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Effects of an external magnetic field on the perpendicular magnetic anisotropy of electrodeposited micro-patterned arrays

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We have investigated effects of an external magnetic field on perpendicular magnetic anisotropy (PMA) of electrodeposited continuous films and micro-patterned arrays. For continuous films, external magnetic field gave rise to a highly aligned grain structure with PMA. Our results indicate that the effect of applied magnetic field is apparent only at specific current density. XRD patterns showed that electrodeposited continuous Co films consist of hexagonal cobalt only and have strong texture for grains with the *c*-axis lying perpendicular to the film plane. The patterned arrays were fabricated by UV-LIGA process, and PMA was modified by changing the aspect ratio of patterned arrays. Our results suggest that there is a critical aspect ratio at which PMA dominates in-plane anisotropy. For the patterned arrays, however, the external magnetic field was not very effective due to a large concentration polarization.

Key words: *cobalt; magnetic field; perpendicular anisotropy; electrodeposition*

1. Introduction

Recently, demands for the electrodeposition of hard magnetic materials have increased significantly due to their potential applications in ultrahigh density magnetic recording and MEMS [1–5]. It has been reported that hard magnetic materials improved the density of recording medias in the field of magnetic recording media, reduced the driving voltage in the operation of actuators, and enhanced the sensibility of sensors [6, 7]. In most cases, however, hard magnetic materials electrodeposited as thin films are easily magnetized in the in-plane direction because of their large shape anisotropy. Therefore, it is important to control the crystallographic orientation and aspect ratio of the magnet arrays in order to produce hard magnet arrays with PMA.

In this study, we report the electrodeposited continuous films and micro-patterned arrays of cobalt, which show a magnetic anisotropy with an easy axis perpendicular to

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the film plane. We also discuss the correlation between structural, crystallographic, and magnetic properties.

2. Experimental

Specimens were prepared by constant current electrodepositing. The working electrode (5 mm×5 mm) was a 100 nm thick Au layer on (100) Si wafer. The current density was varied from 0.75 to 5 A/dm^2 and electrolytic cobalt chips (99.9% purity) in a Ti basket were used as anodes. The electrolyte was a mixed solution of 100 g/dm^3 $CoCl_2 \cdot 6H_2O$, 100 g/dm^3 $CoSO_4 \cdot 7H_2O$, and 100 g/dm^3 NH_4Cl. All solutions were prepared using ultra-pure water (over 18 MΩ at 30±1 °C). The agitation rate was 50 strokes per minute during electrodeposition using the paddle cell [10].

In a CV (cyclic voltammetry) test, the same working electrode was used with the constant current plating. The counter electrode and reference electrode were a graphite plate and a saturated Calomel electrode, respectively. The scan rate was 20 mV/sec. External magnetic field was applied using two magnets (Nd–Fe–B, 0.5 T) facing each other during electrodeposition of the magnet arrays to produce a highly aligned grain structure with perpendicular anisotropy in the magnetic properties. Magnetic properties of prepared specimens were measured with vibrating sample magnetometer, VSM-5, Toei, Japan. Crystal structure and texture were examined by X-ray diffraction (DY983, Philips, The Netherlands) with the operating condition of 30 kV and 20 mA using Mo target.

3. Results and discussion

In Figure 1, there are shown representative *M–H* loops of cobalt continuous films are shown electrodeposited without and with an external magnetic field (0.5 Tesla) measured in a magnetic field parallel (dashed line) and perpendicular (solid line) to the film plane, respectively.

The cobalt film electrodeposited without an external magnetic field shows a typical loop resulting from shape anisotropy with an easy axis parallel to the film plane and a hard axis perpendicular to the film plane (Fig. 1a). The intrinsic coercivity *Hc* was found to be ~ 60 Oe for in-plane direction and ~250 Oe for perpendicular direction, and this difference is thought to be attributable to a mixed anisotropy of shape and magnetocrystalline anisotropy. On the other hand, when a *M–H* loop was measured in the magnetic field perpendicular to the film plane (Fig. 1b), the electrodeposit with an external magnetic field was found to have a small minor-loop-like loop showing coercivity of ~500 Oe which is twice as high as that in Fig. 1a. For in-plane direction, the *M–H* loop in Fig. 1b was very similar to that in Fig. 1a. From these results it is inferred that the external magnetic field might induce the *c*-axis of growing

