Ordered nanoporous nickel films and their magnetic properties

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Abstract

Ordered nanoporous nickel (Ni) films were fabricated by a full-replicated process. Replicated from an alumina membrane, the replicated Ni film has a very high aspect ratio of about 360, an ordered nanopore array structure, and a narrow size distribution of the pore diameters. Due to the peculiar fabrication processes, the replicated Ni film is polycrystalline with clear ferromagnetic behavior, which is totally different from that of conventional electroless deposited Ni films. The replicated Ni film does not possess obvious magnetic anisotropy, which is also different from a typical ferromagnetic thin film.
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1. Introduction

Over the last decade, one-dimensional nanomaterials based on template synthesis have attracted much research interest. Porous alumina membranes are widely used as templates for fabricating one-dimensional nanostructures, including metals [1–5], semiconductors [6–9], carbon [10], and conductive polymers [11]. However, the alumina membrane itself has several disadvantages, such as insufficient chemical stability and low mechanical strength. It is therefore difficult to use alumina membranes for the synthesis of nanowires and nanotubes under severe reaction conditions such as in strong acid and alkali solutions. To overcome these disadvantages, a two-step replication process was developed. Although this has resulted in the successful fabrication of nanoporous replicated films [12–14], there are still some disadvantages. Usually, it is very hard to achieve full replication of the alumina membrane, thus resulting in poor aspect ratio (typically less than 100) of the replicated films. Moreover, the methyl methacrylate

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(MMA) monomer, which is used as the replication medium, is injected into the pores under vacuum conditions. Thus the replication process is complicated and this makes it difficult to be applied widely in industrial manufacturing processes. In this Letter, we demonstrate the fabrication of ordered nanoporous nickel (Ni) films prepared by an improved and simplified method which can result in full replication of the alumina membrane without requiring operation under vacuum conditions. The components, microstructure, and magnetic properties of the replicated Ni films were investigated. The mechanisms of the crystallization of the replicated Ni film were also discussed.

2. Experimental

The replication procedures are outlined schematically in Fig. 1. The anodic alumina membranes, which we used in the replication, were prepared by a two-step anodization process [9,15]. As shown in the right column of Fig. 1a, the anodization of the circular-shaped aluminum (Al) foils was carried out over a circular area, which is about half the diameter of the Al foil. The second anodization was carried out at 40 V in 0.3 M oxalic acid solution at 17 °C for 2 h. After removal of the Al layer on the backside and the barrier layer, a through-hole membrane with pore diameter of about 50 nm (Fig. 1a) was obtained. The thickness and pore density of this anodic alumina membrane are about 20 μm and 10^{10} cm^{-2}, respectively.

Subsequently, the outer annulus of the Al foil was curled up, forming a cylindrical vessel (Fig. 1b). A catalyst pallidium (Pd) layer was then deposited on the surface of the alumina membrane by thermal evaporation at an incident angle of 30° to avoid the clogging of the pores. To obtain a uniform Pd layer on the membrane surface, Pd was evaporated four times in cross directions. A uniform Pd film on the surface is very important for ensuring the regularity of the replicated films. The cylindrical vessel (alumina membrane and Al) was then immersed into the MMA monomer (with 2 wt% benzoyl peroxide) to carry out the pre-polymerization at 85 °C for 16 min and polymerization at 40 °C for 24 h (Figs. 1c, d). The alumina
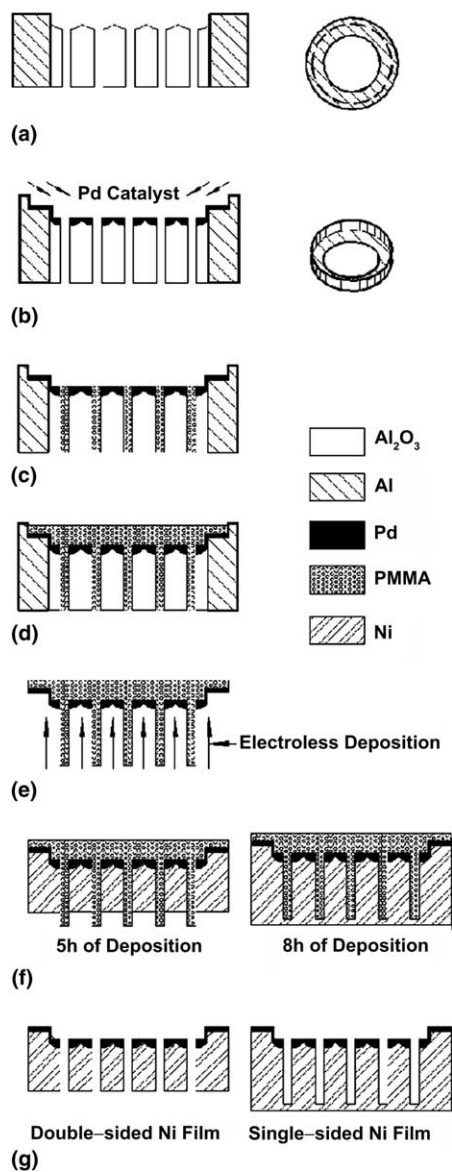

