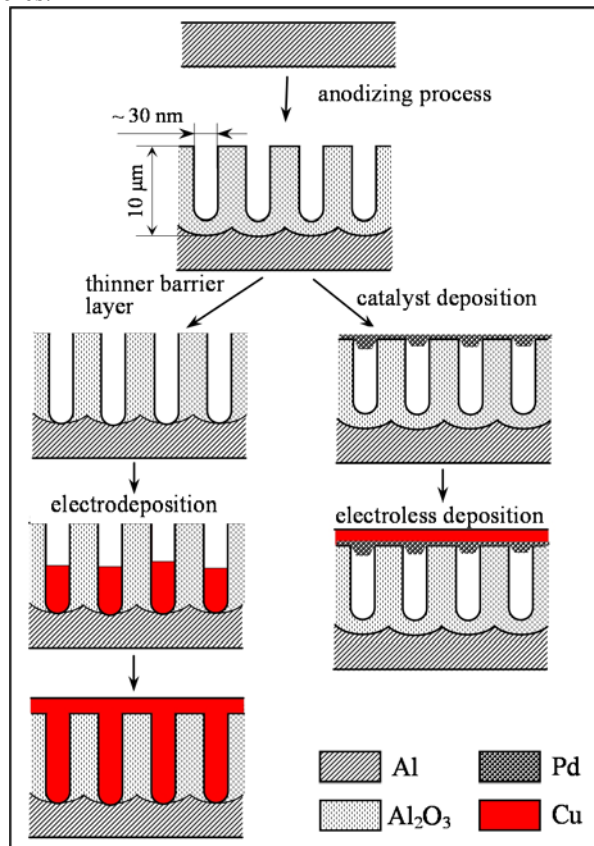


FIGURE 1. FABRICATION PROCESS STEPS

Figure 2-a shows a picture of copper nanowires obtained in neutral copper electrolyte which was grown up to  $\frac{2}{3}$  of the thickness of the alumina oxide layer. At continuing of electrolysis process, the pores are completely filled up and a dense metallic layer is formed on the aluminium oxide (fig. 2-b).

The electrochemical deposition made using that sequence can be used for building up three-ply system Al/Al<sub>2</sub>O<sub>3</sub>+Cu/Cu with anisotropic contact between the aluminium matrix and metallic layer on the surface.

The using of suitable photo-lithographic technique combined with partial dissolving of oxide after the pores was filled with metal, allows the creation of different structures for electronics. By this technology the nano-contact elements [10], a multi-functional solderless interconnectors based on copper nano wires [6], a catalytically activated surface for sensors, etc., can be prepared.

#### B. Chemical metallization of the anodic aluminium oxide

The degree of penetration of the electroless deposited metal inside pores highly depends on the diameter of pores of the anodic aluminium oxide. At used in this work conditions (electrolyte on the base of oxalic acid) the pores with average diameter of 30 nm are obtained. In view of this fact, copper is predominantly deposited only on the

outside surface (fig. 3-a). The grow rate of metallic nuclei close to the outside surface is high enough and the pores openings are plugged up with metal.

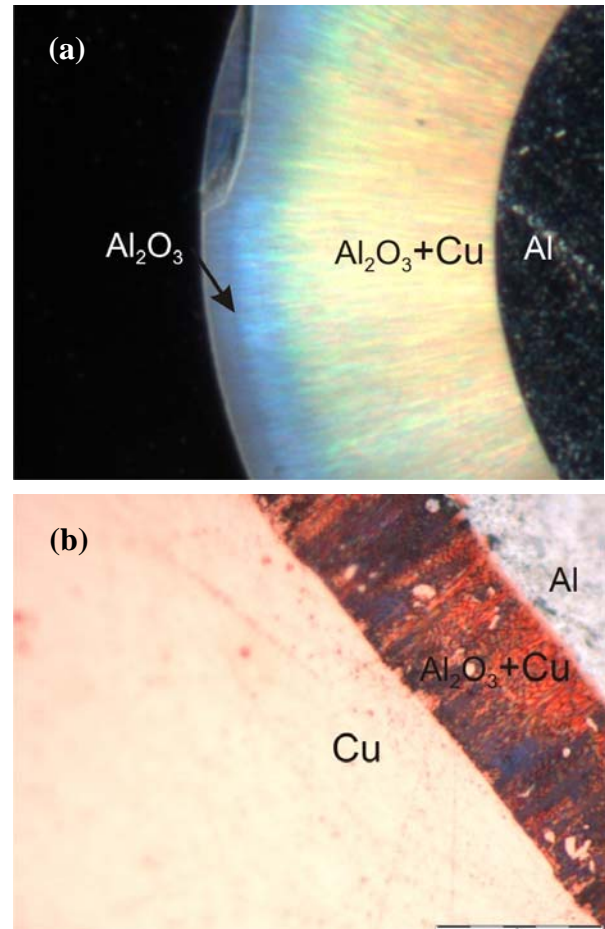


FIGURE 2. ELECTROCHEMICAL DEPOSITED NANOWIRES INSIDE OF THE ANODIC ALUMINA TEMPLATE.

