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Fabrication of micro-Ni arrays by electroless and electrochemical depositions with etched porous aluminum template

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Abstract. Nickel micro-arrays were fabricated by electroless and electrochemical deposition in an etched porous aluminum membrane. The aluminum membrane with metal characteristic could be fabricated from high-purity aluminium by electrochemical method. The aluminum reduced Ni^{2+} into Ni and the formed Ni nuclei served as the catalyst for further reduction of Ni^{2+} in electroless solution. With the help of the membrane, nickel micro-columns of about 1–2 μm diameter were obtained. The surface-deposited nickel layer served as a substrate for the nickel micro-columns, and the resulting material possessed strong mechanical strength. Electrochemical deposition was operated without preparing a conductive layer on the template due to the conductivity of the aluminum membrane. Nickel micro-tubes with an outer diameter of about 1–2 μm and a wall thickness in the order of tens of nm were obtained. The nickel micro-arrays were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

Keywords. Template; nickel; electrochemical deposition; electroless deposition.

1. Introduction

Micro-scale materials with regular structure are of great interest because of their potential applications in many fields, including electronics, catalysis, magnetism, and electrochemistry. The template method is commonly used to prepare this kind of materials. Anodic porous alumina membranes and porous polycarbonate membranes are the two most important templates (Furneaux *et al* 1989; Lakshmi *et al* 1997; Ferain and Legras 2003; Bercu *et al* 2004; Zhu *et al* 2006; Sarkar *et al* 2007). Many novel materials with regular structure can be obtained with these two templates. However, researchers are still not satisfied with the brittleness of anodic porous alumina membrane and the low resistance to chemicals and heat of porous polycarbonate membrane. To fabricate large area membranes with excellent properties, new templates with higher strength and stability are being searched. Metal membranes as templates present unique properties: they are flexible and stable, can normally stand high heat, and cannot be damaged by chemicals. Using metal templates, larger size micro-scale materials can be obtained and some heating and chemical treatments can be used to improve the structure. In addition, the deposition of a conductive thin metal film on one side of the membrane by sputtering or evaporation, necessary in common electrochemical deposition processes to prepare micro-scale materials with templates (Kartopu *et al* 2008; Yang *et al* 2008), can be eliminated with a metal template due to the fact that the metal membrane is conductive.

Several membranes, such as anodic porous alumina membrane (Masuda and Fukuda 1995, 1999; Xu *et al* 2001), porous polycarbonate membrane (Dobrev and Vetter 1999; Vetter and Dobrev 1999), and glass membrane (Pearson and Tonucci 1995) (a mother membrane) are developed to prepare metal templates through the double replication technique. First, the mother membrane is prepared, then the pores of the mother membrane are replicated. After that, the mother membrane is removed. Subsequently, the spaces are replicated by metal. Finally, the duplicates in the pores are removed. It is obvious that the process is complicated and the structure of the metal membrane is strongly dependent on the mother membrane. The disadvantages of the mother membrane are not overcome.

Electroless deposition and electrochemical deposition are widely employed to deposit metals in templates. Electroless deposition method normally requires reducing agents and a noble metal catalyst (Bercu *et al* 2004; Wang *et al* 2004a). The noble metal catalyst is formed

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often *in situ* from its salts with the help of sensitization and activation inside the reaction system prior to electroless deposition. In this paper, we demonstrate that Ni micro-scale arrays are obtained with an etched porous aluminum membrane as template using electroless deposition and electrochemical deposition methods. The metal aluminum membrane is easily obtained through electrochemical method. In the electroless deposition method, sensitization and activation were not needed: nickel deposition was auto-catalyzed by nickel itself, formed by Al reducing Ni^{2+}. In the electrochemical deposition method, no additional conductive metals are needed on the membrane. The membrane is directly applied as a cathode because of aluminum's conductivity.

2. Experimental

2.1 *Chemicals and reagents*

High-purity aluminum foils (99·99%, 90 μm thick) and analytical-grade chemical reagents were used in all the experiments.

