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Magnetic properties of nanometer-size CoPt particles

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We have prepared nanometer-size, isolated CoPt particles. The particles in the range of 100–300 nm in diameter were formed by annealing thin films in the temperature range of 550–800 °C. Films with magnetic coercivity as high as 30 kOe were achieved. The results indicate that the high magnetic coercivity was obtained because the crystallite size approaches that of noninteracting single-domain particles. [S0021-8979(96)04508-3]

I. INTRODUCTION

One of the requirements for practical applications of magnetic devices, such as high-density magnetic recording media, magnetic bias films of magneto resistive elements, and magnetic tips for magnetic force microscopy, is high magnetic coercivity (H_c).[1,2] It is known that an assembly of very fine noninteracting high anisotropy magnetic particles is magnetically hard; i.e., it has a large coercivity. This effect is due to the fact that the particles are single domains and that magnetization reversal takes place only by rotation of M_s vectors against strong anisotropy forces. For randomly distributed single-domain particles, the H_c will be as high as $0.98K/M_s$, where K is the anisotropy constant and M_s is the saturation magnetization.[3]

The CoPt binary alloy is an excellent system because it has both chemical stability and high magnetic anisotropy. CoPt alloy thin films have received significant attention as possible magneto-optic recording media owing mainly to the existence of ordered intermetallic phases with exceptional magnetic properties.[4,5] CoPt compounds are known for their hard magnetic properties. In the bulk form, it shows a high magnetocrystalline anisotropy (4×10^7 ergs/cm^3) and a relatively large saturation magnetization $M_s=800$ emu/cm^3.[6,7] From the calculation using the above equation, one would expect an H_c of 48 kOe in the CoPt alloy. However, early studies showed H_c values of less than 6 kOe in a CoPt binary alloy.[6–8] Recently, Qiu *et al.* have shown that a maximum intrinsic coercivity of about 4.3 kOe was obtained in a mixture of ordered and disordered phases after annealing the rapidly solidified CoPt alloy at 700 °C for 30 min.[9] In thin films, as reported by Tsoukatos *et al.* the maximum H_c observed in CoPt films is of the order of 6.8 kOe.[10] It is known that the hard magnetic behavior of the CoPt alloy is related to the crystal phase transition. The as-cast alloy has a disordered fcc structure which transforms into an ordered fct structure with $c/a=0.98$ after annealing at a temperature below 835 °C. The magnetic hardness of permanent magnets are also influenced by the size of the particles and the interaction between the particles. In order to have a better understanding of magnetic properties of small particles in the CoPt alloy system, we need to prepare films which consist of desired nanostructures.

In this paper, we report a method to prepare films containing nanometer-size particles and show the development of coercivity as high as 30 kOe in CoPt alloy films.

II. EXPERIMENT

The CoPt alloy films were prepared on fused quartz substrates with dc magnetron sputtering. The film thickness was in the range of 10–300 nm. The substrate was fused quartz. The target was made by sintering high-purity Co (99.9%) and Pt (99.99%) powder with 1:1 atomic ratio at 1050 °C for 24 h. The base pressure before introducing the Ar gas was 3×10^{-8} Torr. In order to improve the ordering and to control the crystallite size, the CoPt films were annealed under one atmosphere of Ar/H_2 in the temperature range of 550–800 °C, and the range of annealing time was from 30 min to 40 h. The magnetic properties of the films were measured by SQUID magnetometry. The crystal structure and particle sizes were examined by high-resolution transmission electron microscopy (HRTEM), selected-area diffraction (SAD), nanodiffraction, and atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

Particle growth on a substrate is dependent on the strength of interaction between the atoms of the growing film and the atoms of the substrate. As shown by Pashley, particles as small as 10 nm can be formed in the early nucleation stage.[11] If we choose suitable substrates and growth conditions, CoPt films with well separated particles can be produced. One would expect that particles in the range of 10–500 nm can be prepared by controlling the thickness of films and substrate temperatures.

In this study, we prepared CoPt films with the thickness of 10, 20, and 320 nm on quartz substrates and then annealed them in the temperature range of 550–800 °C. Most metals do not wet insulating surfaces such as quartz, so that the particles are expected to form after the thermal treatment.

