FABRICATION OF ULTRA HIGH DENSITY MAGNETIC RECORDING MEDIA USING SELF-ORGANIZED POROUS ALUMINA NANOHOLE ARRAY

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Abstract

We have investigated fabrication of a high-density magnetic perpendicular nanowire array by means of template-assisted electrodeposition of FePt alloy, which is considered as the most suitable material for overcoming the problem of super-paramagnetism which was caused by shrinkage of dimensions. In order to fill FePt within a high aspect ratio nanohole of AAO that has been grown on Si substrate, we applied DC-pulsed electrodeposition by changing the on- and off-time independently, and found that an off time of more than 100 msec is required to fill the nanoholes. We also investigated a method for controlling the regularity of the single domain nanohole arrangement using a nano-imprinting method, combined with anodic oxidation, and found that it is possible to reduce nanohole pitch to $1/\sqrt{3}$ of the initial pitch of the imprinting mold. This method promises to realize a very fine nanohole array pitch of less than 30 nm.

1. Introduction

The recording density of magnetic recording media has been increasing steadily, and is expected to go beyond 1 Terabit per square inch within a few years. This means that the pitch between neighboring magnetic memory units (i.e. domains) must be smaller than 25 nm. In order to avoid interaction between neighboring domains, a patterned media in which such domains are spatially separated is thought to be the technology of the future. AAO (aluminum anodic oxide) shows typical self-organization phenomena with a regular array of nanoholes perpendicular to the substrate, and it is considered the most suitable structure for realizing nanoscale patterned media. For this reason, there have been extensive studies to fill ferromagnetic materials in nanoholes by electrodeposition[1-6].

Electrodeposition of hard magnetic nanowire into anodized aluminum oxide (AAO) templates is attracting increasing interest in the field of perpendicular magnetic recording. With AAO, it is comparatively easy to control the pore dimensions, length, diameter and the areal density of pore by modulating an applied voltage. We chose FePt as magnetic nanowire because of its excellent hard magnetic properties and good thermal stability even when its size is as small as 3~4 nm. This is due to its large magnetic anisotropy[7-9]. In the present study, we infilled FePt in AAO nanohole arrays by pulse dc electro-deposition, changing the ratio between on- and off- times of the DC pulse.

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Another important task for realization of ultra high density magnetic recording media is to reduce the pitch of nanoholes with a single domain trigonal lattice structure. Nano-imprinting on a flat Al surface using a hard mold, such as SiC that has periodical trigonal array, is very effective for forming a single domain nanohole array by anodic oxidation[10-11]. However, it is very difficult to obtain periodic structures with a few tens of nm, because of the limitation of EB lithography and dry-etching technology. In anodic alumina oxide (AAO), the pitch of nanohole array is determined by anodic voltage, and a $1/\sqrt{3}$ reduction of nanohole pitch was reported by J. Choi et.al.[12, 13] with nano-imprinting using a 500nm pitch mold. In this study, we investigated pitch reduction mechanisms of AAO nanoholes by anodic oxidation after nano-imprinting using a 200 nm pitch SiC master stamp.

2. Experimental

At first, aluminum film (1μm) was deposited on Au(50nm)/Ta(100nm)/Si(100) substrate by sputtering. Then anodic oxidation of Al was carried out in 0.3 M oxalic acid at 3 °C under a constant voltage of 40V, and a 100 nm pitch nanohole array was formed. After the Al film had completely changed to AAO, the alumina barrier layer at the bottom of the nanohole was etched away using diluted phosphoric acid in order to make electrodeposition of the FePt nanowire easier. Since this etching process is isotropic for aluminum oxide, it is called a pore widening process, the pore diameters being widened from 40 nm to 70-80 nm..

