Effect of pretreatment of AAO template on NiCoFe Nanowires Synthesized by Electroless Deposition

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Abstract: The influence of pretreatment of AAO template and deposition process on magnetic NiCoFe nanowire fabricated by electroless method was investigated. The Electroless process carried out at room temperature using DMAB as a reductant agent. SEM and EDX analysis used to characterize the deposited sample. According to the results, sonication during deposition process is not recommended in fabrication of metallic nanowires or nanotubes.

Keywords: Magnetic Nanowire; Electroless; AAO; Pretreatment.

Introduction

Magnetic nanostructures based on self-assembly have recently attracted much consideration due to their potential for increased areal density magnetic storage media and gas sensors [1]. Arrays of magnetic nonodots, nanowires or nanotubes may be fabricated by several methods such as e-beam lithography, imprint technology or template. The porous template can be considered as one quicker and cheaper method to prepare highly perpendicular magnetic anisotropy structure [2]. Using this method, different kinds of nanomaterials have been fabricated, such as metals, semiconductors, polymers, carbon and other materials [3]. There were many reports disclosing the fabrication details of several kinds of templates, such as track-etched membranes, anodic aluminum oxide (AAO), and diblock copolymer [1]. Template synthesis method using AAO has attracted much consideration because the pore channels of AAO template are parallel to each other and the holes can be controlled by properly adjusting the anodizing conditions [4]. It is well known that transition metals such as Fe, Co, Ni and their alloys have higher saturation magnetization and lower crystalline anisotropy. Furthermore, magnetic properties are strongly influenced by the dimension and crystal properties, which also depend on the physical structure of templates and growth mechanism of nanowires or nanotubes. Recently, magnetic properties of nickel nanowires have been investigated because they show important applications in magnetic recording media [2]. Metal nanotubes or nanowires can synthesis in tempelate using chemical vapour deposition[5], electroplating[6], and supercritical fluids[7]. Besides, electroless is the simple method in terms of equipment and processing for syntesis of these materials[8]. Electroless method is actually a chemical deposition process and involves the use of a chemical agent to coat a material onto the template surface. [9]. The significant difference between electrochemical deposition and electroless deposition is that in the former, the deposition begins at the bottom electrode and the deposited materials must be electrically conductive. The electroless method does not require the deposited materials to be electrically conductive, and the deposition starts from the pore wall and proceeds inwardly. Therefore, in general, electrochemical deposition results in the formation of "solid" nanorods or nanowires of conductive materials, whereas the electroless deposition often grows nanowires or nanotubules[9].

In this paper, we describe the effect of different pretreatment and depositing methods on preparing ordered CoNiFe nanowires in AAO template by electroless deposition in an aqueous solution.

Experimental

The AAO templates were prepared by the anodic oxidation procedure in phosphoric acid. Aluminum foil (99.99% purity supplied by Merck) was used as the anode electrode. The Al foil was annealed at 500◦C for 2h. The Al foils were chemically treated in 1M NaOH solution for 3 minutes at room temperature and rinsed with distilled water and acetone. Then, they were eloctropolished in a mixture of $HClO_4$ and ethanol (1:4 in vol.) at 20V below 5˚C. Anodization was conducted under the constant potential of 120V in 0.3M phosphoric acid electrolyte for 20h. The temperature of the electrolyte was maintained at 0-3˚C during anodization using a cooling system. The solution was mechanically stirred in order to accelerate the dispersion of the heat that evolved from samples. Two pretreatment methods were exerted on AAO to fabrication of NiCoFe nanowires. In the first one, after the anodization, the AAO template was directly dipped in an aqueous mixture of $1gl^{-1}$ $PdCl_2$ and $12gl^{-1}$ HCl for 5 min without the sensitization process. In the second method, AAO template firstly was sensitized by sonicating in an aqueous mixture of $19gl^{-1}$ $SnCl_2$ and $50gl^{-1}$ HCl for 10 min and washing with deionized water solution, followed by immersion in an aqueous mixture of $1gl^{-1}$ $PdCl_2$ and $12gl^{-1}$ HCl for 5min. After the surface of treated AAO template was polished with a refined sand paper and fully washed with deionized water, the chemical deposition was carried out at room temperature and different conditions. The chemical composition of the electroless deposition bath is as fallowed: 0.017M $NiSO_4.6H_2O$, 0.017M $CoSO_4.7H_2O$, 0.013M $FeSO_4.7H_2O$, 0.143M lactic acid, 0.07M DMAB. A group of templates were sonicated during electroless deposition and others were immersed in electroless solution and kept at low vacuum environment to enhance the solution into the pores. In order to simplify discussion of the samples, they are nominated in table 1. The morphology of the AAO template and the metallic nanowires were characterized by scanning electron microscopy (SEM). In order to get better morphology of nanowires, partial dissolution of the AAO membrane was carried out in 1M NaOH for 10 min. Furthermore, an energy dispersive spectrum (EDS) was employed to study the chemical composition of nanowires.

