Fe nanodot system fabricated by non-lithographic method and its structural properties

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Abstract. In this work, we study the magnetic structure and morphology of the Fe nanodot system fabricated by the non-lithographic method, using anodic aluminum oxide (AAO) membrane as a template. By the two-steps aluminum anodization, the AAO patterns with the hexagonal pore arrangement have been achieved. Using AAO pattern as a template, under suitable conditions we successfully deposited the iron metal in the pores by the thermal vacuum evaporation. By the exposure of the deposited system from the bottom of the AAO membrane, the hexagonal ordered Fe nanodot system has been obtained. The morphologies of the nanodot system were imaged by the Atomic Force Microscopy (AFM) and Field Emission Scanning Microscopy (FESEM) methods. The magnetic structures were investigated by the Energy Dispersive X-Ray Fluorescence Spectroscopy (EDS) and Magnetic Force Microscopy (MFM) methods. Experimental results confirmed that the MFM image of the fabricated Fe nanodot system is similar to their AFM image.

Keywords: AAO, AFM, MFM, nanodot system, magnetic structures.

1. Introduction
Magnetic nanoparticle monolayer has been proposed as suitable for future ultra-high-density magnetic recording media and other applications [1, 2]. A great deal of brilliant science and engineering involving mesoscopic structures was made possible over the past decade through the use of advanced lithographic technologies. These techniques seem to be economical, but they have technological limits for fabricating one-dimensional (1D) and zero-dimensional (0D) nanostructures. Thereby, creating an alternative technique for fabricating nanostructures fabrication by selective deposition into templates called non-lithographic method is an interesting work.

Non-lithographic fabrications of low-dimensional structures can be performed by either electrochemical or physical methods, using AAO as a patterning template. An attractive approach to get 1D and 0D structures is carried out using anodic aluminum oxide (AAO) template which self-organizes into a hexagonal array of uniform nanopores with pore density up to $10^{12}$ cm$^{-2}$ and pore diameters down to 4 nm [3]. A variety of nanostructures has been successfully fabricated using AAO templates by electrochemical deposition [4-6], but only a few nanostructures created by physical deposition have been reported [7-9]. The electrochemical deposition entails synthesizing the desired material within the pores of a membrane, resulting in nanorod (nanowire) or nanotube formations. The
physical method using AAO as a depositing mask leads to nanodot formation on surface of any substrates. For the electrochemical deposition, the problem of filling the pores is critical and this has been successfully solved by application of some voltage bias with high ac frequency. For the physical deposition, the penetration through the AAO pores of evaporated atoms (particles) is crucial, so it is very difficult to transfer the AAO structure to deposited nanodot system on the substrates. This penetrating process is complicated and still not understood. The process of the selective etching/removal of the deposited product on the template surface is very complicated and in many cases it is impossible.

In this work, we present a unique technique to get symmetric iron (Fe) nanodot system by using AAO templates. We develop a simple technique without selective etching process. The technique involves filling Fe into pores of the AAO. Then the remained aluminum substrate was etched out. Finally, the deposited Fe in the AAO pore was exposed by removing the bottom of the AAO barrier-layer.

2. Experimental

The AAO template was prepared by two-steps anodization of aluminum foil of 3 mm-thick and (5x1.7) cm² in size. First, 99.99% pure Al foil was ultrasonically cleaned in acetone and alcohol for 10 min. and 20 min., respectively. Then the back surface and edges of the Al foil were covered by epoxy, so all steps of AAO fabrication can be proceeded only from the non covered surface of the Al foil. The flatness of the cleaned aluminum foil was obtained by chemical electro-polishing in the 1:4 %vol. perchloric acid and alcohol under voltage of 20V for 2 minutes at 7°C. The anodization process is carried out in 0.3 M oxalic acid solution at the temperature of 15°C under voltage of 40 V and current of 10 mA. The first anodization was carried out for 10 hours. The aluminum oxide was then etched in 1M chromic phosphoric solution at 65°C for 5 hours. The second anodization was carried out for various times from 2 minutes to 10 minutes. Under these anodization conditions, the pore diameter of the initial AAO template was in the range from 15 nm to 20 nm. Pore-widening process was done in the 0.1 M phosphoric solution at 30°C. After widening process, the pore diameter was about 60 nm. Filling of the Fe in the pores was carried out by vacuum thermal evaporation. Vacuum level, deposition rate and source-substrate distance were 10⁻⁷ Torr, 0.2 nm/min. and 50 cm, respectively. Aluminum layer was dissolved in the saturated solution of mercury (II) chloride HgCl₂. Aluminum barrier oxide was removed by etching in 1 M phosphoric solution for 1 hour at room temperature. Figure 1 presents schematic procedure for fabrication Fe dots. The various kinds of Fe clusters or Fe nanotube in the AAO pores depended on the pore diameter and aspect ratio of the pores. In our work, the Fe nanodot system had a symmetry exactly identified with AAO symmetry. The morphology of the AAO template and prepared Fe nanotube system were analyzed by FESEM and AFM methods. The magnetic structure of the fabricated Fe nanodot system was investigated by MFM method.