As shown in Fig. 1, the H_c of CoPt films is in the range of 2–22 kOe, depending on the film thickness and annealing

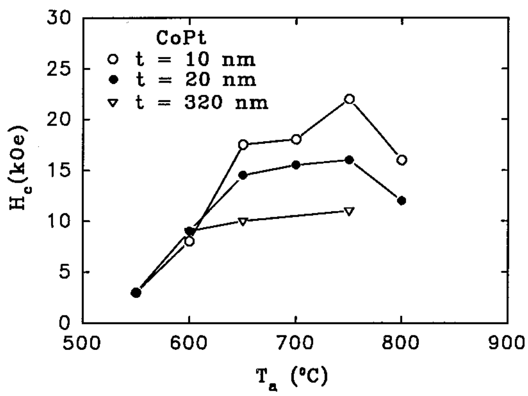

FIG. 1. The evolution of H_c vs the annealing temperature for films with thickness of 10, 20, and 320 nm.

FIG. 2. (a) HRTEM image of as-deposited film. (b) Dark-field image for film annealed at 750 °C for 30 min.

temperature. These films were annealed in the temperature range of 550–800 °C for 30 min in Ar/H_2 atmosphere. The H_c was measured at 300 K with the film surface perpendicular to the magnetic field. The as deposited films regardless of their thickness has a H_c less than 100 Oe. The H_c increases with the increasing annealing temperature. The highest H_c of 22 kOe was observed for 10-nm-thick films annealed at 750 °C. For films annealed at 800 °C, the value of H_c decreased. The H_c of the film with a thickness of 320 nm after annealing at 800 °C also decreased. This datum is not shown in Fig. 1, because it was not prepared in the same sputtering run.

In the CoPt binary system, a disordered fcc and a tetragonal CuAu type structure can coexist in the concentration near 50 at. % Co. This system exhibits excellent hard magnetic properties that depend strongly on the concentration and the degree of crystalline order of the alloy.

As shown in Fig. 2, HRTEM images show that all the as-deposited CoPt films are continuous and composed of 5–10 nm crystallites. The corresponding SAD ring pattern can be indexed using a disordered fcc structure model. After annealing at 750 °C, the crystal structure of the films transforms to the fct structure as identified by the nanodiffraction. The 320-nm-thick film remains continuous after annealing and has crystallite sizes of 50–100 nm. For films of nominal thickness on the order of 10 nm, the alloy forms 50–300 nm particles which grow discontinuously on the substrate. Dark-field images show that there are several crystallites in the large particles. The particles are clearly observed by using atomic force microscopy. As shown in Fig. 3, the CoPt film with a thickness of 10 nm after annealing at 750 °C for 30 min formed many particles with a size range of 50–300 nm. The particle height is in the range of 30–70 nm. This indicated that the film area near the particle was cleaned during the formation of particles.

The observed microstructure is consistent with the early studies that the formation of the tetragonal crystallite and the growth of the crystallite after annealing at high temperature is partly responsible for the increase of H_c.[8–10] It is known that the film annealed at high temperature increases the size of the crystallite which is clearly observed in HRTEM image.

For films annealed at 800 °C, the reduction of H_c may be due to the further crystallite growth which results in the formation of multidomain. In comparison with earlier studies, one of the major differences is possibly that the particle size and the interaction between the particles in these samples prepared by different groups are not the same. In our films, the separated nanometer size particles form a nearly non-interacting system which leads to very high H_c values. This conclusion is also supported by our thickness dependence of the H_c in the films which were prepared from the same sputtering run and annealed together at the same temperature and time duration. Under this preparation condition, the ordering and the size of the crystallite in these films should be the same. One of the major differences between the thin and the thick films is the separation of the particles, i.e., the interactions between the particles is not the same as in these films when they have different thickness. As shown in Fig. 1, the value of H_c of the 10-nm-thick film is about two times higher than that of the 320-nm-thick films.

In order to further understand the effect of the ordering on the H_c, we have examined a series of samples with 10 nm thickness which were annealed at 750 °C for 30 min to 40 h.

