Fabrication of Uniform Magnetic Nanowire Array

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Abstract. Two-dimensional uniform arrays of identical nanometer size nickel wires with high aspect ratios and large packing densities have been fabricated. The arrays were made by electrodeposition into nanochannel glass templates. The templates were polished and etched for enough time to obtain parallel, uniform, cylindrical nano-channels. Obtained nickel wires were circular, each approximately 150 μm long and 80 - 160 nm in diameter, depending on the diameter of the nanochannel of the template. Scanning electron microscopy has been used to characterize the nanostructures. A superconducting quantum interference device magnetometer has been used to investigate the magnetic properties of the nanowire arrays. Preliminary results on fabrication of nickel nano-arrays by supercritical carbon dioxide fluid process were also presented.

1. Introduction
Nanostructured materials exhibit a host of interesting new phenomena directly related to their reduced dimensionality. They provide a means of studying quantum size effect, spin-spin interactions, and low dimensional excitons. The fabrication and investigation of magnetic nanostructures such as nanometer scale particles and wires present interest from both fundamental and technological points of view. Characterization and explanation of the magnetic properties of magnetic nanowire and nanoparticle arrays are extremely important due to their potential wide range applications. One impetus for exploring this new technology is the demand for higher bit densities in magnetic storage and in memories.

Magnetic nanowire arrays with large aspect ratios have been fabricated by various methods, including electron-beam lithography [1], electroplating into anodized aluminum [2,3] and polycarbonate track-etched membranes [4,5], interference lithography [6,7] and physical deposition into selectively etched semiconducting wafers [8]. In this paper, we will describe the fabrication, nanostructures and magnetic properties of extremely uniform magnetic nanowire arrays grown in nanochannel glass (NCG) templates using both electrochemical deposition and supercritical fluid process.

Nanochannel glass [9] a glass matrix containing extremely uniform arrays of hollow channels. The hollow channels are typically arranged in a hexagonal close packed pattern. The channel diameter can be as small as 20 nm and packing densities can be greater than $10^{11}$ channels/m². NCG is fabricated by a draw process similar to that used to fabricate optical fibers. The preparation of the NCG begins by placing an acid-etchable glass rod within an acid-resistant glass tube. The assembly is drawn at elevated temperature to a fiber with a circular cross-section. These core/clad fibers are carefully stacked by hand into a hexagonally shaped bundle. The bundle is then drawn at elevated temperature, reducing its cross-sectional area and fusing the individual glass fibers together. The geometric
regularity of the bundle, as well as its hexagonal cross-section, is preserved by the draw. These resulting fibers can be repacked and redrawn repeatedly until the final desired channel dimension is reached.

2. Experimental procedure of electrochemical deposition
NCG was cut into wafers with thickness at about 1 to 2 mm using a diamond saw. Both surfaces of the wafer were polished to an optical flat and the thickness of the wafer was reduced to approximately 300 µm. The unetched NCG wafer was etched by immersing in 1% acetic acid solution for some time. The etching time is very critical. Etched for longer time, the nanochannels become distorted; for shorter time, the nanochannels are not completely etched. To enhance the etching rate, we periodically took the sample out of the etching solution and rinsed in distilled water. The sample was put into a vacuum chamber to evaporate water inside the nanochannels. It was then immersed in the etching solution again. This process ensures that periodically fresh etching solution enters nanochannels to enhance the etching rate. The total etching time was about 18 hours.

One side of the NCG template was sputtered with a thin copper layer (100 nm) to serve as the electrical connection. After sputtering, the sputtered side of the template was mounted on a silicon substrate coated with a thin layer of copper. It was imperative that the copper layer on the template was firmly in contact with the copper layer of the substrate to establish good electrical pass way for the electrochemical deposition.