3. Results and discussion

The typical surface and cross-section morphology of the prepared two-steps anodization AAO template are presented in figure 2 These images apparently show the hexagonal arrangement of the pores and the pore uniformity both in horizontal (figure 2a) and vertical shapes (figure 2b). As shown in the figure 2, the obtained AAO structure has the pore-pore distance of ~ 95 nm corresponding to the pore density of about 4x10¹¹ cm⁻². The pore diameter is about 60 nm that means the thickness of the porous aluminum anodic oxide wall is ~ 35 nm.

Experimental data indicated that, the penetration of the evaporated iron (atoms or group of atoms) into AAO pores was strongly dependent on the pore diameter and aspect ratio of the AAO pore. For the initial AAO pattern with pore diameter about 20 nm, most of the iron evaporated products tend to perform clusters during penetration into the pore. As a result, various small Fe clusters distributed along the pore wall were observed as seen in figure 3a. It is clear that, under these conditions, the AAO structure cannot make uniform Fe systems. To overcome this problem, we have developed a technique for widening the diameter of the pore. When the pore diameter is larger, about 60 nm and
pore aspect ratio is less than 10, the evaporated iron metal successfully penetrated along the pore wall. The evaporated iron metal created the single Fe nanotube in each pore, as seen in figure 3b. It is clear that, the bottom of the tubes is closed. As mentioned above, the iron nanodots deposited in the AAO pores were exposed from the bottom side by removing barrier aluminum oxide. The SEM image (figure 4a) clearly shows the typical surface morphology of prepared Fe nanodots. From figure 4a, it is clear that the iron dots have semispherical shape after removing the AAO barrier. We can note that the arrangement of the Fe nanodots was identical with the pore arrangement of the used AAO template.

It is found from the EDS characterizations (figure 4b) that the peaks at 6.398 keV and 7.057 keV corresponding to the Fe element. Experiment results presented in figure 4(a, b) indicated that we had successfully realized all steps for the Fe nanodot system by using AAO template. It is noted that using the developed technique, Fe nanodots with highly uniform arrangements can be formed. This system consists of hexagonal Fe nanodots separated each other by porous anodic aluminum oxide wall.

![Figure 1. Schematic procedure for fabrication Fe dots.](image1)

![Figure 2. Surface (a) and cross-section (b) morphology of the 60 minutes widened AAO.](image2)
It is well-known that MFM is the direct method to observe the magnetic structure of magnetic materials. However, for a system of nanometer size, this method still needs to be improved and developed [10]. In order to get MFM image of a nano system, it is necessary to distinguish the effect caused by the Van der Waals forces and the effect caused by the magnetic forces. In principle, comparing the MFM image of the sample surface with its tapping AFM mode image, we can evaluate the influence of the Van der Waals forces to the MFM tip. But it is impossible to get AFM image of the tapping mode by the magnetic tip. So, it is impossible to simultaneously get the MFM and AFM tapping mode images. To solve this problem, we chose indirect comparison. We compared the AFM image measured by the contact mode with the ones by the tapping mode; then we compared the AFM contact mode image with the MFM image. The result of the comparison between AFM contact mode and AFM tapping mode is shown in figure 5.

It must be noted that these images were simultaneously obtained by scanning line by line in the sequence of one line AFM contact mode and one line AFM tapping mode. It is clear that the AFM contact mode image and AFM tapping mode image show the same structure, except the small difference in the width of the AAO wall. Comparing with that from FESEM image (figure 4a), it is clear that the difference of width also appeared. This difference is due to the resolution of different applied AFM modes and measured methods. But the important conclusion is that all obtained images show the same arrangement of the pores and nanodots. These results confirm that the AFM image of the contact mode (figure 5a) presents the real geometrical distribution of the Fe nanodots. Figure 6 presents the typical result of the comparison between AFM contact mode and MFM mode.
The MFM image was obtained by tip-scanning at a distance of 60 nm from the sample surface. Here, we emphasize that the AFM and MFM images were simultaneously measured, so the AFM and MFM signals had provided images of the same position. Firstly, we note that the dot distribution in the MFM image determined by magnetic forces is identical with that from AFM contact mode measured due to the Van der Waals forces. Secondly, it seems to be the large domain in the MFM image, which looks like clouds (figure 6b). We propose that the cloud-like signals related with the size difference of Fe dots. A similar result concerned with the size of the magnetic particles was reported in [11] and has been explained by the collective behavior of the Fe dots. Based on the dot distribution and the cloud-like distribution, we can confirm that the obtained MFM image presented in figure 5b is really due to magnetic forces. The dot distribution is due to individual magnetic dipoles of the Fe nanodots, and the cloud-like distribution is due to the dot interaction. Finally, experiment results indicate that by the developed technique we successfully fabricated the hexagonal ordered Fe nanodot system, which has the magnetic structure identified with their topology.

4. Conclusion
By two-step aluminum anodization, the AAO patterns with the hexagonal pore arrangement have been achieved. Using AAO pattern as a template, we successfully deposited iron metal in the pores by the thermal vacuum evaporation. The deposited hexagonal ordered Fe nanodots have been exposed by etching aluminum and alumina oxide layers from the bottom of the AAO template. The morphology of
the Fe nanodot system can be clearly identified by SEM and AFM studies. EDS and MFM were employed to confirm the existence of Fe in the nanodot system. The fabricated Fe nanodot system has the magnetic image similar to their topography.

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