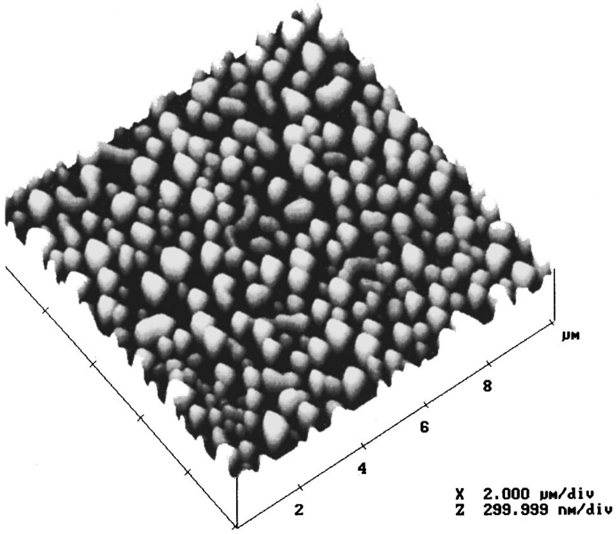

FIG. 3. The atomic force microscopy picture of a nominal 10-nm-thick CoPt film annealed at 750 °C for 30 min.

The result is shown in Fig. 4. The magnetic coercivity of CoPt films dramatically increases upon annealing at 750 °C for 3 h, and then decreases to roughly 24–25 kOe after 20 h annealing. The hysteresis loop of the film with the highest H_c measured at 300 K is shown in Fig. 5. The measured intrinsic coercivity in this film is 30 kOe. Here we should note that the measured value may not be the actual H_c due to the low applied magnetic field (5.5 T). The ordering of the crystallites should improve after a long annealing time, so the H_c of the film should also improve if the ordering is the most important factor. The reduction and the leveling off of the H_c in the films after long annealing indicates that the crystallite growth is more important than the further ordering in these films. The increase of H_c at the beginning of the annealing stage is likely due to the growth of the crystallites which reach the size of a magnetic single domain. After further annealing, the drop in H_c of the films may be due to the increase in the crystallite size which results in multidomain formation.

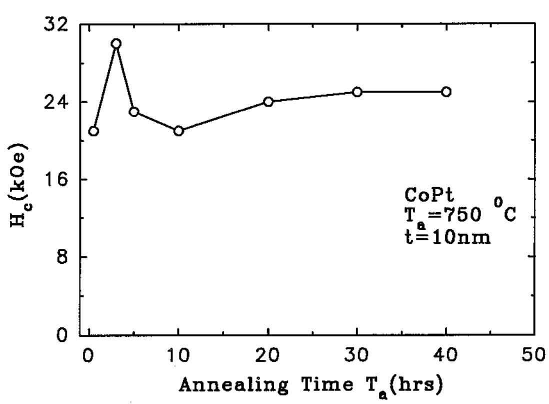

FIG. 4. The H_c of CoPt films with a nominal 10 nm thickness annealed at the temperature of 750 °C for 30 min to 40 h.

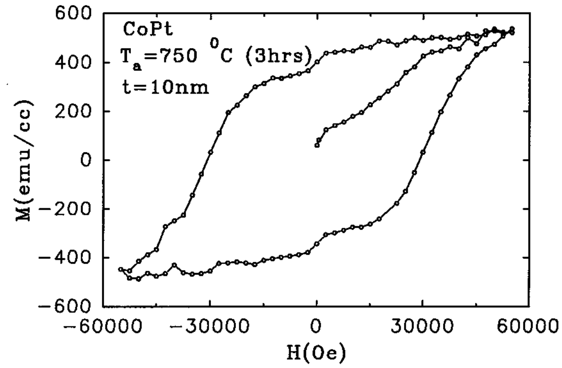

FIG. 5. The hysteresis loops of a CoPt film with a nominal 10 nm thickness that was annealed at 750 °C for 3 h.

IV. SUMMARY

As revealed by high-resolution transmission electron microscopy and atomic force microscopy, we have prepared well separated and nanometer-size CoPt particles (in the range of 100–300 nm). The smaller particles form a nearly noninteracting system and have dimensions close to the single-domain particle size which leads to a very high coercivity value of about 30 kOe. This value is about five times higher than the early studies which show coercivity values of less than 6 kOe and is close to the theoretical estimate of 48 kOe for the CoPt alloy.

ACKNOWLEDGMENT

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