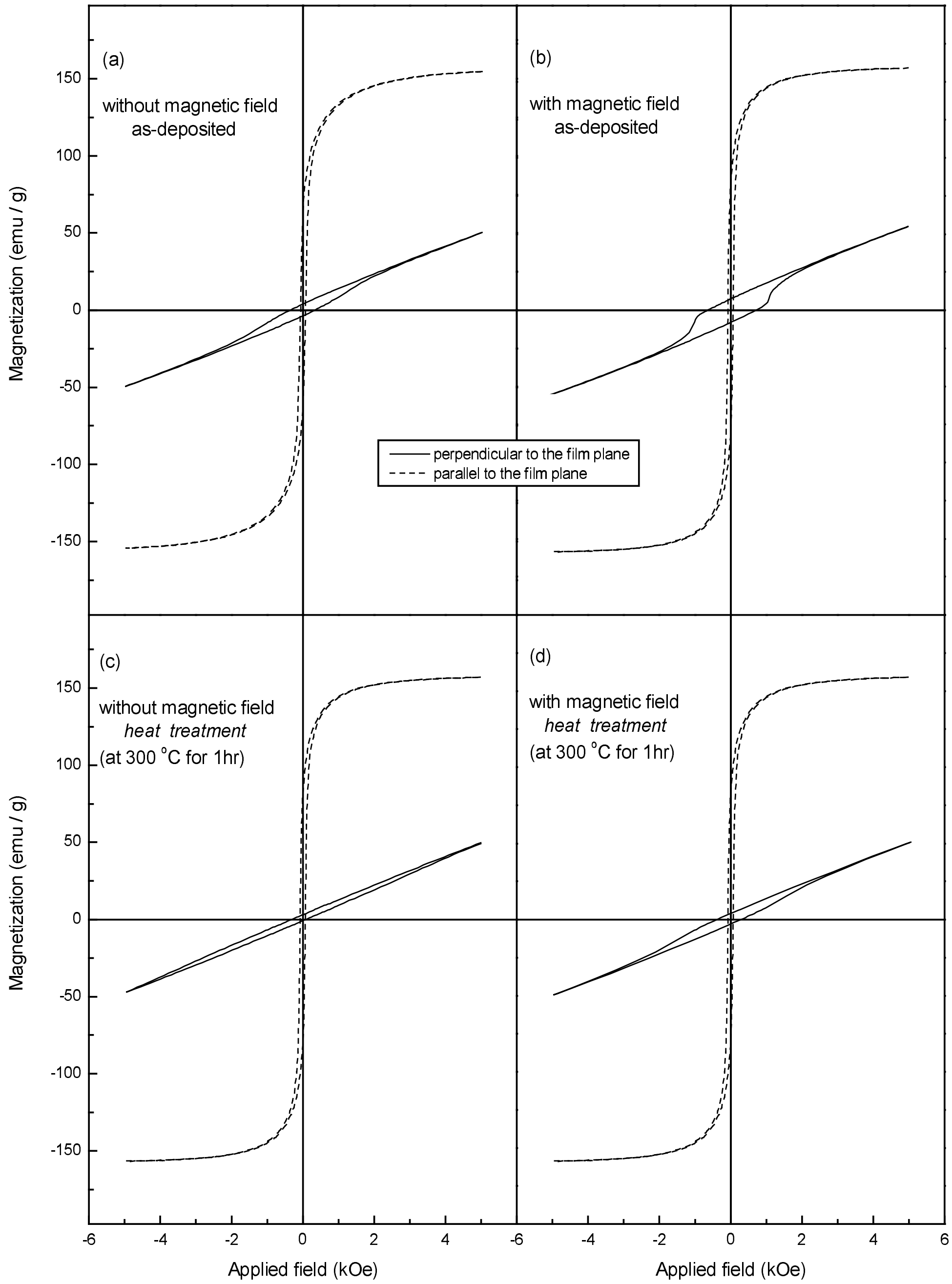

Fig. 1. *M–H* hysteresis loops of the electrodeposited Co films:
a) without magnetic field (as-deposited), b) with magnetic field (as-deposited),
c) without magnetic field (annealed at 300 °C for 1 hr),
d) with magnetic field (annealed at 300 °C for 1 hr)