2.2 *Preparation of etched porous Al membrane*

The etched porous aluminum membrane was prepared as described in literature (Lu *et al* 2009). The high-purity aluminum foil was used as the anode and graphite was used as the cathode in an electrolytic cell. The electrolyte solution was a mixture of HCl and H_2SO_4. The pore structure of the etched aluminum membrane was controlled by changing the current density, the ratio of HCl : H_2SO_4, the temperature and the etching time.

2.3 *Fabrication of Ni arrays by electroless deposition*

The deposition solution contained $NiSO_4{\cdot}6H_2O$ as the source of Ni^{2+}, lactic acid as complexing agent, and $NaH_2PO_2{\cdot}H_2O$ as the reducing agent. The pH value was adjusted with CH_3COONa and $NaHCO_3$. The solution contained 25·0 g/L $NiSO_4{\cdot}6H_2O$, 21·0 ml/L lactic acid, 20·0 g/L $NaH_2PO_2{\cdot}H_2O$, 20·0 g/L CH_3COONa and 12·0 g/L $NaHCO_3$ (pH = 4·8).

Nickel micro-arrays were obtained as follows. One side of the etched porous aluminum membrane was covered by adhesive tape and then immersed into the deposition solution at 60°C in a water bath. The temperature was kept at 60°C for 4 h. After reaction, the deposited membrane sample was moved into a 5% NaOH solution in order to dissolve the aluminum membrane. Until aluminum was completely leached out, the sample was divided into two pieces. The piece of obtained Ni micro-arrays was thoroughly rinsed with distilled water, and then dried in air.

2.4 *Fabrication of Ni arrays by electrochemical deposition*

Electrochemical deposition was carried out in a two-electrode electrochemical cell at room temperature. The Al membrane was used as the cathode and a Ni plate as the anode. The deposition solution included 350 g/L $Ni_2SO_4{\cdot}7H_2O$ and 30 g/L $H_3BO_3{\cdot}NaOH$ was used to adjust pH to about 4·3. The current density was 5·0 A/dm^2. After deposition, the deposited membrane sample was prepared to be analyzed by a method similar to that in §2·3.

2.5 *Analytic methods*

The crystal structures of the etched porous aluminum membrane and the resulting sample obtained in 2·4 were analysed by X-ray diffraction (Philip X'Pert Pro MPD). The resulting sample obtained in 2·3 was analysed by X-ray photoelectron spectroscopy (VG Microlab MKII). The images were obtained by a SEM instrument (JEOL JSM-5900LV).

3. Results and discussion

3.1 *Characteristic of etched porous aluminum membrane*

The membrane presents a typical metal appearance and has good conductivity. Furthermore, it can be obtained with large areas and good flexibility, and is not easily ruptured. Its XRD pattern and a schematic diagram of structure are presented in literature (Lu *et al* 2008).

3.2 *Parameters of electroless deposition*

Electroless deposition of Ni was widely researched. Distinct parameters were chosen at different conditions for certain uses. In this process, pH of solution cannot be too low or too high because of the amphoteric characteristics of Al. No obvious change on the surface of the etched Al membrane was observed at lower pH (< 4·2), whereas a suspended solid was formed at higher pH (> 6·0). The results show that a pH of 4·8 is optimal.

Temperature and concentration of the Ni^{2+} resource are important factors affecting the formation of Ni micro-arrays. Their influences are similar to those in the electroless deposition of Cu (Lu *et al* 2008).

3.3 *Micro-columns of Ni fabricated by electroless deposition*

In the electroless deposition, Al can reduce Ni^{2+} into Ni. Nickel nuclei were formed on the surfaces of the Al