For electrodeposition of FePt alloy in nanoholes, an electrolyte composed of H_2PtCl_6, $FeSO_4$ and Na_2SO_4 was used. The counter electrode was a Pt sheet, and as a reference electrode, we used an Ag/AgCl electrode. The pulse electrodeposition was carried out using a rectangular voltage pulse, as shown in Fig 1. Pulse on-voltage was V_{on} = -820 mV and off-voltage was V_{off} = 0 mV; on-time was T_{on} = 48 ms and off-time was varied such as T_{off} = 24, 48, 144, 480 ms. The atomic ratio of Fe to Pt was 50:50 when -820 mV was used in the case of a FePt film deposition. After electrodeposition, we annealed samples at 600 °C in a vacuum with a pressure of 1 x 10^{-6} Torr. Fig 2 shows a cross-sectional scanning electron microscopy (SEM) image of the sample formed with T_{off} = 48 ms. A small amount of inhomogeneously-filled FePt nanowire was observed at the bottom of the nanohole. Fig 3 shows a cross-sectional SEM image of the sample formed with T_{off} = 480ms. Nanoholes were almost completely filled with FePt, and a FePt film was formed on the AAO nanohole array due to further deposition. In this case, we need to polish away the FePt film to separate each FePt nanowire to be suitable for magnetic recording media.

These results suggest that some duration of pulse off-time, typically longer than 100 msec, is essential for the successful filling of nanoholes. In the case of a 48msec off-time, a continuous FePt film was formed on AAO, while only a few nanoholes were deposited with a depth of less than half. The reason for FePt deposition on AAO comes from the weak electrical conductivity of AAO porous aluminum oxide film. Electrodeposition may proceed both at the top of nanohole as well as at the bottom where the gold electrode is exposed. When pulse off-time is long enough, the Fe and Pt ion concentration may be sufficiently large to maintain FePt deposition by ion diffusion from top to bottom of the nanoholes. On the other hand, diffusion fluxes of Fe and Pt ions are not sufficient for deposition when pulse off-time is too short.

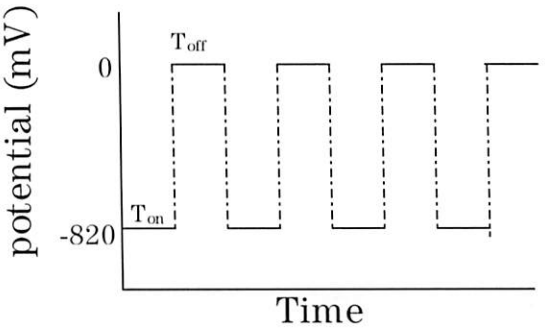

Fig. 1 Pulse cycle for pulse dc electrodeposition.
T_{on} = pulse duty time and T_{off} = pulse relaxation time.

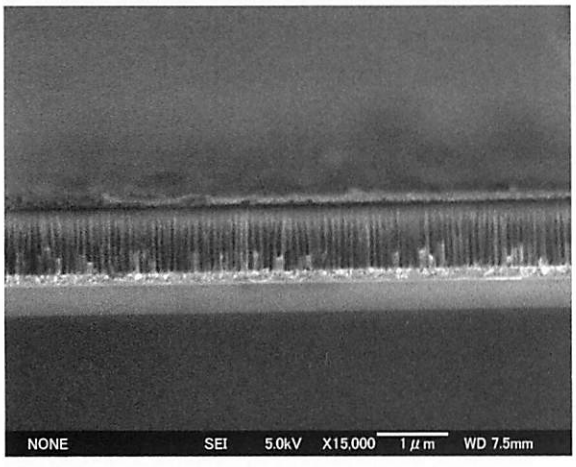

Fig. 2 Cross-sectional SEM image of AAO nanoholes after dc pulse electrodeposition (T_{on} = 48 ms and T_{off} = 48 ms)

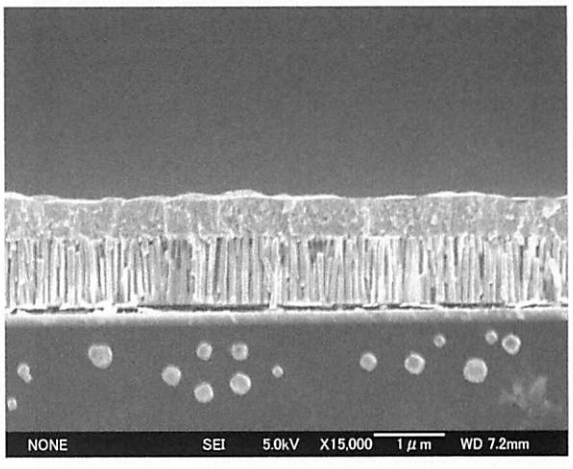

Fig. 3 Cross-sectional SEM image of AAO nanoholes after dc pulse electrodeposition (T_{on} = 48 ms and T_{off} = 480 ms)

