THE EFFECTS OF ANODIZING CONDITION AND POST TREATMENT ON THE GROWTH OF NICKEL NANOWIRES USING ANODIC ALUMINUM OXIDE

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Abstract: *The effects of anodizing condition and post treatment on the growth of nickel nanowires, were investigated. A two-step anodizing process was applied in phosphoric and oxalic acid solution. Nickel electrochemical plating was applied to fill Anodic Aluminum Oxide (AAO) pores. For pore filling enhancement, AAO surfaces were treated by silver predeposition. After electroplating, aluminum and oxide layer of some specimens were removed. The results showed that silver preplating increases the pore filling and as the applied voltage becomes higher, the pores diameter decreases.*

Keywords: *anodizing, nanopores, aluminum oxide, deposition*

1. INTRODUCTION

Nanotechnology is attracting wide attention and is expected to have a profound impact on our economy and society in the coming decades. A template approach, which is based on confined deposition of materials inside the nanometer-scale pores of self-organized anodic aluminum oxide (AAO), could be potentially used for fabrication of metallic tips. High efficiency electron emission sources are central to the development of vacuum microelectronic devices.

When aluminum is polarized anodically in an electrolytic solution, an oxide film will be formed on its surface and this process is called anodizing [1]. When aluminum is being anodized in sulfuric, oxalic or phosphoric acid, a porous oxide film, as shown in Figure 1, with honeycombed structure will form on the aluminum surface that each cell contains a cavity [2].

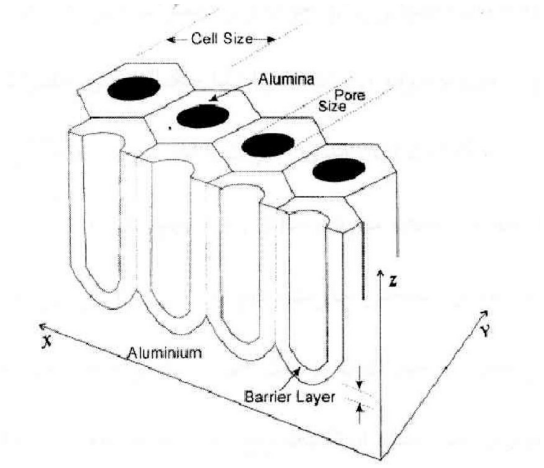

Fig.1. porous oxide films, with honey combed structure formed on the aluminum surface

The special arrangement and structure of cavities in anodic aluminum oxide make it a pattern for growth of nanostructures in the cavities. Arrangement and shape of the cavities in anodic aluminum oxide depend on the applied voltage, temperature, concentration and type of the acid [3]. In the first stage of anodizing, the structure of the cavities is not well arranged and the diameter of the cavities is not the same which means that those are not aligned parallel to each other. To produce well arranged cavities that are straight and parallel to each other, like Figure 2, the two-step anodizing is applied.

After removing the aluminum oxide layer by acid, a thin layer of oxide, that is called barrier layer, remains and covers the end of the cavities. The barrier layer is not a hard layer. As shown in Figure 2 periodic vicissitudes are formed on aluminum's surface. This structure acts as a pattern for growth of cavities in two-step anodizing. If the condition of anodizing in the first step is repeated in the second step, then a

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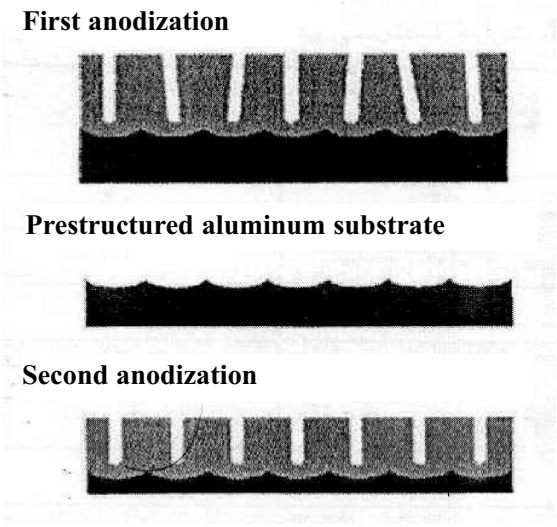

Fig. 2. Formation of periodic vicissitudes on the aluminum surface

well arranged array of nanocavities will produce.