Table 1. Nomination of samples

Sample	A	B	C	D
Preatreatment	Sn+Pd	Pd	Sn+Pd	Pd
Condition	Sonicated		Vaccum	

Sn+Pd:Sonicating in $SnCl_2$ solution + immersion in $PdCl_2$ solution
Pd: immersion in $PdCl_2$ solution

Results and Discussion

Chemical deposition, as a self-catalysis process, can first react on the surface of catalytic carriers. Metallic ions are reduced to metal and deposited onto the active surface; reductant agents are oxidized and generate free electrons that can reduce metallic ions on the active surface[4]. In this investigation, the deposition of NiCoFe was carried out at room temperature. The Pd nuclei catalyze the borane oxidation thereby facilitating localized metallic ions reduction by the reducing agent. This is followed by an autocatalytic metallic on NiCoFe metal deposition process where the metal deposited catalytically oxidises the reducing agent to continue the deposition [8]. Thus, deposition rate will decrease when Pd is completely covered with NiCoFe [4]. The pH value of deposition bath adjusted to around 7–8 because higher pH value with strong alkali will not only corrode the AAO membrane, but also accelerate the metal deposition rate, making it difficult to control the formation of metallic nanowires. The lower pH value with strong acid will also corrode the AAO membrane [3].

Figure 1 shows the SEM image of the AAO template fabricated in this study. Figure 2 indicates the top-view image of the sample A prepared by electroless deposition under sonicating. It shows that NiCoFe film cover the face surface of the AAO template and prevent from diffusion of solution into pores and deposition on the pores wall. In this case, although the face surface of the AAO was polished and did not have catalytic properties, high energy of sonicating leads to start the electroless deposition process on the face of AAO template as well as container wall. Sample B which activated by $PdCl_2$ solution without sensitization and deposited under sonicating has same result as sample A.

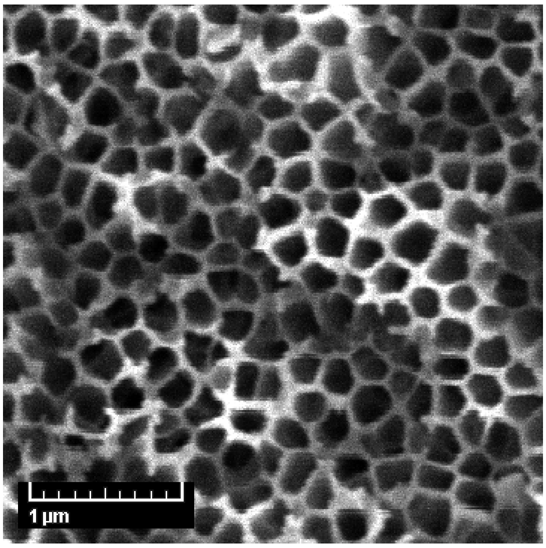

Fig 1. SEM image of AAO template

Surface morphology of sample C that prepared with both solution of $SnCl_2$ and $PdCl_2$ and deposited in low vacuum environment presented in Fig.3. It shows formation of irregular nanowires, furthermore the undesirable metallic coating is formed on some areas that can affect negatively on nanowires fabrication.