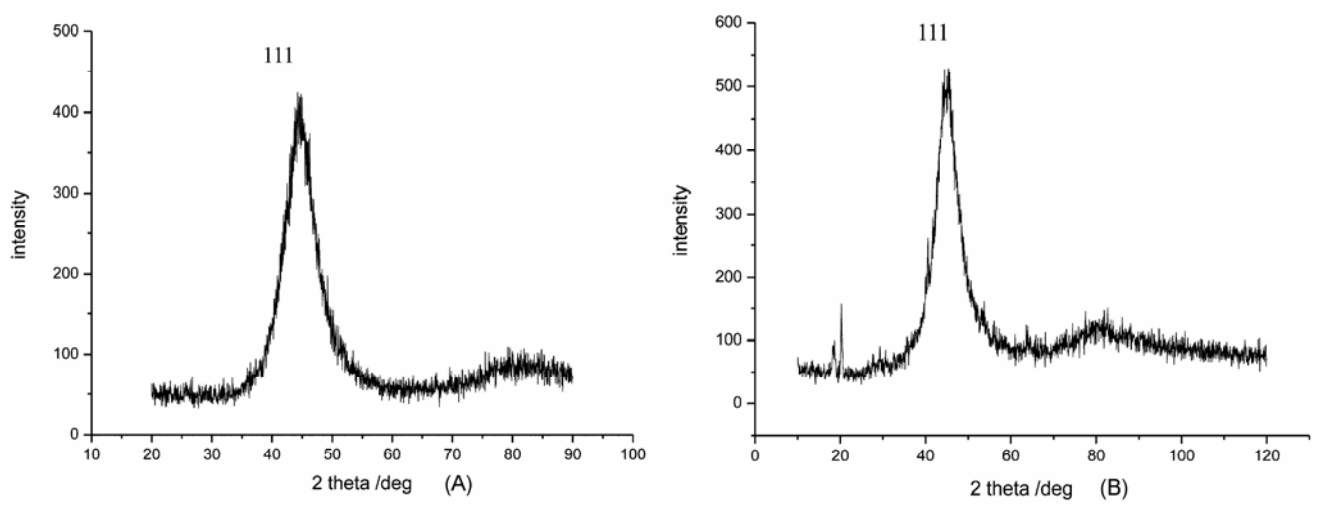

Figure 1. XRD pattern of Ni arrays by electroless deposition: (**A**) grey-silver side and (**B**) black side.

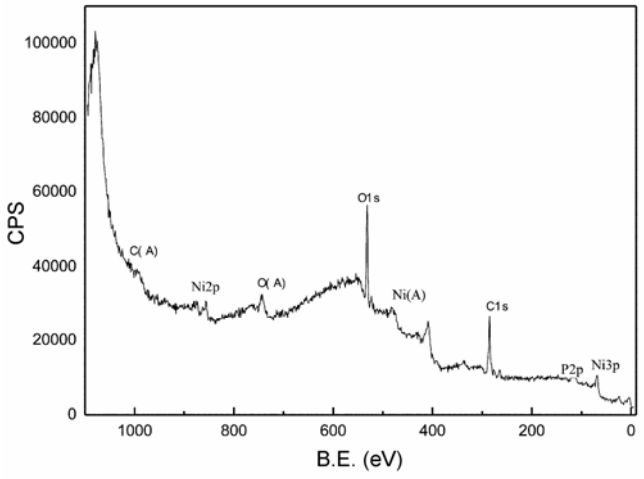

Figure 2. XPS pattern of Ni arrays of the grey-silver side from electroless deposition.

membrane and the pore walls. The initially formed Ni nuclei serve as the catalyst for the reduction of Ni^{2+}, and so noble metal was not needed and any sensitization or activation, employed in conventional electroless deposition with templates such as anodic porous alumina membrane or porous polycarbonate membrane, was unnecessary.

Ni was deposited into the pores on one side of the aluminum membrane. When aluminum inside the deposited membrane was completely leached out with NaOH solution, the mirror-image replicated Ni film was obtained. The side exposed to the electroless solution presented a silver-grey colour, whereas the inner side was black, indicating that it possessed micro-scale particles. The two sides are conductive.

XRD patterns of typical sample are shown in figure 1. Figure 1A denotes the silver-grey colour side, and figure 1B refers to the black side. One can see that its peak is at $2\theta = 44{\cdot}8°$ which indicates the (111) of Ni.

XPS results also testified that Ni formed and further revealed that the grey-silver side consisted of P (figure 2, at binding energy, 130·0 eV) whereas no P existed in the black side. The appearance of C1*s* and O1*s* can be thought as impurities.