Electrochemical deposition was performed by a bipotentiostat (Pine Instrument Company). The electrolyte was composed of saturated NiSO₄ aqueous solution with a pH value of 1~2. The deposition potential was chosen to be -1.3 V versus a saturated calomel electrode based on cyclic voltametry experiments performed in the electrolyte solution employed [10]. The electrochemical deposition time varied with the channel size of nanochannel samples.

3. Results and discussion
The electrochemical deposition begins at the metal surface at the bottom of the channels and continues uniformly up the channels toward the open ends of the channels. This results in highly uniform filling of the NCG template. By control of the electrochemical deposition chemistry, pH value and current density, nickel nanowire arrays with good magnetic properties were obtained. Fig. 1(a) is a SEM micrograph of the surface of the nickel nanowire arrays after polishing off the copper layer. The nickel arrays in the channels appear uniform and continuous. Fig. 1(b) shows a SEM image of the cross-section view of a nickel array sample with 180 nm channel diameters. This image was taken at the

![Figure 1](image-url)

**Figure 1.** (a) Scanning Electron Microscope (SEM) image of top surface of etched but filled with nickel. The channel diameter of template is 192 nm; (b) SEM image of cross-section of etched but filled with nickel with channel diameter of 192 nm.
boundary between the nanowires (bottom part) and empty channels (top part). The total lengths of the nickel nanowires in this sample were about 140 µm measured by the scanning electron microscope. The picture shows that there was some unevenness in the growth of Ni nanowires. The uneven growth was probably due to the unevenness in diameter of the etched channels. The length difference was about 1 - 5 µm, which was very small in comparison with the 140 µm of the total length.

Figure 2. Magnetization curves versus applied field of the nickel nanowire arrays of 100 nm in diameter and 150 µm in length measured at 70 K. (a) Magnetic field is parallel to the length of the wires. (b) Perpendicular to the length of the wires.

The magnetization of nickel nanowire arrays was measured using a Superconducting Quantum Interference Device (SQUID). Fig. 2(a) and (b) shows hysteresis curves of nickel nanowire arrays, with a diameter of about 80 nm and a length of about 150 µm for the applied field parallel and perpendicular to the plane of arrays at 70 K, respectively. From the hysteresis curves it is observed that for field applied parallel and perpendicular to the long axis of the wires, the coercivities are $H_c=240$ Oe and $H_c=130$ Oe, respectively. The orientation of magnetization looks more likely in the parallel direction, which indicated an anisotropic behavior [11]. The curves are highly sheared indicating strong interwire interaction between nanowires [12].

3. Filling the voids by supercritical fluid process

The process described above can produce nanowire arrays with very high aspect ratio. In some applications uniform arrays with wires that have well defined aspect ratio are required. For example, for discrete perpendicular magnetic recording [13] discrete magnetic elements with cylinder shape uniformly embedded in a nonmagnetic matrix are required [14]. To that end, we have carried out a preliminary experiment to fill the voids in the NCG from top by a supercritical fluid process (SFP) [15]. One end of a piece of NCG was polished to optical flat. The piece was immersed in the acetic acid solution for a few minutes to etch out the etchable materials. The depth of the voids was about a few micrometers deep. Using Ni(hfa)$_2$ . $x$H$_2$O as precursor nickel materials have been deposited onto polished end of the sample by SFP. The details of SFP could be found elsewhere [15,16]. Fig. 3 shows the SEM images of the top and cross-section views. The existence of Ni inside the nanochannel was confirmed by the EDX analysis.
Figure 3. SEM pictures of the sample processed by SFP. (a) The top view. (b) The cross-section view.

5. Summary
We had shown the ability to grow uniform arrays of nickel nanowire with high aspect ratio and wire diameters as small as 80 nm. SEM and SQUID have been applied to characterize the nanostructures and magnetic properties. The obtained arrays looked regular and continuous. Moreover, the magnetic orientation tended to be in parallel with the long axis of arrays. Deposition of Ni into nanochannels by the supercritical fluid method was also reported.

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