Fig. 1. Schematic outline of the fabrication of nanoporous Ni film: (a) through-hole alumina membrane, (b) deposition of the Pd catalyst layer, (c) immersion of alumina membrane in MMA and pre-polymerization of MMA, (d) polymerization of MMA, (e) removal of alumina membrane and electroless metal deposition, (f) double-faced and single-faced nanoporous Ni films and (g) removal of PMMA.

membrane and Al were then removed in NaOH solution. Electroless deposition was then carried out by immersing the PMMA cylinder array in a

Ni electroless deposition solution: 25 g/L $NiSO_4 \cdot 7H_2O$, 25 g/L $NaH_2PO_2 \cdot H_2O$, 30 g/L NH_4Cl, 12.5 g/L $Na_3C_6H_5O_7 \cdot 2H_2O$, 60 g/L $Na_4P_2O_7 \cdot 7H_2O$, and 100 g/L $N(CH_2CH_2OH)_3$, using $N(CH_2CH_2OH)_3$ to adjust the pH to 9. Finally, the PMMA was removed with acetone (Fig. 1g). The deposition times of the double-faced and single-faced Ni film are 5 and 8 h, respectively.

3. Results and discussion

3.1. Characterization

Fig. 2 shows the scanning electron microscope (SEM) images of the replicated Ni films obtained using the JEOL JSM-6300. The pore regularity is very high on the upper surface (Fig. 2a). This is a result of the uniform distribution of Pd on the surface of the alumina membrane before replication. Pore arrays can be clearly seen on the bottom surface of the 5 h-deposition film (Fig. 2b), indicating that the electroless-plating rate is quite even at different catalyst positions. Fig. 2c shows that the nanopores are cylindrical, parallel to each other, and have a very high aspect ratio. The thickness of the 5 h-deposition film is about 18 μm (Fig. 2d), resulting in an overall aspect ratio of about 360 for the pore arrays. This extremely high aspect ratio originates from the high aspect ratio of the PMMA cylinder array, which is the result of the immersion of the anodic alumina membrane in the MMA monomer. The MMA monomer can fully penetrate into the pores of the alumina membranes, resulting in a PMMA cylinder array with a very high aspect ratio. Since the MMA monomer penetrates the pores by simply immersing the alumina membrane in it, there is no longer a need for operation under vacuum conditions. This results in a highly simplified replication process.

3.2. Magnetic properties

The hysteresis loops of the replicated Ni membranes were measured using a superconducting quantum interference device (SQUID) magnetometer (QMPMS-2) with the magnetic field applied parallel and perpendicular to the

plane of the film (Figs. 4c, d). For comparison, a conventional Ni film was fabricated using the same electroless plating process as that of the
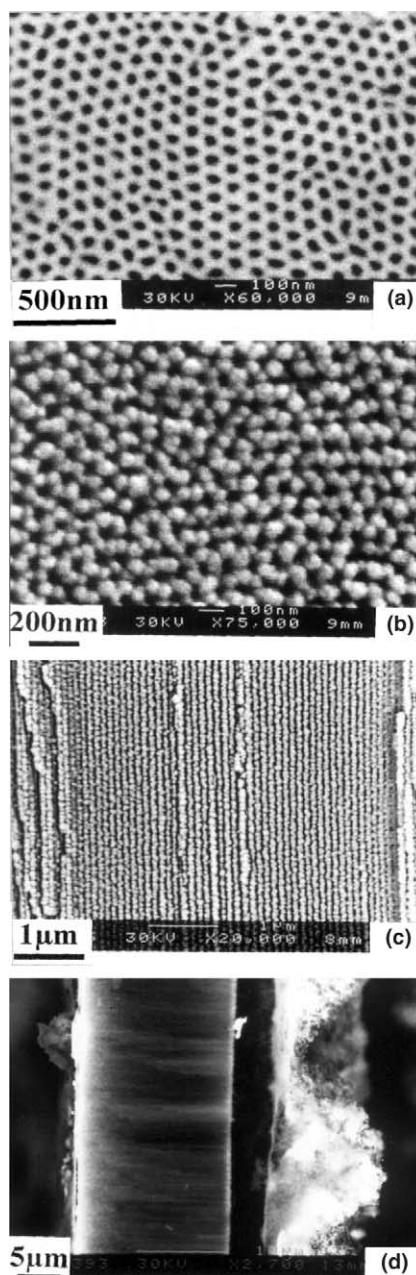