The mechanism of self-organization in anodic aluminum oxide is that electric field across the barrier layer controls the growth of oxide layer and the local increase in electric field at the end of cavities (at the interface of electrolyte and barrier layer) solves the oxide layer. There is a balance between oxide film growth at the interface of metal-oxide and dissolution with the aid of electric field [2]. Figure 3 shows a schematic growth of the oxide layer. Because of this balance, and with prolonging the time, the growth of oxide layer will cease and the thickness of the oxide layer will remain constant. In addition, the electrolyte's anions at the interface

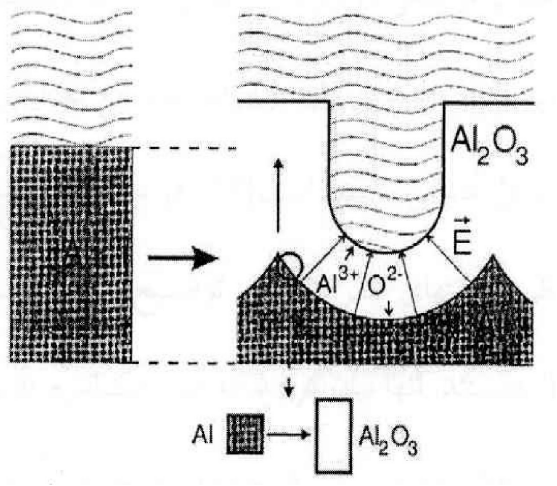

Fig. 3. A schematic growth of the oxide layer

of cavities and electrolytes will be absorbed by the oxide layer and penetrate the barrier layer structure.

Growth of aluminum oxide layer at constant voltage happens while keeping the other parameters of anodic aluminum oxide film unchanged. Creation of oxide film happens at constant rate that is defined by average of present electric field at oxide layer. On the other hand, rate of solution of oxide layer that is done by electric field is defined by local field present at the end of cavities. This depends on radius of curvature at the end of cavities and so any trend, towards decrease or increase of cavities curvature, depends on the changes of used voltage [2]. Jessensky et al. have considered these explanations not satisfactory enough and have expressed a systematic relation between the volumetric expansion during phase transformation of Al into Al_2O_3 in anodizing, applied voltage and creation of self-organizing structure [4].

Anodic aluminum oxide is used as chemical sensors, multi-part nanowires for studying moving properties of electrons in nanoparticles [5].

For the magnetic nanowires that have high aspect ratio (for example 50%), the magnetic saturation across the wires will occur by less magnetic field [6].

By benefiting from well arranged structure of cavities in anodic aluminum oxide it is possible to produce denser field emission arrays. Furthermore, by concerning the diameter of cavities in anodic aluminum oxide that are in order of nanometers, the size difficulties of lithographic methods will be resolved.

There are different methods in order to fill the cavities of anodic aluminum oxide such as chemical vapor deposition (CVD), sol-gel method, and electro-less deposition and etc. One of the most common ways is the electrochemical process that is used for filling the nanosize cavities by conductive materials for producing connected wires with high aspect ratio.

The aim of this research was to investigate the effect of anodizing conditions on the growth of nickel nanowires on AAO template.