It is well known that a Ni–P alloy is obtained in which the ratio of P varies with the electroless deposition condition. The reactions are as follows:

$$H_2PO_2^- + H_2O \rightarrow HPO_3^{2-} + H^+ + 2H,$$

$$Ni^{2+} + 2H \rightarrow Ni + 2H^+,$$

$$H_2PO_2^- + H^+ + H \rightarrow 2H_2O + P,$$

$$2H \rightarrow H_2.$$

Literature (Hu *et al* 1998) shows that Ni deposition begins first; co-deposition then occurs when pH is low enough to reduce the electrical potential below –1·21 V. In this work, at the initial deposition stage Ni is deposited in the holes and on the surface of etched Al membrane. In the subsequent period, the diffusion of solution is restricted because of the blocked holes. The reaction in the holes slowed down; thus, the concentration of H^+ is not high enough to induce P deposition, and micro-scale Ni crystals are formed within the holes. However, at the surface of the etched Al membrane, continuing reduction of Ni brings about enough H^+ to lower the pH under which P can co-deposit with Ni. We can then obtain the thin material with particular properties: it has different constituents on each side; furthermore, the scales of the two sides of granules are so different. One can distinguish it by the distinct colour. The silver–grey side has enough strength to form large size thin films.

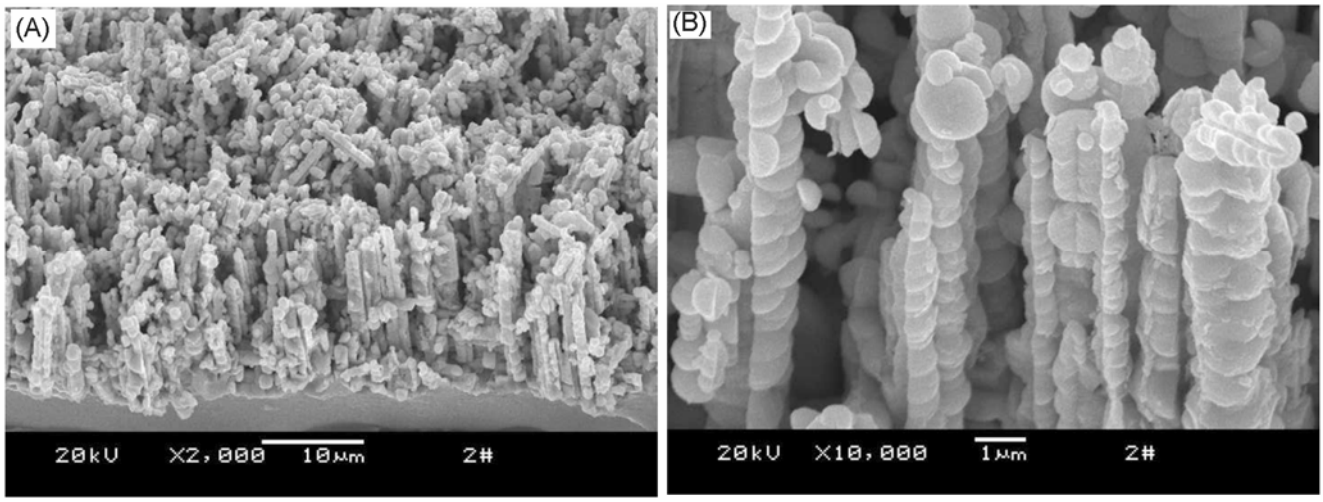

Figure 3. SEM images of Ni arrays by electroless deposition (**A**. ×2000 and **B**. ×10000).

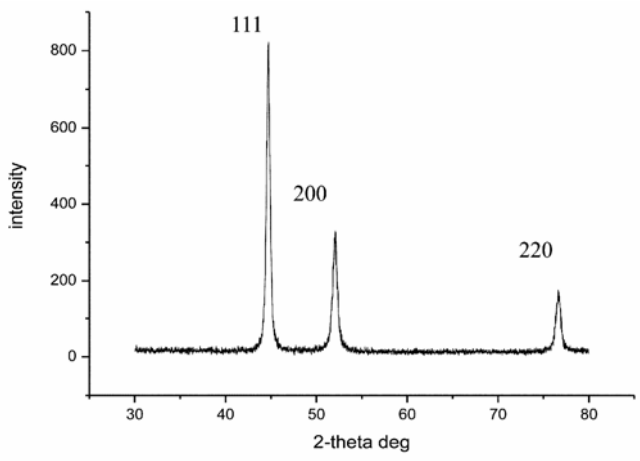

Figure 4. XRD pattern of Ni arrays by electrodeposition.

