MAGNETIC PROPERTIES OF COBALT ELECTRO-DEPOSITED ALUMITE FILMS

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Abstract... The paper was investigated that the temperature and the pH of the Co solutions and the geometric structure of the films affects the orientation of the c-axis of the electro-deposited Co particle. That is, the coercive force H_c and the uniaxial magnetic anisotropy energy K_u variations are due to the change of the orientation of the c-axis and geometric structure of the Co particles in the Co electro-deposited anodic oxide films affected strongly the magnetocrystalline anisotropy of the films.

It is shown that the magnetic properties of the Co electro deposited anodic oxide films can be changed in a wide range than Fe electro-deposited films decided by the geometric structure almost, because we can select and control both the Co solutions conditions and the geometric structure.

1.Introduction

Kawai et al. studied about Fe,Co and Ni electro-deposited anodic oxide films and suggested a possible application of these films as magnetic recording media[1].

Recently, the study of Fe electro-deposited films as perpendicular magnetic recording media had been done with some detail[2][3][4][5]. As a result, it became clear that the magnetic properties of Fe electro-deposited films were determined mainly by the geometric structure of the electro-deposited Fe particles in the anodic oxide film and the influence of the crystalline magnetic anisotropy of Fe particles upon the properties is small.

However in films with electro-deposited Co particles having large the crystalline magnetic anisotropy ($K_u: 4.5 \times 10^6$ erg/cc), only the geometric structure of the particles seems to be insufficient to predict completely their magnetic properties.

In this paper, Co electro-deposited films are investigated in order to make the magnetic properties of the films clear. We also investigated the dependence of the magnetic properties of Co deposited films on the electro-deposition conditions.

2.Experimental

We used rolled aluminum plates (purity 99.99%, thickness 95 μm) as the preparing substrate of the anodic oxide films. The aluminum plates were degreased and neutralized for one minute in water solutions of NaOH (1.2 mol/l) and then of HNO_3 (0.8 mol/l). The substrates were anodized in a solution (30 °C) of H_2SO_4 (1.6 mol/l), oxalic acid (0.34 mol/l) and H_3PO_4 (0.52 mol/l).

Next, the pore diameter of the anodic oxide films were widened in a solution (20 °C) of H_3PO_4 (0.1 mol/l, 30 °C), and the barrier layer of the films were thinned in a mixed solution (20 °C) of H_3BO_3 (0.5 mol/l) and sodium tetraborate (0.050 mol/l).

The electro-deposition of Co in pores was carried out in a mixed solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and H_3BO_3 (pH 4.5, 20 °C) and the current density is 0.6 A/dm². In order to make the length of the electro-deposited Co particles equal, the buff polishing with alumina powder of the size 0.3 μm was performed.

The magnetization of the samples was measured by a VSM and the magnetic anisotropy was measured by a magnetic torque meter. In these experiments, disks of diameter 6mm ϕ punched from the original samples were employed. The measurement of

the crystalline orientation was done by an X-ray diffraction method with a Co target, the Co electro-deposited magnetic particles were extracted chemically from the films and their shape observed by a TEM.

3. Results and discussion

3-1 Dependence of pore diameter.

Figure 1 shows the dependence of the coercive force H_c perpendicular ($\perp$) and parallel ($\parallel$) to the film plane on the pore diameter (particle diameter). Where, packing density P (porosity) is 0.2 and the deposited particle length is from 1.0 to 1.5 μm . The $H_c(\perp)$ is 1800 Oe when the pore diameter is 200 $\text{\AA}$, and as the pore diameter increases the coercive force decreases. In

Figure 1. The dependence of the coercive force H_c on the pore diameter.

this case, the declination is slower than that of Fe deposited films as shown in Figure 2.

When the pore diameter is larger than 1000 $\text{\AA}$, the coercive force $H_c(\perp)$ reaches almost a constant value of 500 Oe. This value is larger than that of Fe deposited films. The coercive force $H_c(\parallel)$ decreases slowly from 1000 Oe to 600 Oe, as the pore diameter increases.

