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The synthesis of silver nanowires in anodic Aluminum Oxide template

Nguyen Van Dan[1], Tran Huy Nam[1] and Tran Thanh Tam[1]

[1]Department of Metallic Materials, Faculty of Materials Technology, Ho Chi Minh City University of Technology, Viet Nam;

Abstract

Studied the synthesis of silver nanowires by pyrolysis of $AgNO_3$ was realized in anodic aluminum oxide (AAO) templates at different temperatures of 140, 170 and 180 ° C for 60 minutes .The fiber crystalline structure of silver nanowires was successfully prepared by reduction of silver nitrate in support of ethylene glycol (EG) and polyvinyl pyrrolidone (PVP).

By controlling the molar ratio PVP/$AgNO_3$ of 8/1, crystalline silver nanowires can be obtained while EG concentration is constant (6 ml/l). The optimum pyrolysis temperature was 170 ° C. Dimension distribution of silver nanowires showed their best diameter and length of around (70÷80) nm and about 2 μm respectively.

Scanning Electron Microcopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Diffraction (XRD) were employed to characterize anodic alumina oxide templates and silver nanowires

Keywords*: Silver nanowires, AAO template*

1. Introduction

Silver nanowires have been interested to study for many years due to their potential in applications such as electronic, catalytic and photonic materials; sensing devices, nano-antenna and bacteria- and mold-resistant paint for hospital ... [1].

There are some methods of synthesis of silver nanowires such as chemical [1, 2-4], electrochemical [5], photochemical [6, 7]. The synthesis of silver nanowires based on anodic aluminum oxide (AAO) template has been widely used [4, 5, 8, 9]. The fiber structure of silver nanowires was successfully prepared by reduction of silver nitrate, using ethylene glycol (EG) and polyvinyl pyrrolidone (PVP). By controlling the molar ratio of PVP and $AgNO_3$, silver nanowires can be achieved with constant EG concentration [8, 10, 11]. Yugang Sun and Younan Xia [10] have combined EG solution (6 ml/l) and solution of PVP and $AgNO_3$ (molar PVP/$AgNO_3$ ratio was 6/1), followed by a pyrolysis of $AgNO_3$ at 160 ^oC for 30 minutes. Due to presence of PVP added to the system the removal efficiency of silver ions to elemental silver increased ... However, in their study [10] silver nanowires were prepared by polyol method, not in AAO template.

In our study, silver nanowires were synthesized by pyrolysis of silver nitrate in support of EG and PVP in AAO template at 170 °C for one hour. Effect of various molar PVP/$AgNO_3$ ratio (1.5/1, 3/1, 6/1, 8/1 and 10/1), while EG concentration is maintained constant (6 ml/l), on formation of silver nanowires will be discussed.

2. Experimental

2.1. Preparation of AAO template [12]

First of all a high-purity aluminum (Al) foil with thickness around 100 μm was used for making an ordered porous oxide film by anodization (Fig. 1). It is also noticed that the aluminum should be annealed for at least 5 hours at 400 ^oC to remove crystal defects and promote grain growth. Then, the surface impurity of Al foil was cleaned in a mixed solution containing 100 (g/l) NaOH, 60 (g/l) Na_2CO_3 and 30 (g/l) $Na_2SiO_3.9H_2O$ during 3 min at 80 ^oC. After that, the surface roughness of the annealed Al was reduced by polishing in acidic solution including 70 (ml) H_3PO_4, 25 (ml) H_2SO_4, 5 (ml) HNO_3 at 85 ^oC for 3 min.

The anodization was realized in two steps. In the first step, the aluminum sample was anodized with a $H_2C_2O_4$ (0.3M) solution at 55 V, 15 ^oC for 10 min. Then, the first layer of alumina film was removed in acidic solution of H_3PO_4 (3.5 %) and H_2CrO_4 (20 g/l) at 80 ^oC. In the second step, the anodization was performed in the same solution at 55 V, 15 ^oC for 75 min. An ordered porous alumina film was formed.

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After anodization, the alumina surface of sample was cleaned in the same solution used for removing of first layer. In order to separate the alumina film completely from the Al substrate, the solution of hydrochloric acid (20 %) and $CuCl_2.2H_2O$ (0.1 M) was utilized. Then, the barrier in the film bottom was dissolved by using H_3PO_4 (5 %). This step also widened the pore size.