Fig. 2. SEM images of the upper surface (a), bottom surface (b) and cross sections, (c) and (d), of the double-faced nanoporous Ni film after 5 h of electroless deposition.

replicated Ni film and its hysteresis loops are also shown (Figs. 4a, b). Typically, the as-deposited Ni films (in most cases, these are actually Ni–P films) by electroless plating can be either polycrystalline or amorphous depending on the phosphorous (P) content [16–19]. The low-P content Ni–P film is polycrystalline and changes to amorphous once the P content is higher than about 7 wt%. The amorphous Ni–P alloy and its heat-treated products, such as Ni_3P and Ni_5P_2, are paramagnetic or superparamagnetic. Only the face-centered cubic (fcc) Ni particles in Ni–P alloys show typical ferromagnetic properties [20].

The solution we used for the Ni electroless plating is a high-P solution; it results in conventional Ni films with 12 wt% of P content which will give rise to amorphous films. Figs. 4a, b show a typical set of hysteresis loops of the conventional Ni film, with applied field parallel to and perpendicular to the plane of the sample, measured at room temperature. It can be seen that no easy axis appears and the magnetization is still unsaturated in an applied field of up to 10 kOe, showing typical superparamagnetism. This behavior is rather like that of nanostructured magnetic powder and magnetic granular films in which nanoscale single domain magnetic granules are randomly embedded in either an insulator or a metallic matrix [21].

The replicated Ni films, however, have a typical ferromagnetic behavior at both 5 and 300 K (Figs. 4c, d). This suggests that the replicated Ni membranes are polycrystalline with a Ni fcc structure. X-ray diffraction (XRD) measurements, using MAC Science Ltd., MXP18AHF, confirm this point (Fig. 3). The diffuse XRD peak (curve (b) in Fig. 3) of the conventional Ni film shows its amorphous microstructure while the Ni (1 1 1) peak in curve (a) in Fig. 3 indicates the polycrystalline structure of the replicated Ni film. The crystallite size of about 30–50 nm can be estimated from the half-peak width of the Ni (1 1 1) peak by

Fig. 4. Magnetization hysteresis loops with the magnetic field applied parallel and perpendicular to the plane of the Ni film: a conventional Ni film, fabricated by the same electroless plating process as that of the replicated Ni film, measured at 300 K (a) and (b); nanoporous Ni films measured at 5 K (c) and 300 K (d).
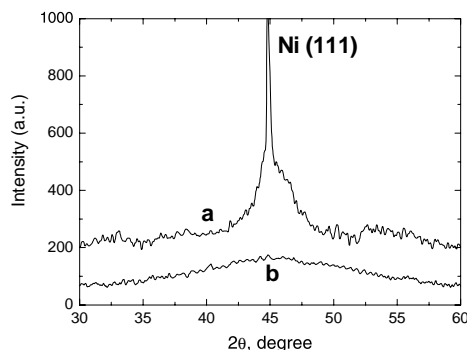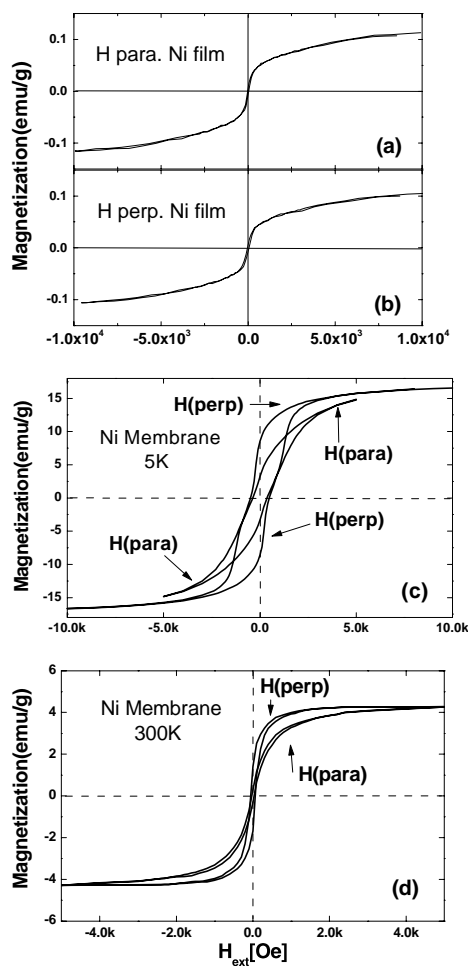