2. EXPERIMENTAL PROCEDURE

In order to prepare anodic aluminum oxide, a

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Table 1. The chemical composition of the Aluminum

Al	Si	Fe	Cu	Mn	Mg	Zn	Ti	Others
99.5%	0.2%	0.04%	0.05%	0.05%	0.05%	0.05%	0.03%	0.03%

Table 2. Solution used for partially dissolution of the cavities

Temperature ºC	Others	Phosphoric acid	Chromic acid
80-90	Distilled water	50 cc/L	20 gr/L

Table 3. Composition of the solution used for A 1 and A2

Temperature ºC	Sulfuric acid (H_2SO_4)	Boric acid (H_3BO_3)	**Silver Nitride** ($AgNO_3$)
room	10 gr/L	20 gr/L	5 gr/L

99.5% purity 1050 aluminum plate with 0.5mm thickness was used. The chemical composition is shown in table 1. Eight specimens with code numbers of (A1, A2, A3 and A4) and (B1, B2, B3) were cut into 40×150 mm pieces and were degreased in ultrasonic apparatus. Chemical polishing of specimens were carried out at 80-90 ºC in proper solution.

The "A" labeled specimens were anodized in oxalic acid and the "B" labeled specimens were anodized in phosphoric acid.

A1, A2 and A3 samples Anodizing were done in 0.04M Oxalic acid solution in 5 ºC for 2 hours in the first step and 40 minutes in the second step in 85 V.

The A4 specimen was anodized at 2 ºC in 0.3M Oxalic acid at 45 V for 8 hours for the first step and 80 minutes for the second step.

In order to remove the porous aluminum oxide layer which was produced during the first step, a solution with composition mentioned in table (2) was used for 20-25 minutes.

Partially dissolution of cavities was applied for thinning the barrier layer, increasing the diameter of cavities and homogenizing of oxide surface. The specimens were placed in 5Wt% phosphoric acid. A1 and A2 were partially dissolved for 20 minutes and A3 and A4 for 5 minutes.

The A1 and A2 specimens were electroplated by silver for 10 minutes in a solution with composition mentioned in table 3. This process was done in direct and constant voltage of 2 V and 0.01 A. For A3 and A4, the silver electroplating was done in alternative current of 15 V and 50 Hz.

In the next step, nickel electrochemical deposition was done in solution with composition mentioned in Table 4 for A1 specimen and for other specimens the solution in Table 5 was used. After electrochemically deposition, the specimens were immersed in 6M soda for 6 hours in order to remove the aluminum and aluminum oxide completely.

The "B" labeled specimens were first underwent a two-step anodizing in 0.4 M phosphoric acid and in 20ºC for 1 hour in 140 V which was the condition for both steps. In between the porous oxide layer formed from the first step was removed with the aid of phosphoric and chloric acid solution. After anodizing, in order to increase the cavities diameter and thinning the barrier layer, all the specimens were partially dissolved in 5Wt% phosphoric acid for 3 hours.

Table 4. The composition of bath used for Ni electrochemical deposition

PH	Temperature ºC	Nickel sulfate	Boric acid (H_3BO_3)
2-3	40	53.6 gr/L	30 gr/L

Table 5. Solution used for A 1 and other specimens

PH	Temperature ºC	Wetter agent	Boric acid (H_3BO_3)	Nickel sulfamate
3.77	45	2 cc/L	30 gr/L	270 gr/L

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Table 6. Composition used for removing Aluminum

Temperature ºC	Water	$CuCl_2$	Choloridric acid (HCl)
10	100 mL	3.4 gr	100 mL

The B1 specimen was pore filled by nickel with the same condition as for A1 specimens but in another bath that its composition is shown in table 4 for 3 hours.

The B2 specimen was underwent the same as B1; its aluminum was removed in a bath with composition shown in table 6 and after that, its oxide layer was partially removed in 1M soda for 8 minutes in ambient temperature.

The B3 specimen after being partially dissolved its cavities as B1 specimen was silver electroplated as A1 specimen, after that it was nickel pore filled like B1 specimen and after that, its aluminum and oxide layer between the nanowires was removed in 3M soda.

