An Alternative Method to Fabricate Metal Nanohole Arrays

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A new replication method was developed to produce metal nanohole arrays with highly ordered honeycomb-like structure. In this process, porous anodic alumina was used as template; hot-press and electroless plating techniques were introduced to fabricate polycarbonate nanopillar arrays and Ni metal nanohole arrays, separately. With this method, metal nanohole arrays with precise replication of the porous anodic alumina can be fabricated on a large scale simply and rapidly.

Since Masuda and Fukuda[1] successfully prepared an ordered porous alumina template (PAT) by a two-step anodization method in 1995, PAT as one of the most commonly used templates has attracted considerable attention owing to its versatile application for fabrication of nanostructural materials. Compared with other templates, such as porous polymer templates,[2] and colloidal crystal templates,[3] PAT has many advantages: highly ordered pore arrangement over a large area, adjustable pore size and interpore distance, uniform channels, reliable fabrication process, low cost of production, and good thermal and chemical stability. These make it useful in many fields, such as photocatalysis,[4] magnetics,[5,6] energy storage,[7] photonics,[8] and biosensors.[9]

In order to further expand the applicability of PAT, Masuda et al.[10] developed a process for fabricating a nanohole array in which PAT with a honeycomb-like structure is replaced by metal. In this process, a negative poly(methyl methacrylate) (PMMA) structure was obtained by embedding PAT in methyl methacrylate monomer before polymerizing. Ni was electrochemically deposited from one side into the cavities of the negative PMMA to form a Ni nanohole array of about $1 \times 1\,mm^2$ area with geometric structure identical to that of PAT. This process enables the precise replication of PAT with high aspect ratios, but large scales of metal nanohole arrays cannot be obtained because the dissolution of PAT and the deposition of Ni are difficult to conduct through a slender aperture.

There is another replication method to fabricate metal nanohole structures. In this process, metal is sputtered on PAT substrate;[5,11] the metal layer self-assembled and retained the same shape as the surface of the PAT. This process enables the replication of large area of PAT simply and rapidly, but with the increasing thickness of the metal layer, the diameter of the nanoholes are reduced and disappear finally. Therefore, a high aspect ratio and uniform channel structure cannot be obtained by this method.

Here, we report a new replication method using hot-press[12,13] and electroless plating techniques to fabricate nickel nanohole arrays with highly ordered honeycomb-like structure identical to that of PAT. The microstructure was studied by a LEO1530 VP field emission scanning electron microscope (FE-SEM).

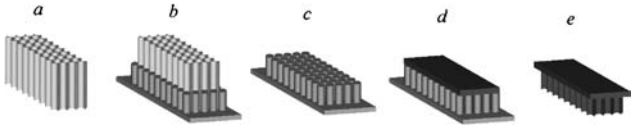

Figure 1. Fabrication of metal nanohole arrays: (a) PAT with through-hole structure; (b) hot-press of the PAT on PC substrate; (c) removal of the PAT; (d) electroless nickel plating into the interspace of the negative PC; (e) removal of the negative PC.

The fabrication sequence of nickel nanohole array is shown in Figure 1. First, a PAT of $1 \times 1\,cm^2$ area and a mass of 50 g was placed on the surface of PC substrate, and then moved into an oven and heated to 150–160 °C for 1 h. After the temperature became below 40 °C, the PAT was dissolved completely in 5% phosphoric acid to form the negative PC structure. Next, a nickel nanohole array was fabricated by electroless plating of nickel into the interspace of nanopillars in the negative PC. Finally, a nickel nanohole array was obtained by dissolving the negative PC in toluene.

A PAT with through-hole structure was fabricated by a two-step anodization process according to ref 11.

Electroless plating of nickel was performed using a sodium hypophosphite bath (Table 1). Nickel sulphate was the source for metal ions, sodium hypophosphite was the reducing agent, citrate acid was used as a complexing agent, and sodium acetate acted as a buffering agent to control pH of the bath during the plating process. All chemicals were analytical reagent grade. The electroless plating was conducted with vigorous stirring at 85 °C. Prior to electroless plating, the sample was immersed in a solution of palladium chloride ($PdCl_2$: 1 g/L, $SnCl_2 \cdot 2H_2O$: 72.45 g/L, $NaSnO_3 \cdot 7H_2O$: 7 g/L, HCl: 300 mL/L) at 30 °C for 5 min, rinsed, and then reduced in hydrochloride acid (HCl: 100 mL/L) at 45 °C for 2 min. After electroless plating, the sample was washed thoroughly with distilled water several times and dried in an oven at 90 °C for 2 h.