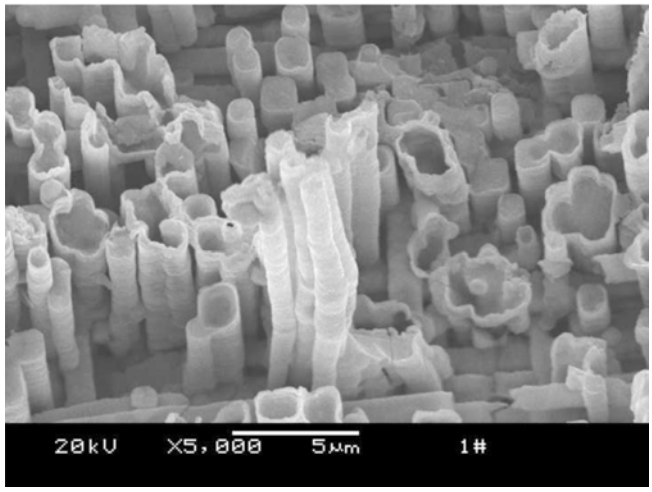

Figure 5. SEM image of Ni-arrays from electrodeposition.

SEM images of the black lining are shown in figure 3. One can see that micro-scale arrays are formed. The square columns are perpendicular to the surface of the etched Al membrane, similar to TiO_2 and Cu micro-tubes (Lu *et al* 2008, 2009). Thicker walls compared to those of Cu micro-tubes are formed because of long deposition time. The different coarseness of crystallite may also be due to the varied growth time of the crystal.

3.4 *Micro-tubes of Ni fabricated by electrochemical deposition*

Electrochemical deposition is carried out with etched porous Al membrane as cathode without any pretreatment. Figure 4 shows the XRD pattern of the final material obtained in §2·4. The diffraction peaks at $2\theta = 44{\cdot}7(111)$, $52{\cdot}0(200)$, $76{\cdot}6(220)$ were detected, respectively which indicated that the material was *fcc* Ni, and the intensity of (111) is strongest. The low surface energy of (111) resulted in priority growth compared to (200) and (220), whose surface energies are $1{\cdot}63\,J{\cdot}m^{-2}$, $1{\cdot}76\,J{\cdot}m^{-2}$, and $1{\cdot}98\,J{\cdot}m^{-2}$, respectively (Wang *et al* 2004b). The fine difference in surface energy brought about the formation of Ni polycrystals, which is significantly different from that formed in electroless deposition solution. The average size of crystal granules was 25·9 nm.

SEM (figure 5) was used to observe the morphologies of the material obtained in §2·4. It was seen that micro-

tubes with square holes were obtained which nearly replicate the structure of holes of etched Al membrane (Lu *et al* 2009). One can see that the wall of tubes is thinner. The hole of etched Al membrane was saturated with the electro-deposition solution before electric current passed. Absorbed Ni^{2+} was reduced at the interface of holes under the action of electricity in the initial stage. A compact layer, formed on the surface of etched Al membrane, covered the holes so that the diffusion of Ni^{2+} ions from the bulk solution to the holes became more difficult as the electro-deposition proceeded. The deposition rate and amount in the holes slowed down, so thicker walls of tubes could not be easily obtained. It may be possible to fabricate a composite with the expected properties in the tubes using other methods afterwards.

4. Conclusions

The etched porous Al membrane was used to fabricate Ni micro-scale arrays by electroless deposition with neither sensitization nor activation and Ni micro-tubes by electro-deposition without preparing other conductive layer on the etched porous Al template. Obtained Ni thin film from the two methods are conductive with different colour sides in which one side is grey-silver and the other is black. A Ni–P alloy was formed on the grey–silver side in the electroless deposition. The methods used to prepare Ni micro-tubes were novel and the materials obtained by the methods could have potential applications such as in electrodes and in composite fabrication.

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