cobalt crystallites in the direction perpendicular to the film plane, and make the grain size close to the single domain size. Figures 1c and d also show the variations of the *M–H* loops of the cobalt films electrodeposited without (Fig. 1c) and with (Fig. 1d) an external magnetic field after the samples were annealed at 300 °C for 1 hr. When the sample was electrodeposited without an external magnetic field, the *M–H* loop was independent of the heat treatment except that the perpendicular coercivity decreased to some extent. In Fig. 1d, however, the minor-loop-like loop disappeared after annealing, which indicated the shape anisotropy gradually becoming dominant in the mixed anisotropy, but the magnetocrystalline anisotropy was still effective (this may be deduced from the fact that the value of the coercivity remained ~500 Oe regardless of the heat treatment). These results demonstrate that the application of an external magnetic field during electrodeposition can affect both the crystallographic orientation and the grain size. Figure 2 presents X-ray diffraction patterns of the continuous films of cobalt electrodeposited without (Fig. 2a) and with (Fig. 2b) an external magnetic field, respectively.

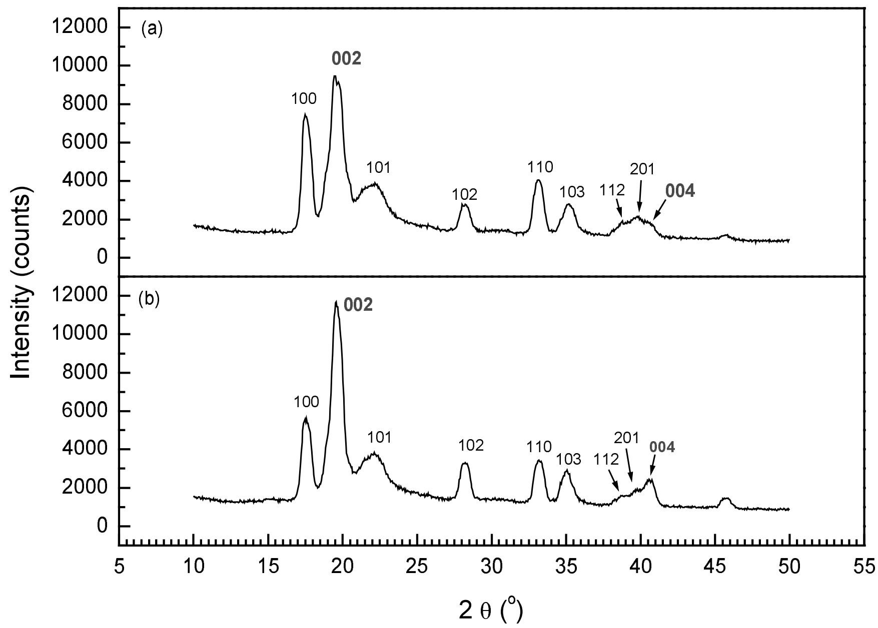

Fig. 2. X-ray diffraction patterns of the Co film electrodeposited without (a) and with (b) an external magnetic field. The electrodeposition was conducted at 1 A/dm^2

In Figure 2b, two peaks from *hcp* cobalt (002) and (004) planes are observed more apparently than in Fig. 2a. This means that the application of an external magnetic field during electrodeposition leads cobalt grains to grow preferentially and form (002) texture. Considering that cobalt grains with the (002) orientation have the *c*-axis perpendicular to the film plane, the difference between Figs. 1a and 1b can be easily understood.

Figure 3 is a comparison of the cyclic voltammograms measured without (dashed line) and with (solid line) an external magnetic field. The switching potential at which the scanning direction changes from cathodic to anodic one was fixed at –1.1 V in order to eliminate a possible interference from the hydrogen evolution reaction.