Table 1. Composition and operating parameters of electroless plating bath for Ni

Composition/Operation parameters	Specification
$NiSO_4 \cdot 6H_2O/g \cdot L^{-1}$	19.2
$NaH_2PO_2 \cdot H_2O/g \cdot L^{-1}$	23
$CH_3COONa \cdot 3H_2O/g \cdot L^{-1}$	14.88
$C_6H_8O_7 \cdot H_2O/g \cdot L^{-1}$	8
$C_4H_6O_4/g \cdot L^{-1}$	8
$H_2NCNH_2/mg \cdot L^{-1}$	0.5
$CH_3CHOHCOOH/mg \cdot L^{-1}$	0.48
$KIO_3/mg \cdot L^{-1}$	1
Poly(ethylene glycol)/$mg \cdot L^{-1}$	0.12
Temperature/°C	85
pH	5.2

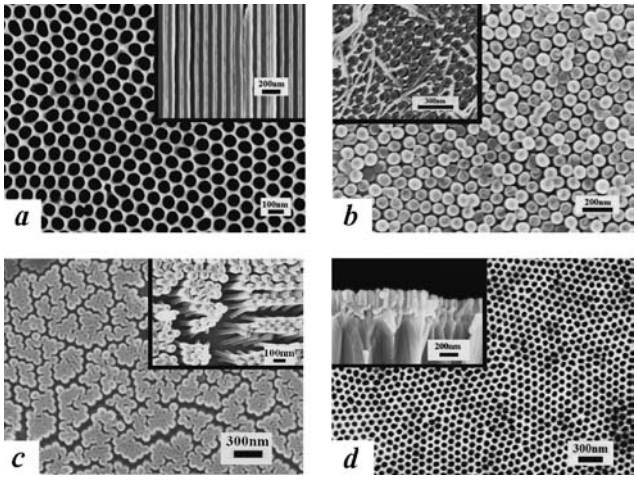

Figure 2. (a) FE-SEM images of the PAT with through-hole structure. (b) FE-SEM images of the negative PC prepared at 150 °C after the PAT was dissolved completely, and inset (b) shows the image of the PAT dissolved partially. (c) FE-SEM image of the negative PC prepared at 160 °C after the PAT was dissolved. (d) FE-SEM image of a nickel nanohole array. Electroless plating was carried out at 85 °C for 30 min.

Figure 2a shows typical FE-SEM images of the fabricated PAT. The thickness and the diameter of the nanoholes were 100 μm and 85 nm, respectively. The aspect ratio of the nanohole was about 1180, the distance between two nanoholes was about 104 nm, and the density of the nanoholes was about $10^{10}/cm^2$. Hexagonal nanoholes were aligned orderly, normal to the surface of the PAT and parallel to each other.

Figure 2b inset shows an FE-SEM image of the negative PC prepared by hot pressing the PAT on the PC substrate at 150 °C and then dissolving the PAT in 5% phosphoric acid for 2 h. From this image, it can be seen clearly that the PAT was not removed completely and that the PC nanopillars were still embedded in the hexagonally packed hole array of the PAT. The PC nanopillars have a uniform diameter of about 85 nm, which is about the same size as that of the nanoholes in PAT. After dissolving the PAT completely, it was found that all the nanopillars stood upright, parallel to each other (Figure 2b). These results indicate that hot press is a simple and effective method to produce negative PCs with highly ordered honeycomb-like structure identical to that of the PAT.

With increased hot-press temperature from 150 to 160 °C, we note that the length of nanopillars increased, and the nanopillars with a uniform diameter randomly tangled together after the PAT was dissolved completely (Figure 2c). This indicates that more PC could be pressed into the nanohole of the PAT with increase of the PC ductibility. The hot-press temperature is a very importance parameter that determines the formation of nanopillars. Figure 2c inset shows a negative PC prepared at 160 °C, the length of the nanopillars is about 400 nm. This result shows that only low aspect ratio of nanopillars can be obtained by this method.[13]

Figure 2d shows a surface FE-SEM image of the nickel nanohole array,[14] obtained by dissolving the negative PC after the electroless nickel plating for 30 min. The negative PC was prepared at the hot-press temperature of 150 °C. From this image, it is seen that the nanoholes with uniform diameter and interval were hexagonally arranged in high regularity. The mean diameter and the interval of the nanoholes measured from the image in Figure 2d were in accordance with the dimensions of the PAT over a large scale area of $1 \times 1\,cm^2$. Figure 2d inset is a cross section image of the nickel membrane. The top layer of the membrane is the nickel nanohole arrays with the length of about 250 nm.

In Figure 2c inset, a diameter enlargement is observed at the upper end of nanopillars. This enlargement is caused by hot deformation of nanopillars during the process coating Au on the surface of the sample for FE-SEM observation. Unordered interspace of nanopillars by hot deformation is also observed in Figure 2b. Nevertheless, uniform nickel nanohole arrays (Figure 2d) can be formed because this process is unnecessary for nickel deposition.

In conclusion, nickel nanohole arrays with highly ordered honeycomb-like structure identical to that of the PAT was successfully fabricated using hot-press and electroless plating techniques. This new method enabled the precise replication of the PAT simply and rapidly over a large scale area. Such a method can be readily extended to prepare other metal and metal alloy, such as Pd, Pt, Fe, Sn, and Ni–Co–B, Co–Fe–B alloy. In addition, this nickel nanohole arrays is an antidot structure of magnetic storage media with high storage density. Therefore, an alternative method to fabricate magnetic storage media is provided.

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Published on the web (Advance View) July 19, 2008; doi:10.1246/cl.2008.884