Next, we investigated reduction of nanohole pitch by adjusting anodic oxidation voltage against a 300 nm pitch imprinting SiC mold. The electro-polished aluminum plate (99.999%) was pressed by a master stamp having a lattice constant of 200 nm (triangular array of protrusions) under a pressure of 80MPa. The anodic oxidation of the Al sheet was carried out at various voltages between 43 and 50V for the purpose of obtaining $1/\sqrt{3}$ times the pitch of the master stamp (Fig 4), with 0.3M oxalic acid at 1°C. Anodic oxidation time was 1 hour, and after anodic oxidation, alumina nanoholes were enlarged slightly by wet chemical etching (5wt% phosphoric acid 30°C, 20min). Subsequently the oxide membranes were removed by dipping

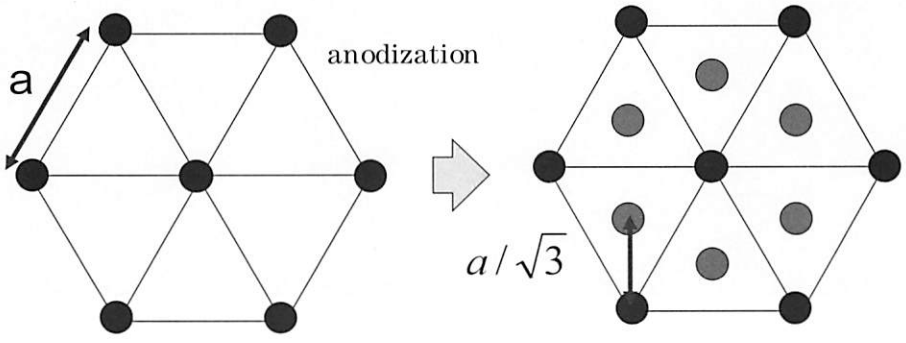

Fig. 4 Pitch reduction of alumina nano-hole array

the Al plate into aqueous mixture of phosphoric acid (6wt%) and chronic acid (1.8wt%) at 60 °C for 1 hour. The surface of the AAO plate and Al film after removal of AAO membrane are shown in the SEM images in Fig 5, for anodic voltages of 44, 46 and 48V. There are trigonal lattice of the large holes for every case just after anodic oxidation (Fig 5 a, b and c), which corresponds to imprinted locations with 200 nm pitch.