In an earlier paper, it was reported for Fe electro-deposited films that the

magnetization reversal is determined to follow the curling mode from the results such as the dependence of the $H_c(\perp)$ on the pore diameter. However in the case of Co electro-deposited films, the large magnetocrystalline anisotropy of Co particle plays an important role of the magnetization reversal mechanism, and the difference of the pore diameter dependence of the $H_c(\perp)$ between the Co and Fe deposited films seems to be caused by this effect. That is to say, the easy axis of the magnetization of Co particles declines toward the film plane and as a result, the $H_c(\perp)$ becomes lower than calculated value from the curling mode.

Figure 2. The dependence of the coercive force perpendicular $H_c(\perp)$ on the pore diameter for the Co and Fe deposited films.

Figure 3 shows the relationship between the uniaxial magnetic anisotropy energy K_u and the pore diameter. When the pore diameter is larger than 200 $\text{\AA}$, the K_u drops rapidly and slowly increases after having a minimum around 400 $\text{\AA}$. This result means that the crystalline anisotropy besides the shape anisotropy of deposited Co particle have a great contribution to the effective anisotropy.

Figure 4 shows the crystalline orientation of these samples.

A vertical axis gives an X-ray diffraction

Figure 3. The uniaxial magnetic anisotropy energy K_u dependence of the pore diameter.

Figure 4. The X-ray diffraction intensity ratios dependence of the pore diameter.

intensity ratio of the (002)plane / (100)plane and (101)plane/(100)plane. The smaller these values is comparing with these of random orientation, the closer the direction of crystalline c-axis of the Co particles becomes to the film plane. In the sample of the pore diameter 200 Å, it shows the maximum value of the intensity ratio of (002)plane / (100)plane, and it drops rapidly as the pore diameter is larger than that value. In the pore diameter 350 Å both ratios have minima together.

From this result, we can find the c-axis declines toward the film plane, and in the film with the pore diameter of 350 Å, this declination is the largest. This

result also indicates the great contribution of crystalline anisotropy as shown in figure 3.

3-2 Dependence of packing density

All the samples referred in this section have pore diameter 450 Å and particle length equal about 1.5 μm . The pH of the Co solutions is 4.5.

Figure 5. The dependence of the coercive force perpendicular $H_c(\perp)$ on the packing density.

The dependence of the coercive force $H_c(\perp)$ on the packing density P is represented in Figure 5. The two curves correspond to Co solutions with pH 4.5 and 5.5. For Fe electro-deposited films, $H_c(\perp)$ is independent of the P and has a constant value. However, Co electro-deposited films have a different behavior. The $H_c(\perp)$ of Co electro-deposited film is different with the pH of the Co solutions, and decreases rapidly when the P increases until 0.26. For the P higher than 0.26 the dependences of the $H_c(\perp)$ on the P as well as the pH becomes small.

It was investigated the crystalline orientation for the Co particles as a function of the pH of the Co solution. Figure 6 represents the dependence of the X-ray diffraction intensity ratios of $I_{(002)}/I_{(100)}$ and $I_{(101)}/I_{100}$ on the packing density. As we can understand from

the figure, the diffraction intensity of the (100) plane increases with increasing of the packing density P up to 0.26, that is the c -axis declines more towards the film plane. However it almost does not change at the P more than 0.26. The change of the diffraction intensity on the packing density P agrees qualitatively to the dependence of coercive force $H_c(\perp)$ on the P as shown in Figure 6. The coercive force $H_c(\perp)$ decreases when the c -axis declines more towards the film plane.

Figure 6. The X-ray diffraction intensity ratios relation of the packing density.

From this fact we can say that the relation between the packing density P and the coercive force $H_c(\perp)$ is due to the difference of the orientation of the c -axis of Co particles mainly.

Figure 7 shows the dependence of the uniaxial magnetic anisotropy energy on the packing density P . The broken line shows the calculated value of the magnetic anisotropy obtained by considering the magnetostatic energy[6].