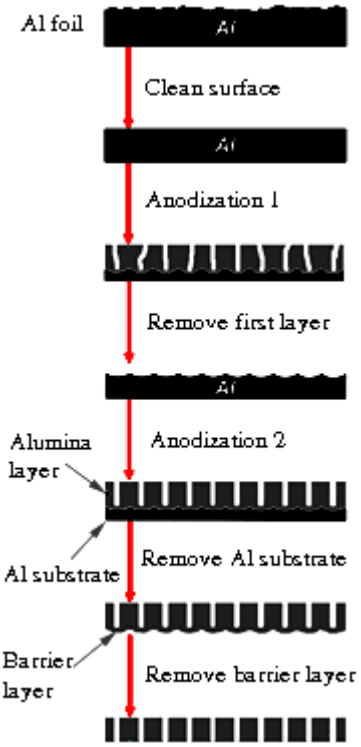

Fig 1. Schematic diagram describing the fabrication of AAO template

2.2. Fabrication of silver nanowires

In a typical synthesis of silver nanowires, the EG (6 ml/l) solution, heated under stirring for 30 minutes, was mixed with solutions containing $AgNO_3$ (40 g/l) and PVP of various concentrations. The morphology and dimension of silver nanowires strongly depend on the molar ratio of PVP and $AgNO_3$. In our study this ratio was alternated as 1.5/1, 3/1, 6/1, 8/1 and 10/1.

The ready mixture of solutions was dropped on the top surface of porous AAO template under vacuum at room temperature. Reduction of silver ions was performed in the furnace at different temperatures of 140, 170 and 180 ° C for 60 minutes at a heating rate of about 1 ° C / s .

The silver nanowires were collected when the template framework was dissolved in NaOH (1M) in few minutes. After that, silver products were washed in water, acetone and ethanol to remove completely EG and PVP.

SEM, EDS and XRD techniques have been employed to characterize anodic alumina oxide templates and silver nanowires.

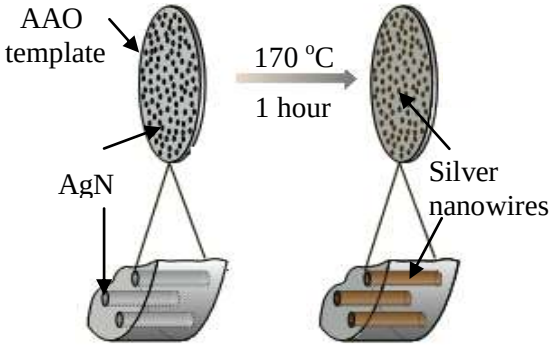

Fig 2. Schematic drawing of the formation of silver nanowires in AAO template

3. Result and discussion

A porous aluminum oxide membrane was shown in Fig. 3 with the pore size D determined by the formula (1.1):

$$D = \frac{D_1 + D_2 + ... + D_n}{n}, \quad (1.1)$$

where D_1, D_n are measured pore diameters and n is number of pores. The pore diameter of membrane prepared in oxalic acid solution was around 95.3 nm (Fig. 3).

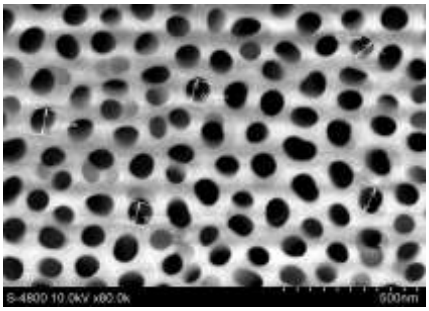

Fig 3. FE-SEM image of the top surface of AAO membrane

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Table 1: The result of EDS analysis

Element	wt. %	at. %
O-K	15.21	25.58
Al-K	71.21	71.03
Ag-L	13.58	3.39
Total	100	100

The elemental silver formed in the AAO template after impregnating with mixture solution of EG, PVP and $AgNO_3$ was proved by FE-SEM and EDS analysis (Fig. 4). Table 1 shows concentrations (at. %) of aluminum and oxygen as 71.03 and 25.58 respectively, corresponding to Al_2O_3. The silver content of 3.39 % was accounted for two Ag-L peak positions at 2.8 and 3.5 keV (Fig. 4b).