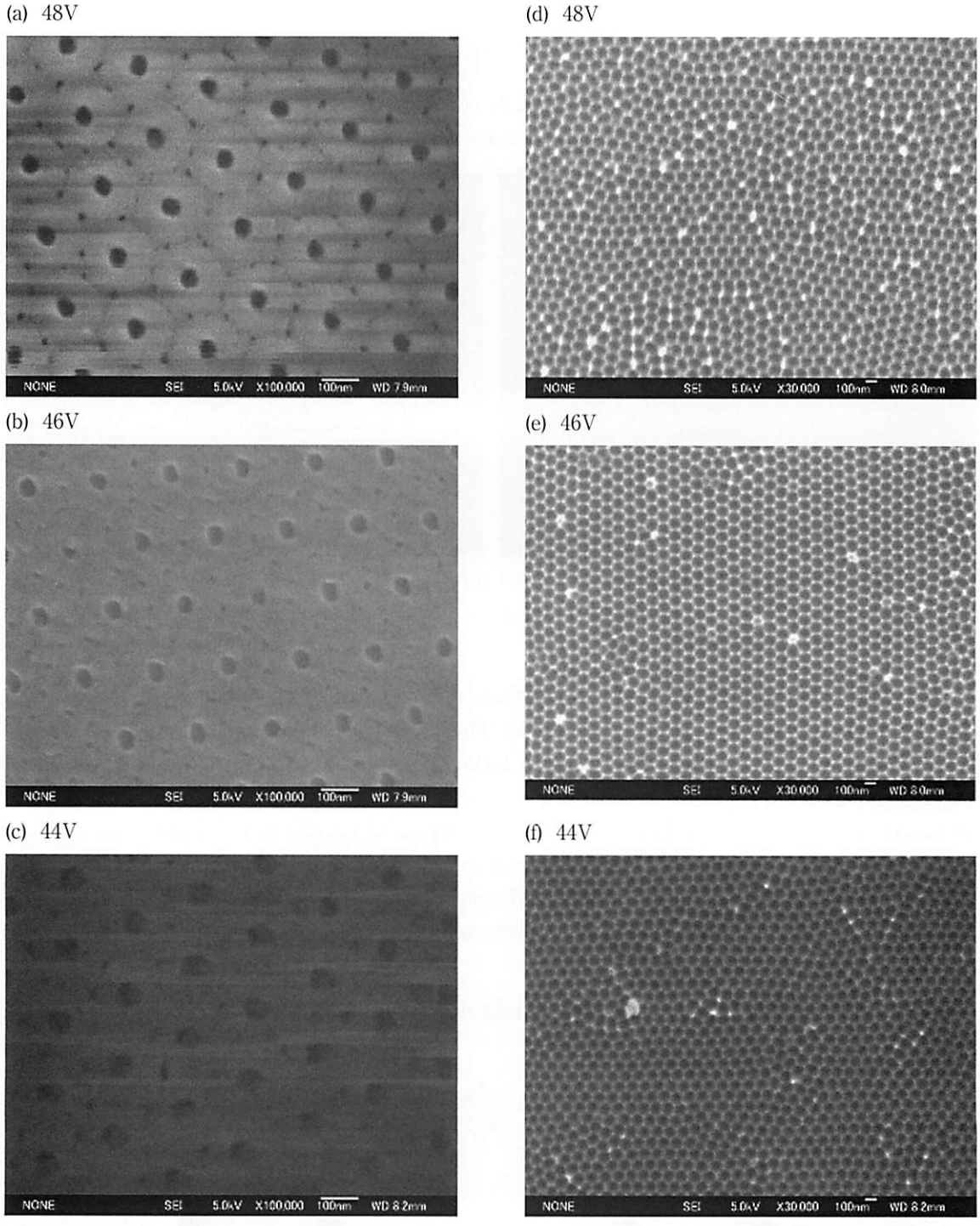

Fig. 5 Top view SEM images of the surface of the AAO membrane just after anodic oxidation (a, b, c), and of Al film after removal of AAO membrane (d, e, f).

Many small holes are also observed on the hexagonal lattice boundaries. During anodic oxidation of 1 hour, AAO film thickness becomes about 10 μm. Figs 5 d, e and f show aluminum surface morphology after removal of AAO film. Periodic arrangement of hexagonal lattice that reflect nanohole bottoms is clearly shown for the case of 46 V (Fig 5 e). It should be noted that the pitch of the nanohole bottom is 115 nm that is $1/\sqrt{3}$ of the master stamp. However, regularity of nanohole bottoms is not so good for the case of 48V(Fig 5d), or 44 V (Fig 5f).

We analyzed these SEM images by two-dimensional FFT to evaluate the voltage dependence of nanohole regularity. Fig 6 shows FFT images of the nanohole arrangement