The experimental value has a maximum 4×10^5 (erg/cc) with the packing density P of 0.16, is zero about $P = 0.26$, and becomes negative for the P larger than 0.26, that is, the easy direction of magnetization changes from perpendicular to parallel of the film plane. In this figure all the experimental values are smaller than

Figure 7. The uniaxial magnetic anisotropy energy K_u dependence of the packing density.

calculated values. This disagreement is caused by the declination of the crystalline c -axis toward the film plane as shown in Figure 6.

3-3 The variation of Co electro-deposited conditions.

In this experiment, we investigated whether the coercive force H_c is vary or not by changing the pH and temperature of the Co solutions during the preparation of the anodic oxide magnetic films.

Figure 8 shows the dependence of the coercive force $H_c(\perp)$ and $H_c(\parallel)$ on the temperature of Co solution. In this experiment, the pore diameter and packing density are kept 200 Å and 0.2 respectively. The lengths of Co electro-deposited particles are 1.0-1.2 μm. At 20 °C, the coercive force H_c decreases slightly with decreasing the pH, and at the pH lower than 3.6, the H_c suddenly drops down. That is to say, the coercive force $H_c(\perp)$ and $H_c(\parallel)$ fall to values smaller than 1200 Oe and 700 Oe at the pH of 3.2. When the pH get lower, the $H_c(\parallel)$ decreases a little more, but the $H_c(\perp)$ turns to increase. The

Figure 8. The coercive force H_c dependence of the pH of the Co solutions.

same behavior is observed at every temperature, and the lower the temperature is, the higher the pH at which the H_c drops rapidly is. Furthermore it becomes wider of the range of pH having the minimum of the $H_c(\perp)$ with decreasing the temperature.

Figure 9. The relation of the X-ray diffraction intensity ratios on the pH of the Co solutions.

Figure 9 shows the dependence of the X-ray diffraction intensity on the pH at the solution temperature of 20 °C.

With decreasing the pH, the X-ray diffraction intensity drops down at the pH of 3.6. At the pH of 3.1, the X-ray intensity of (002) plane or (101) plane can hardly be observed. In this condition it seems that the c-axis of Co particles is almost completely in film plane. At the pH lower than 3.1, the X-ray diffraction intensity ratio of $I_{(002)}/I_{(100)}$ increases a bit. This tendency is correspondent with a change of the coercive force $H_c(\perp)$ qualitatively. From this result, we can find that the coercive force H_c can be varied by selecting the condition of the pH and the temperature of the Co solutions. For example for a Co electro-deposited film with the pore diameter of 200 Å, the coercive force $H_c(\perp)$ changes from 2000 to 1200 Oe.

Next, we had investigated the dependence of the coercive force H_c on the packing density P . The result is showed in Figure 10. In this experiment, the temperature of the Co solution was 10 °C and pH was 3.5~4.0. From this figure we can find that both $H_c(\perp)$ and $H_c(//)$ do not depend on the packing density.

Figure 10. The dependence of the coercive force on the packing density.

At the pore diameter 450 Å, the dependence of the coercive force H_c on the pH and the temperature of Co solution is shown in the figure 11. In this case the dependence of the pH and the temperature on the coercive force $H_c(\perp)$ and $H_c(\parallel)$ are almost the same as pore diameter 200 Å.

Figure 11. The dependence of the coercive force on the packing density.

4. Conclusions

The dependence of the magnetic properties such as coercive force H_c and magnetic anisotropy energy K_u on the pore diameter D_p and packing density P for the Co electro-deposited anodic oxide magnetic films were investigated.

The results obtained are as follows.

(1) Coercive force H_c and magnetic anisotropy energy K_u are influenced considerably by the effect of crystalline anisotropy as well as the shape anisotropy of Co electro-deposited particles. As the c-axis of Co particles declines strong toward the film plane, the coercive force

$H_c(\perp)$ and magnetic anisotropy perpendicular to the film plane decrease.

(2) The orientation of the c-axis of the electro-deposited Co particles can be controlled by changing the pH and the temperature of the Co solution, and as a result, the magnetic properties such as the coercive force and the perpendicular magnetic anisotropy can be controlled.

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