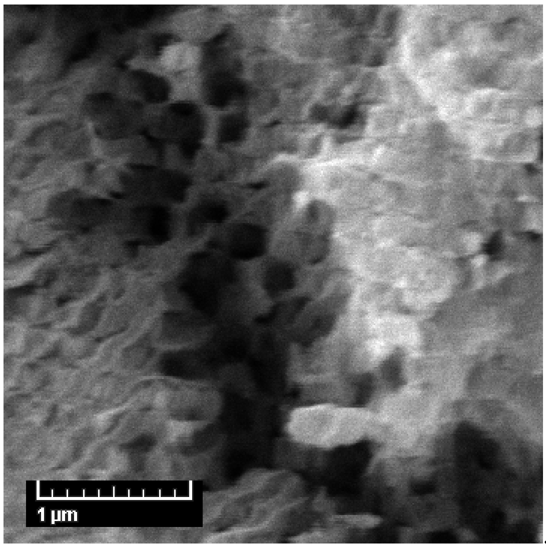

Fig 2. SEM image of the sample A

In the pretreatment process of sample C, the adhesive ability of $SnCl_2$ on the pore wall is limited. Even some $SnCl_2$ sensitizers become colloidal particles in the pores of AAO template by hydrolyze reaction. Subsequently, the Pd^{2+} cations are deoxidized to Pd on the surface of the colloidal particles [4].

During the chemical deposition process, NiCoFe deposits not only on the Pd particles immobilized on the surface of pore wall, but also on the Pd particles which transmitted out of AAO pores under applied vacuum [4]. This process leads to formation of metallic coating on the face of template. Figure 4 shows NiCoFe nanowires of sample D fabricated in one stage activated AAO under vacuum. The diameter of nanowires is corresponding well to the pores size of the AAO template. Thus, the diameter of the nanowires can be adjusted by choosing the AAO template with different pore sizes.

In pretreatment of the sample D, the formed Pd grains are small particles with large specific surface area. In terms of thermodynamics, Pd prefers to deposit on the surface of pore walls rather than in the pores for reducing the Gibbs energy [4]. So the NiCoFe deposition only occurred on the pore walls and result in nanowires. The EDS spectrum of the sample D shown in Fig.5 indicates the presence of nickel, cobalt and iron elements. The O and Al signal come from the AAO template and the Au and Ag signals related to Au/Ag spattered coating. The EDS analysis indicates that the nanowires of sample D are an alloy with composition of $Ni_{84.5}Co_{9.25}Fe_{6.25}$.