Some of the specimens were subject of pores widening in 5% phosphoric acid solution. Because of the anisotropic properties of anodically formed aluminium oxide his dissolution in this weak electrolyte is taking place mainly on the vertical of the walls. The concentration gradient inside pores regarding hydrogen ions leads to predominantly widening of pores on the outside surface of the oxide and when the oxide is thicker the form of the pores becomes conical [11]. By different duration of stay in the widening solution the depth of penetration of metallic layer into oxide layer can be controlled. (figure 3-b). After 30 minutes widening, the hole surface of the pores beside the barrier layer is covered with deposited metal. In this case in some separate points (sites with accumulation of defects) it is possible that the dielectric properties of oxide to be deteriorated.

Figures 4-a and 4-b display cross-section of the aluminium oxide surface, partially covered with metal, obtained respectively without and after partial surface widening of pores during 10 minutes. On the figure 4-c the entire filling of the pores can be seen (on the right part of the picture) after widening - 30 minutes in phosphoric acid solution. On the pictures it can be noticed clearly that the bigger diameter of pores of the aluminium oxide allows its uniform filling with metal up to the bottom. In the both

cases infiltration of metal layer in  $\text{Al}_2\text{O}_3$  provides high adhesion since there is not in practice borderline between the separate layers.

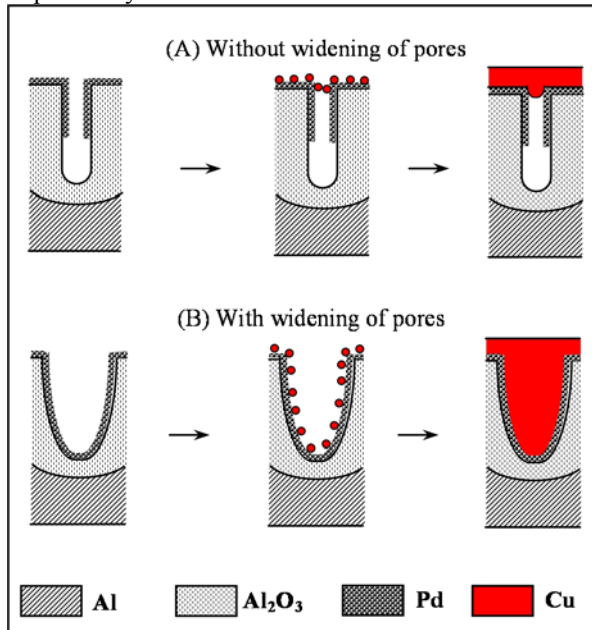


FIGURE 3. EFFECT OF WIDENING OF PORES ON THE PENETRATION OF ELECTROLESS METAL DEPOSITION.