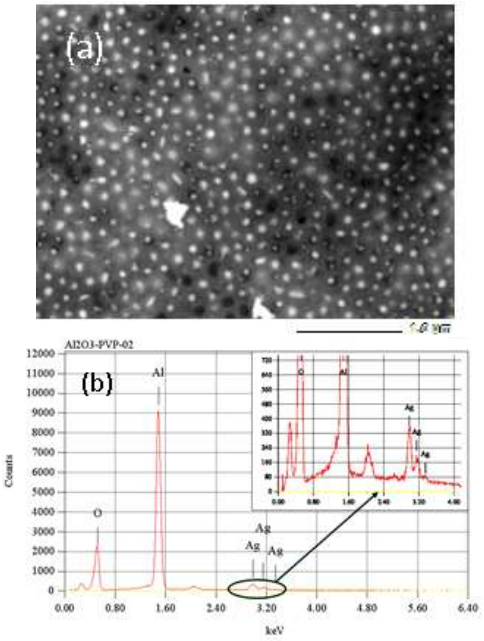

Fig 4. (a) SEM image and (b) EDS spectrum of aluminum oxide membrane containing silver elements after pyrolysis

The SEM image shows that most pores were filled by elemental silver. The reduction process and the formation of silver nanowires were surveyed according to the molar PVP/$AgNO_3$ ratio mentioned above. Fig. 5 shows the morphology of the silver nanowires depending on the molar ratio.

With the molar PVP/$AgNO_3$ ratio of 1.5/1 only silver nano-clusters of large size were produced, their shape was not defined and a discrete distribution found (Fig. 5a). Increasing this ratio favored the formation of more distinct silver nanowires (Fig. 5b, c, d). For example, when the ratio was 8/1, the silver nanowires were identified explicitly with diameters of (70-80) nm and a length of about 2 micron (Fig. 5d). A further increasing the PVP/$AgNO_3$ ratio to 10/1 resulted in formation of silver nanoparticles (Fig. 5e).

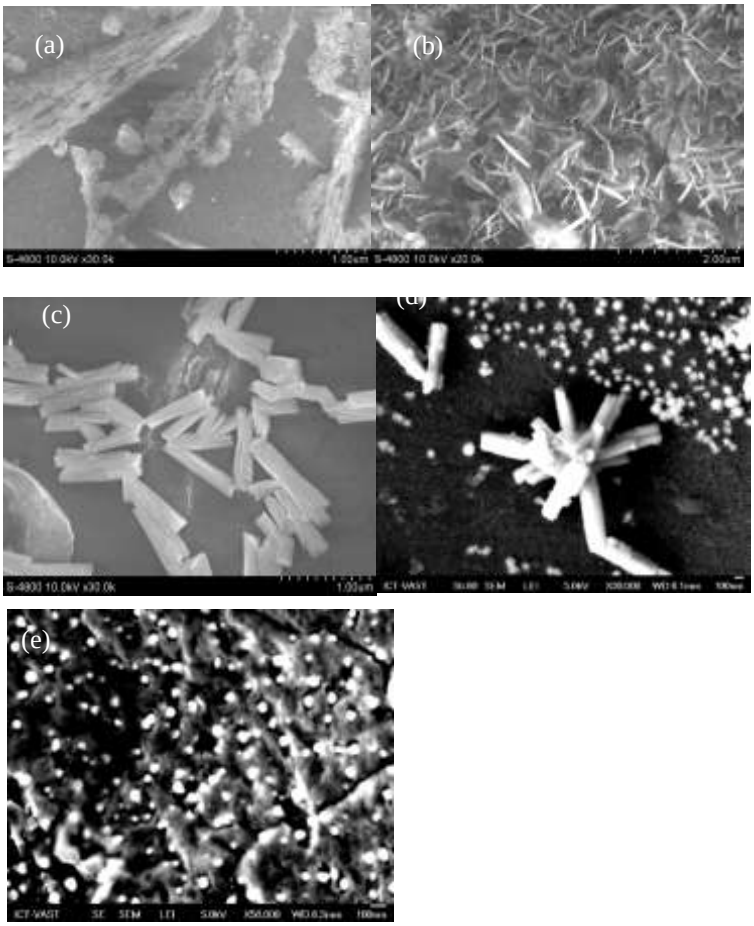

Fig 5. SEM image of silver nanowires corresponding to the various molar PVP/$AgNO_3$ ratios:
(a) 1.5/ 1, (b) 3/1, (c) 6/1, (d) 8/1 and (e) 10/1.

The formation mechanism of Ag nanowires in AAO template has been described in [13, 14]. In initial moment, the first silver nuclei are often formed in the decahedral shape during reducing by EG. The presence of PVP is very helpful because of its absorbency on {100} crystal planes. It determines probability of elemental silver to be deposited on {111} planes of decahedral structure and developed into silver nanowires with face-centered cubic structure.