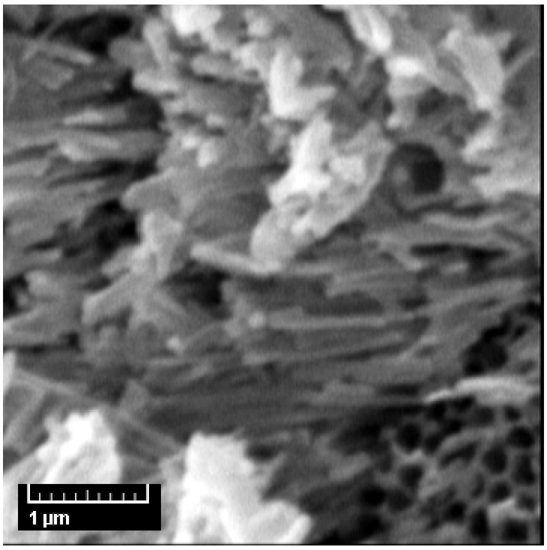

Fig 3. SEM image of the sample C

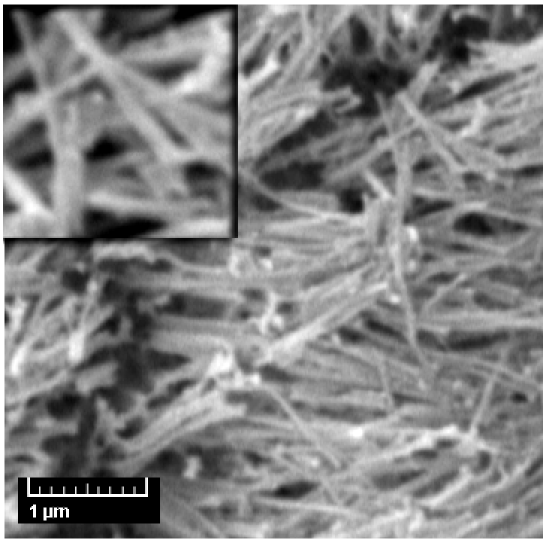

Fig 4. SEM image of the sample D

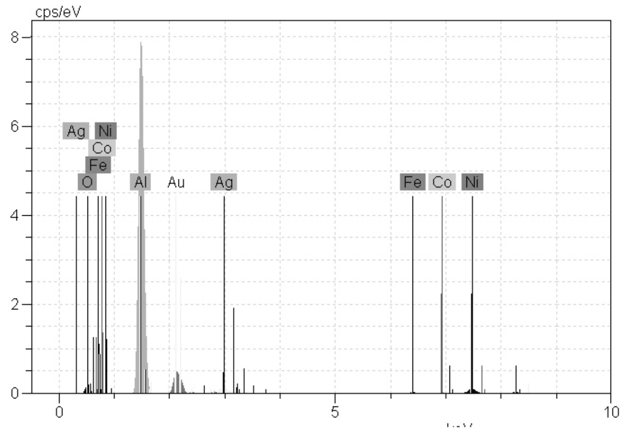

Fig 5. EDS spectrum of the sample D

Conclusion

The effect of pretreatment and deposition process on fabrication of NiCoFe nanowires by electroless method using AAO membranes as template were investigated. Sonicating during deposition is not useful in fabrication of nanowires or nanotubes. This study indicates that using sensitization and activation together as pretreatment and vacuum during deposition process does not have a good result in formation of nanowires, whereas applying the one step activation as pretreatment will culminate in formation of the acceptable nanowires.

References

[1] F.E. Atalay, H. Kaya, S. Atalay, S. Tari, “Influences of deposition time and pH on magnetic NiFe nanowires fabrication”, Journal of Alloys and Compounds 469 (2009) 458–463.

[2] S.C. Lin, S.Y. Chen, S.Y. Cheng, J.C. Lin, "Synthesis and magnetic properties of highly arrayed nickel-
[3] W. Wang, N. Li, X. Li, W. Geng, S. Qiu, "Synthesis of metallic nanotube arrays in porous anodic aluminum oxide template through electroless deposition", Materials Research Bulletin 41 (2006) 1417–1423.
[4] X. Ren, C.H. Jiang, X.M. Huang, D.D. Li, "Fabrication and magnetic behavior of chemical deposited Ni–P nanowire and nanotube arrays", Physica E 41 (2009) 349–352.
[5] M.K. Li, M. Lu, L.B. Kong, X.Y. Guo, H.L. Li, "The synthesis of MWNTs/SWNTs multiple phase nanowire arrays in porous anodic aluminum oxide templates", Materials Science and Engineering A 354 (2003) 92-96.
[6] X. Ren, C.H. Jiang, X.M.Huang, D.D. Li, "Fabrication and magnetic behavior of chemical
phosphate nanotubes", Solid State Sciences 7 (2005) 896–900.
deposited Ni–P nanowire and nanotube arrays", Physica E 41 (2009) 349–352.
[7] J. Xu, W. Zhang, M.A. Morris, J.D. Holmes, "The formation of ordered bismuth nanowire arrays within mesoporous silica templates" Materials Chemistry and Physics 104 (2007) 50-55.
[8] J.F. Rohan, D.P. Casey, B.M. Ahern, F.M.F. Rhen, S. Roy, D. Fleming, S.E. Lawrence, "Coaxial metal and magnetic alloy nanotubes in polycarbonate templates by electroless deposition", Electrochemistry Communications 10 (2008) 1419–1422.
[9] G. Cao, D. Liu, "Template-based synthesis of nanorod, nanowire, and nanotube arrays", Advances in Colloid and Interface Science 136 (2008) 45–64.