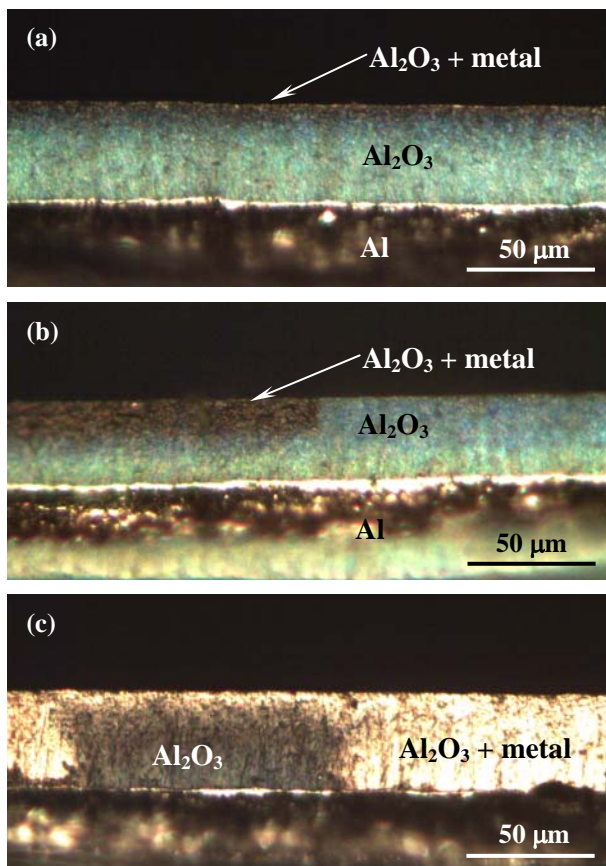


FIGURE 4. CHEMICAL DEPOSITED METAL ON OXIDE (A), INTO OXIDE AFTER 10 (B) AND 30 MINUTES WIDENING OF THE PORES (C).

By using of photolithography the described above three-ply structures can be formed only on separate sites of the surface receiving different conductive images on the dielectric substrate from anodic aluminium oxide on

aluminium matrix (figure 4-b). The deposited in this way chemical metallic layer can be used for preparing of different kind of sensors (for gas, temperature, pressure, etc.), micro-heaters and so forth.

The electrochemical and chemical metalizing allows a uniform deposition of metal on surfaces with shaped form (such as cylinder surface - fig. 2-a), which is difficult when PVD methods are used.

#### IV. CONCLUSION

In the present work the technologies for electrochemical and chemical copper deposition into and on nanopores of anodic aluminium oxide are presented. In the first case the filling of pores of aluminium substrate is achieved, as in the second (electroless) - deposition only on the outer surface without contact between the metallic layer and the aluminium is possible. By an intermediate process of pores widening the depth of penetration of chemically deposited metal into pores can be increased. The applied chemical methods for metal deposition in this work allow formation of different conductive images and structures suitable for application in the electronics.

#### REFERENCES

- [1] A.A. Poznak, Modified anodic alumina and composite materials bases on it, BSU, Minsk, 2007 (in Russian)
- [2] C. Cheng, R. Kanth Gonela, Q. Gu, D.T. Haynie, Self-Assembly of Metallic Nanowires Aqueous solution from Nano Lett., 2005, Vol. 5, pp 175-178.
- [3] R.M. Dickson, L.A. Lyon, Unidirectional Plasmon Propagation in Metallic Nanowires, J. Phys. Chem. B, 2000, Vol. 104, pp. 6095-6098.
- [4] E.C. Walter, R.M. Penner, H. Liu, K.H. Ng, M.P. Zach, F. Favier, Sensors from electrodeposited metal nanowires, Surf. Interface Anal., 2002, Vol. 34, pp. 409-412.
- [5] D. Al Mawlawi, N. Coombs, M. Moskovits, Magnetic properties of Fe deposited into anodic aluminium oxide pores as a function of particle size, J. Appl. Phys., 1991, Vol. 70, pp. 4421-4425.
- [6] Vh.Nguyen, P. Castelan, Z. Khatir, T. Lebey, V. Bley, N. Sewraj, Qh. Luan, B. Schlegel, Fabrication of bottom die substrate solderless interconnection based on nano copper wires, Proceedings of Power Electronics and Application, 2009, EPE'09.13<sup>th</sup> European Conference, pp. 1-9, 2009
- [7] J.-H. Kim, S. U. Jang, K. H. Park, S.-J. Kwon, Effects of Applied Voltage on Barrier Oxide Layer in Porous AAO Fabrication, Proc of 3<sup>rd</sup> Int. Nanoelectronics Conference 2010, pp. 499-500.
- [8] Chun-Ko Chen, Sheng-Hui Chen, Analysis of Nano-channel Array fabricated by Multi-step Anodic Aluminum Oxide Method, Proc of 4<sup>th</sup> Int. Nanoelectronics Conference 2011, pp. 1-2
- [9] A. Saedi, M. Ghorbani, Electrodeposition of Ni-Fe-Co alloy nanowire in modified AAO template, Materials Chemistry and Physics, 2005, Vol. 91, pp. 417-423
- [10] V. Videkov, V. Porkun, I. Vrublevsky, S. Tzanova, Brush Type Bonding with Nano-Needle Structure for Carrier Wafer Bonding in Microelectronics, Proc. of Nanotech Northern Europe (NTNE 2007), Helsinki, pp. 70-74.
- [11] J. Cui, Y. Wu, Y. Wang, H. Zheng, G. Xu, X. Zhang, A facile and efficient approach for pore-opening detection of anodic aluminum oxide membranes, Appl. Surf. Sci., 2012, Vol. 258, pp. 5305- 5311