3. RESULTS AND DISCUSSION

3.1. Oxalic Acid Anodized Specimens

As shown in Figure 4, the nanowires are not grown up along the cavities in A1 specimen which was nickel deposited in a solution with chemical composition shown in table 4. Figure 5 shows the structure of A2 specimen that was nickel pore filled in different bath from A1 that included wetter agent.

Figure 6 shows the structure of developed nanowires in A3 specimen that was silver

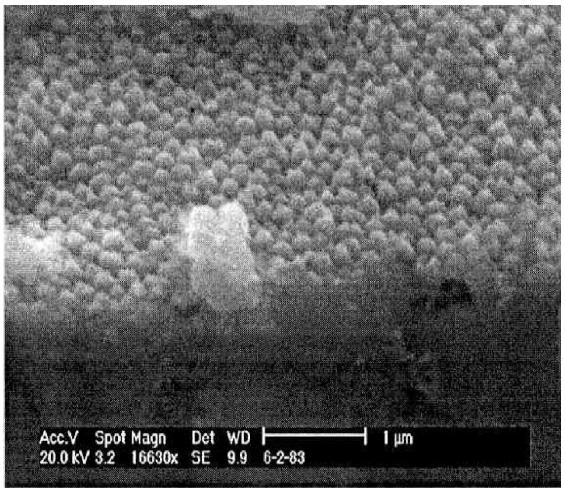

Fig. 4. Grown up nanowires in A1 specimens

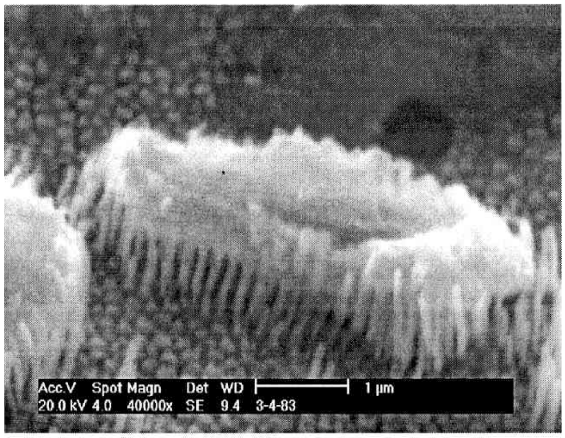

Fig. 5. The structure of nickel tips of specimen silver electroplated in DC mode

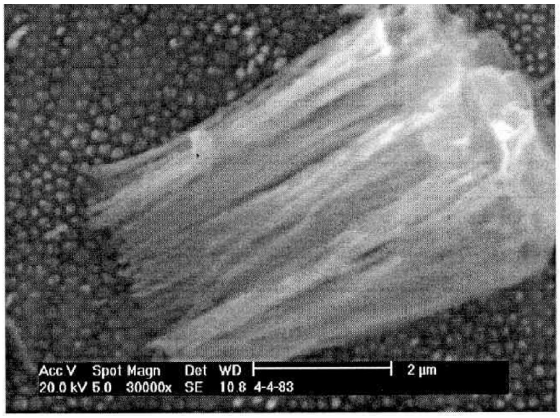

Fig.6. The structure of Ni tips of specimens silver electroplated in AC mode

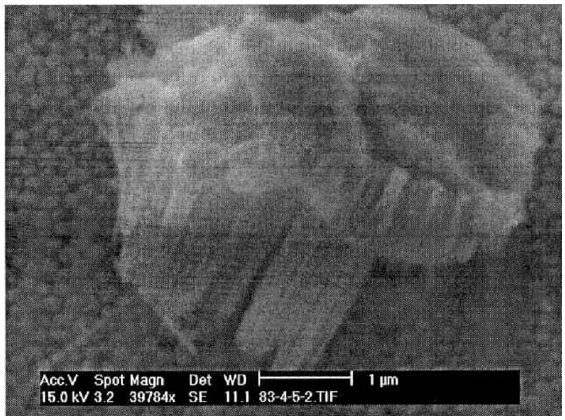

Fig. 7. Showing the nickel nanowires

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electroplated before pore filling.