When the PVP/$AgNO_3$ ratio is low, i. e. less amount of PVP is not enough to be absorbed on the {100} system, the nano-silver tends to set free (clustering). Then, when this ratio increases, the PVP amount is sufficient to soak up the {100} planes and therefore, there is only way the silver atoms are deposited onto the {111} planes to

generate silver nanowires. Once the ratio is too high, the excess PVP amount will be adsorbed on whole {111} system, thereby preventing the aggregation of nano-silver [14].

The formation of silver nanowires in AAO template reported above is similar to that for the mentioned polyol method, but the difference is that the fiber diameter and length may be controlled by these ones of the AAO template pores. In addition, the molar PVP/$AgNO_3$ ratio in our study showed a greater value (8/1) compared with that (6/1) for polyol method used by Yugang Sun and Younan Xia [10] with the same EG concentration (6 ml/l). The reason could be a harder formation of silver nanowires in AAO template, so a higher PVP concentration should be applied. However, the fiber diameter and length can be controlled in a wide range.

Figure 6 demonstrated the X-ray diffraction pattern of crystalline silver nanowires synthesized in AAO template with a molar PVP/$AgNO_3$ ratio of 8/1, then subjected to pyrolysis at different temperatures of 140, 170 and 180 ° C for one hour.

Looking at Figure 6, only the samples were pyrolyzed at 170 and 180 ° C to form the Silver nanowires. Thus, the optimum pyrolysis temperature was 170 ° C.
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4. Conclusions

The silver crystalline nanowires have been successfully synthesized inside nano-pores of the AAO template with a molar PVP/$AgNO_3$ ratio of 8/1 and a constant EG concentration of 6 ml/l. The pyrolysis at 170 °C for 1 hour provided silver nanowires with diameters of (70-80) nm and a length of about 2 micron.

The molar concentration ratio of PVP and $AgNO_3$ in this study, as showed, must be greater (8/1) in comparison with that for the polyol method (6/1) while the same EG concentration (6 ml/l) used.

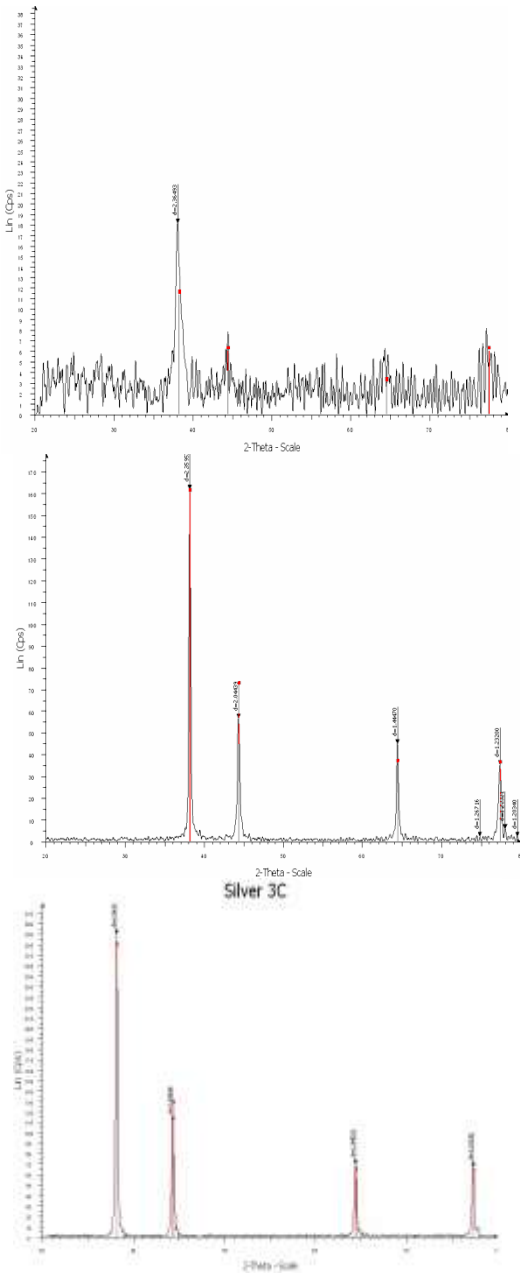

Fig 6. X-ray diffractogram of samples pyrolysed at different temperatures of 140, 170 and 180 ° C for one hour

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