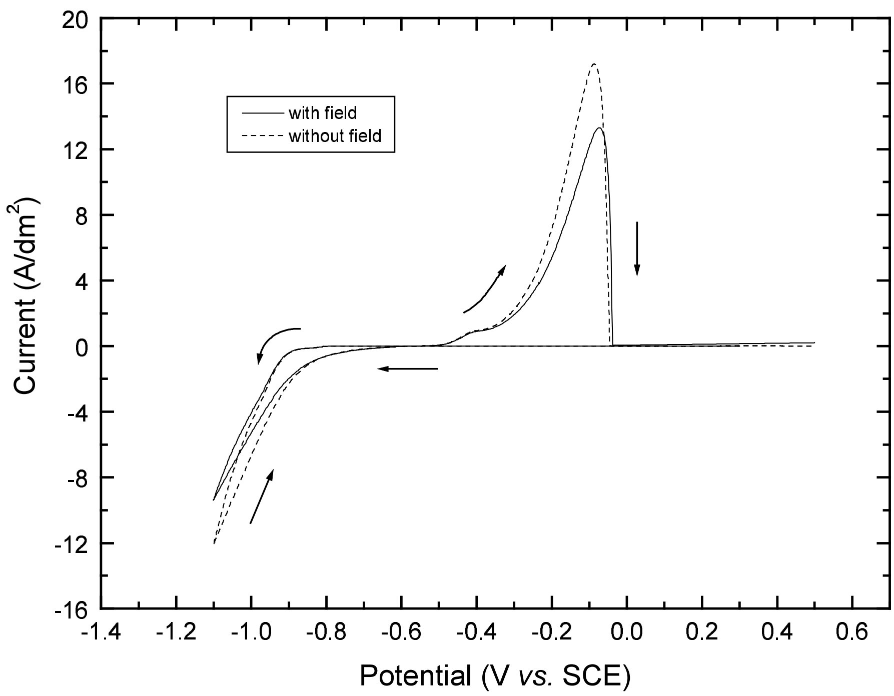

Fig. 3. Comparison of the cyclic voltammograms measured without (dashed line) and with (solid line) an external magnetic field

The shapes of the cyclic voltammograms in Fig. 3 are similar to each other, but the polarization during the cathodic scan reveals different polarization values. With an external magnetic field of 0.5 Tesla, the polarization is larger and it is well known that the polarization has a close correlation with the size of grain in the electrodeposited alloys, producing small grains when the alloy is electrodeposited at high polarization condition [5, 8, 9]. It can be expected that the application of an external magnetic field induces an increase in polarization and the grain size of Co films may become smaller. The reduction of grain size caused by an increase in polarization has been ascertained by transmission electron microscopy (TEM) in our previous work [5]. Interestingly, the effect of applied external magnetic field was apparent only at specific current density, 2.5 A/dm^2. For higher current densities, it seems that the electrocrystallization cannot proceed sufficiently due to large concentration polarization.

For the micro-patterned arrays of cobalt as in Fig. 4, typical *M–H* loops were measured in perpendicular (Fig. 5a) and in-plane (Fig. 5b) directions to the film plane depending on the variation of aspect ratios.

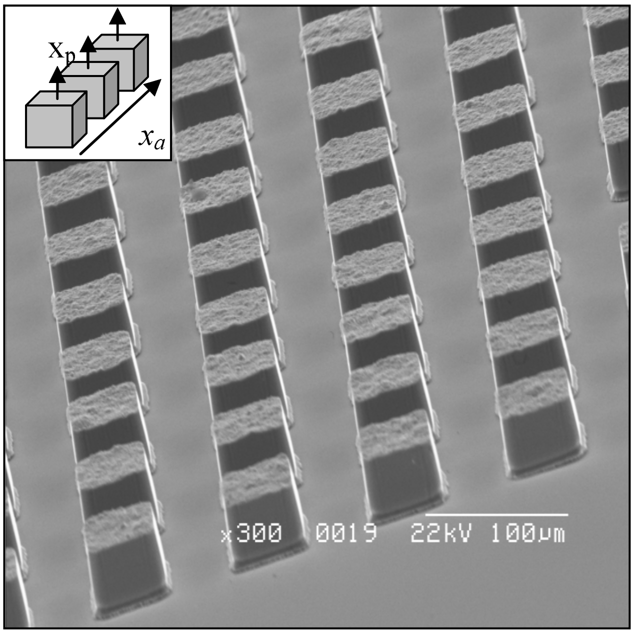

Fig. 4. Scanning electron micrographs of cobalt arrays (50 µm×50 µm×50 µm) stripped the photoresist