Figure 7 shows the structure of developed nanowires in A4 specimen that was anodized in 0.3M oxalic acid and silver electroplated like A3 specimen.

3.2. Phosphoric Acid Anodized Specimens

Figure 8 shows B1 fracture surface of anodic aluminum oxide that includes nickel naowires and Figure 9 shows the spot analysis of the nanowire indicated in Figure 8.

Figure 10 shows the structure of B2 specimen, which the aluminum and oxide layer are removed.

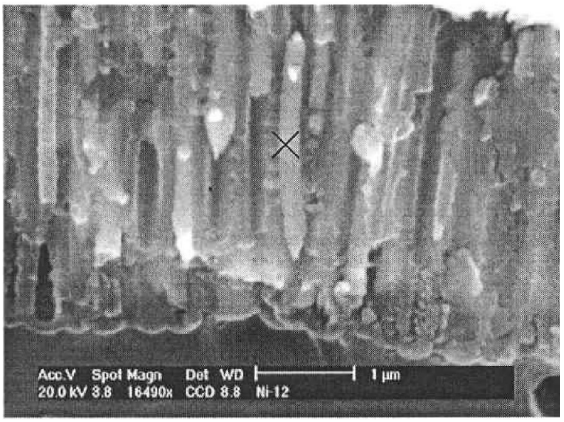

Fig.8. EDX showing Ni nanowires

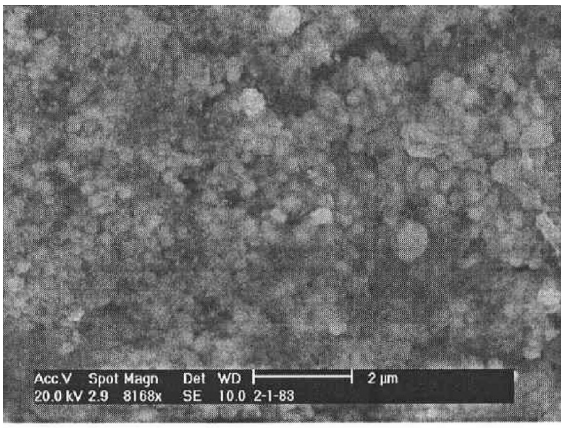

Fig.10. Showing the cavities not filled by Ni

Figure 11 shows the B3 specimen that was silver electroplated before pore filling.

The diameter of cavities is directly proportional to the applied voltage [7]. In order to produce nanowires with different diameters, anodizing voltages were chosen 45 and 85 V. Maximum order and arrange are gained where the voltage, acid concentration and temperature are optimum. Anodizing in 45 V is common in most of the research done in order to reach a well arranged structure. With regard to the fact that an increase in anodizing voltage will increase chemical dissolution at interface of acid-solution, [1] the concentration of used acid in 85 V was