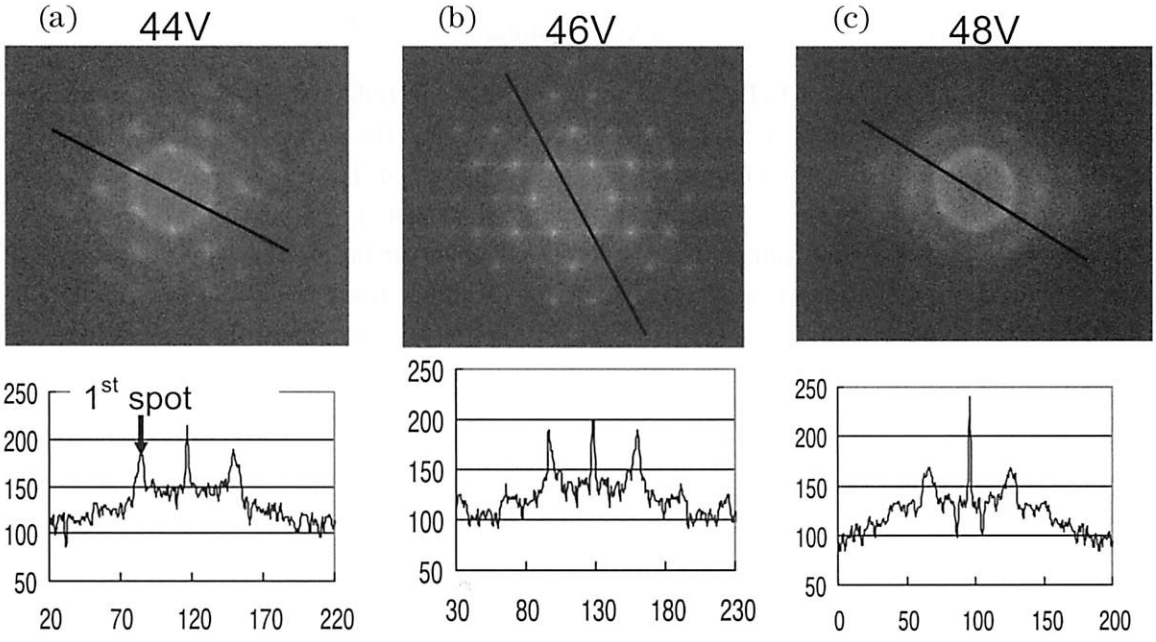

Fig. 6 Two-dimensional FFT images of the nanohole arrangement, as shown in Figs 5d, e, and f which were observed after removal of thick (10 mm) AAO membrane. Line scans of FFT intensity distribution along the red line are shown below.

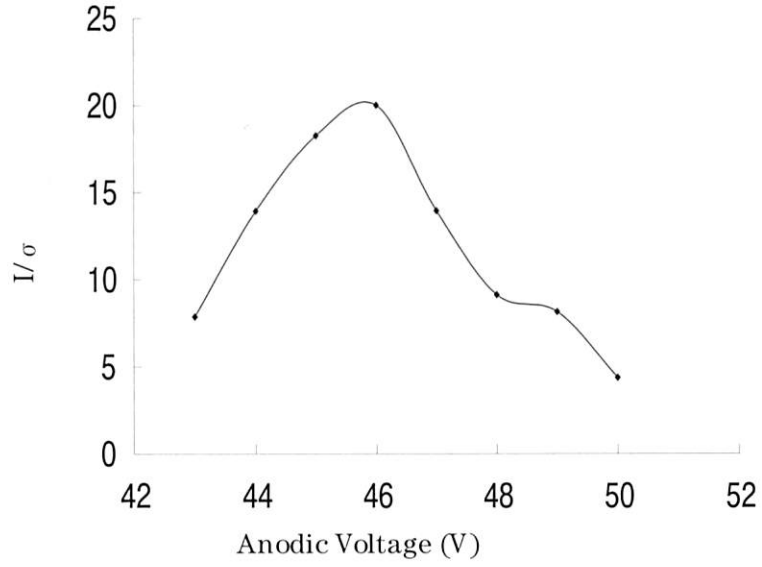

Fig. 7 Voltage dependence of nanohole regularity

shown in Figs 5d, e, and f which were observed after removal of thick (10 μm) AAO membrane. Line scans of FFT intensity distribution along the red line are shown below.

In cases of 44V and 46V, a trigonal array of spots as obtained by FFT, while only coaxial rings were observed in the case of 48V. The regularity of nanohole arrangement is typically well-represented as an intensity of 1st order spots.

Hence, we chose a spatial order parameter I/ó as the 1st peak intensity I divided by its FWHM σ. I/ó is shown as a function of anodic voltages in Fig 7, which shows that the highest regularity is obtained at 46 V.

3. Conclusions

We have studied filling of FePt in AAO nanoholes by controlling the pulse duty ratio. The relaxation time (T_{off}) seemed to act effectively for improving the filling performance of FePt, and we have succeeded in the complete fill of nanoholes when T_{off} was larger than 400msec. We also confirmed that the most appropriate voltage to realize $1/\sqrt{3}$ pitch is 46V in the case of a master stamp of 200nm pitch. When voltage is smaller or larger than 46V, regularity of hole arrangements gets poorer and average hole pitch differs from 115 nm ($1/\sqrt{3}$ pitch). The present study suggests that any pitch of imprinting the master stamp can be reduced to $1/\sqrt{3}$ times by adequate choice of anodic voltage, and the limitation of Top-Down Technology can be overcome by self-organization.

Acknowledgement

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