Although Co cubic (50 µm×50 µm×50 µm) array was expected to have the same *M–H* loop in x_p direction as in x_a direction in Fig. 4, it exhibits different magnetization values according to the direction of the field applied. For example, when the field applied was 2000 Oe, magnetization measured in the x_p direction was 58 emu/g, being 81 emu/g in x_a direction. From this result it can be inferred that Co array has shape anisotropy to be magnetized in the x_a direction.

In Figure 5, when two patterned arrays of the same dimension (50 µm×50 µm ×50 µm) are compared with each other, they exhibit almost the same *M–H* loops. This means that application of an external magnetic field is insufficiently effective to improve PMA for the electrodeposited patterned array. It has been reported that in a through-template electrodeposition like this work, mass-transfer effects are significant, and diffusion of ions through the template is a rate-determining step [6,11]. In these conditions, a large concentration polarization appears. The reason why the application of an external magnetic field was not effective for patterned arrays can be attributed to an insufficient electrocrystallizaton due to the large concentration polarization. It is not ascertained whether if cobalt patterned arrays have any magnetocrystalline anisotropy.

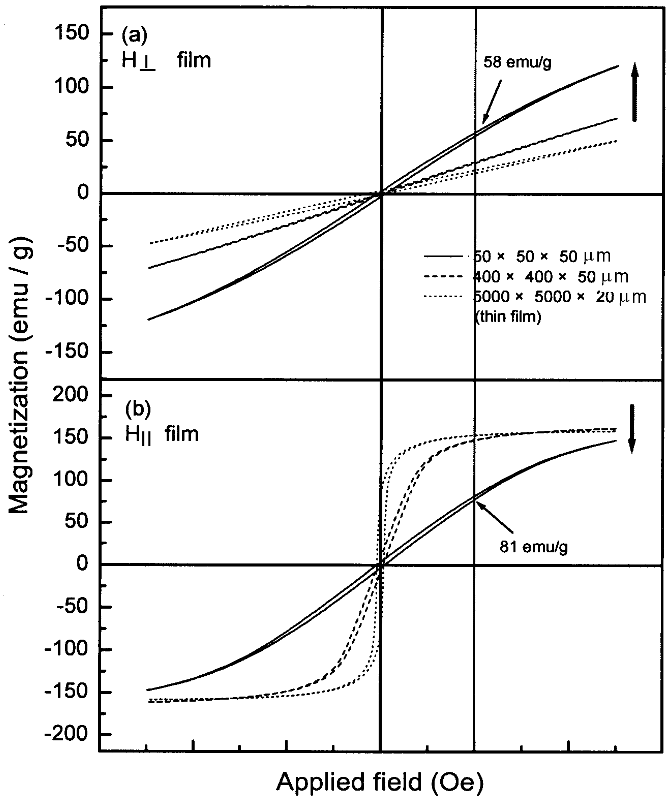

Fig. 5. *M–H* hysteresis loops of patterned Co arrays according to the aspect ratio. Loops were measured in perpendicular (a) and in-plane directions (b) to the film plane

4. Conclusion

We studied the effects of an external magnetic field on continuous films and micro-patterned array in order to improve the PMA of cobalt electrodeposits. Our experimental results give evidence that an external magnetic field leads to the (002) preferred crystallographic orientations of continuous cobalt film and the reduction of the grain size. We also found that the patterned cobalt array shows a predominant PMA in competition with in-plane shape anisotropy. Our results indicate that application of an external magnetic field is effective to improve PMA for electrodeposited continuous film, but little dominant for patterned array due to large concentration polarization during electrodeposition.

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