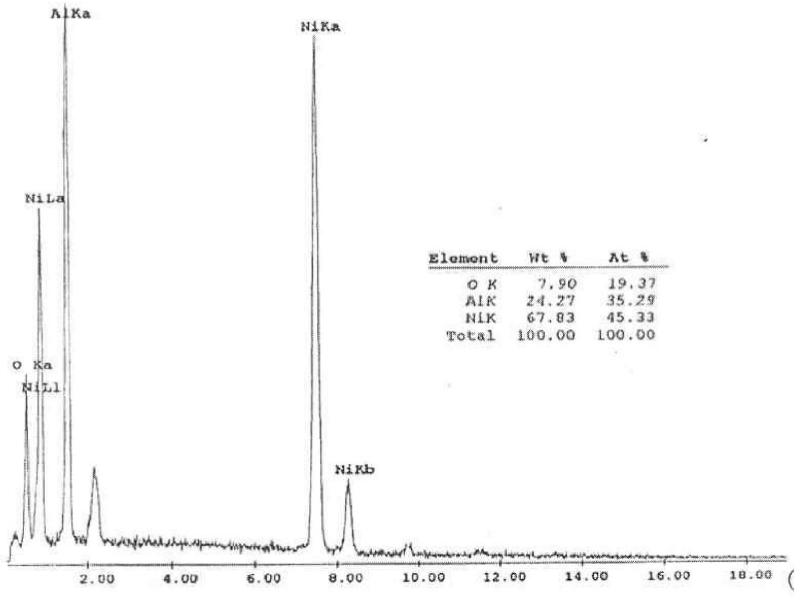

Fig. 9. EDX spot analysis of nanowires

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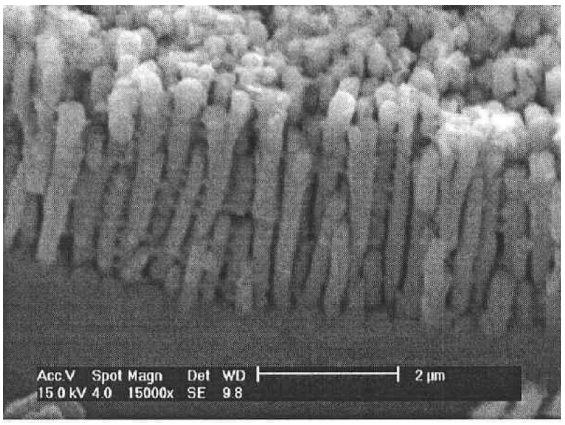

Fig.11. High percentage of cavities filled by Ni

chosen much less than 45 V.

The reason for not growing of nanowires in A1 specimen can be due to the lack of ability to wet the cavities by the used bath. For A2 specimen, another bath with composition shown in table 5 was used that included the wetter agent and as can be seen from Figure 5, the nanowires are grown across the cavities. Before chemical deposition, the specimens underwent a silver electroplating by direct and alternating current. The cavities of the specimen that electroplated in DC mode were partially dissolved for 20 minutes for decreasing the barrier layer thickness enough for the electrons to be able to tunnel through. The specimen that electroplated in AC mode, was partially dissolved for 5 minutes. The reason that AC mode could be used is the rectifying property of the barrier layer for the current. Electrical resistance of the specimens after silver electroplating was measured and in both cases there was a decrease in that. This can be explained by considering the formed silver layer on the surface of the cavities. Figure 5 shows the structure of nickel tips of specimen that silver electroplated in Dc mode and in Ac mode in Figure 6. The diameter of nano-wires is about 95 nanometers and in both cases, most of the cavities are filled. In order to produce nickel nanowire with small diameter, aluminum anodizing was done in 45 V. This condition is used by other researchers [8, 9]. As shown in Figure 7, the diameter of naowires is about 65 nanometers.

Figure 9 shows the EDX spot analysis of the nanowire indicated in Figure 8. The presence of Oxygen and Aluminum is due to the oxide film around the nanowire.

In order to investigate the pore filling percentage, B2 specimen was prepared by removing the aluminum and oxide. As shown in Figure 10, many cavities are not filled by nickel. Many researchers have investigated this phenomenon and have explained that the reason is due to the side cathodic reactions like Hydrogen release reaction [10, 11]. As a result of this reaction, PH will increase at the end of cavities and dissolves the oxide layers. So cavities form at barrier layer and metal deposition will locally occur at higher rates at some cavities. By silver electroplating, the barrier layer will have no role in pore filling and as shown in Figure 11 high percentage of cavities are pore filled by nickel.

4. CONCLUSIONS

1. Diameter of nanowires decrease with decreasing the applied voltage in oxalic acid solution anodizing
2. The solution in which the specimens anodized in phosphoric acid were electrochemically nickel deposited, does not wet the cavities for specimens anodized in oxalic acid.
3. Silver electroplating decreases the electrical resistance and increases the filled percentage of cavities both for specimens anodized in oxalic and phosphoric acid.
4. Silver electroplating in Ac mode increases the filled percentage of pores more than DC mode.

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