Fig. 3. XRD patterns of a double-faced nanoporous Ni film (a) and a conventional Ni film (b), fabricated by the same electroless plating as that of the replicated Ni film.

the Sherrer's formula [22]. Using energy-dispersive X-ray analysis measurement, we found that the P content in the replicated Ni films is only about 5.1 wt%, which is much lower than the estimated 12 wt% P content of the conventional Ni film.

The electroless plating process of the replicated Ni film is initiated from the catalyst areas around the roots of the PMMA cylinders and is carried out in the nanoscaled voids among the PMMA cylinders. This could be responsible for the unusual low-P content of the replicated Ni films. The Ni electroless plating, using sodium hypophosphite (NaH_2PO_2) as the reductant, involves two reactions which results in Ni (reaction (1)) and P (reaction (2)) as follows [16,17]:

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O$$
$$= Ni + 2H_2PO_3^- + H_2 + 2H^+ \quad (1)$$

$$H_2PO_2^- + H = P + OH^- + H_2O \quad (2)$$
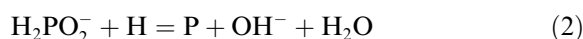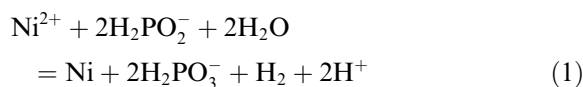
It is seen that Ni^{2+} and $H_2PO_2^-$ ions are consumed in the plating process. The P content in the deposits is dependent not only on the deposition conditions, such as temperature and pH value, but also on the composition of the deposition solution [16,17]. The mole ratio of the $H_2PO_2^-$ ion to the Ni^{2+} ion in the plating solution will greatly affect the P content in the deposits. With a decrease in the above-mentioned mole ratio (i.e., relatively less $H_2PO_2^-$ than Ni^{2+}), the P content decreases. In the electroless deposition of the conventional Ni film, which is initiated from the catalyst film on the substrate, the reaction sites are completely 'open' to the plating solution and thus there is ample supply of the Ni^{2+} and $H_2PO_2^-$ ions from the solution to the reaction sites. However, in the case of the replicated Ni film, the channels for the solution supply are nanoscaled voids among the dense PMMA cylinders with a quite high aspect ratio. Thus the reacting materials need to pass through these tiny PMMA-surrounded deep channels prior to arriving at the reaction sites from the bulk solution. As a well-known reductant, sodium hypophosphite has been used in some organic chemical reactions [23,24] and can react with the organic compounds with unsaturated groups such as carbonyl and alkene [25,26]. Therefore, with the plating solution passing through the tiny channels surrounded by the PMMA cylinders, some amount of $H_2PO_2^-$ ions may be consumed by reducing the carbonyls on the PMMA surface. On the other hand, the adsorption of $H_2PO_2^-$ ions on the PMMA cylinder surface is also possible [27,28]. These factors lead to a reduced supply of the $H_2PO_2^-$ ions to the reaction sites than that of the Ni^{2+} ions, which will result in a lower mole ratio of the $H_2PO_2^-$ ion to the Ni^{2+} ion at the reaction sites than that of the bulk solution. This explains the unusual low-P content in the replicated Ni film.

There is no clear indication of magnetic anisotropy (i.e., no clear preferred magnetization direction) for the replicated Ni film at both 5 and 300 K, as the magnetic coercivities (H_c) of the in-plane and perpendicular hysteresis loops are almost identical in Figs. 4c, d. This is quite different from that of a typical ferromagnetic thin film which has an obvious preferred magnetization direction parallel to the film plane. The reason for this difference is likely due to the elongated morphology of the pore walls of the nanoporous replicated film.

4. Conclusions

Ordered nanoporous Ni films were fabricated using a full-replication process. The process is a total replication of the alumina membrane into the Ni film, resulting in a high aspect ratio of the fabricated films. The nanometer-sized reaction sites of the electroless deposition among the PMMA cylinders caused the crystallization of the replicated Ni film, which is consistent with the ferromagnetic behavior of the replicated Ni film. Due to the special nanostructures and the unusual magnetic properties of the replicated Ni films, it is worthy of further study in the future.

Acknowledgements

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