Elongated prolate ellipsoid CoPt nanocrystals embedded in graphite-like C magnetic thin films

J.-J. Delaunay*, M. Tomita, T. Hayashi

NTT Environmental Technology Laboratory, 3-1 Morinosato-Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan

Abstract

In nanogranular CoPtC thin films, the CoPt nanocrystals embedded in graphite-like C were found to have an elongated prolate ellipsoid-like shape. The long axes of the ellipsoids were perpendicular to the film plane, that is, in the film-growth direction. The shape magnetic anisotropy resulting from the shape of the CoPt ellipsoids gave rise to a magnetization component out of the film plane. The easy axis of the magnetization remained as that of the film plane. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Magnetic granular films offer attractive features as high-density recording media [1]. CoC and CoPtC granular thin films have been studied for their potential use as a high-density magnetic storage medium [2–5]. The films were found to be composed of Co or CoPt nanocrystals embedded in a graphite-like C matrix. Particular attention was given to the crystalline phase of the Co nanocrystals because the crystalline structure is responsible for the magnetocrystalline energy, which is one of the physical properties that control the coercivity of the films. Adding Pt to CoC was found to suppress the formation of the Co cubic phase and increase the coercivity in the film plane, which is the plane of easy magnetization. Coercivities as large as

2000 Oe have been obtained with CoPtC films, and longitudinal media based on CoPtC thin films have been fabricated and analyzed.

Because these microstructure analyses were mainly done using transmission electron microscopy (TEM) to observe the plane view of the films, the shape of the Co nanocrystals in the direction perpendicular to the film plane could not be observed. Knowing the actual shape of the nanocrystals, i.e., spherical or ellipsoidal, is important for understanding the film-growth mechanism and magnetic properties. Magnetic shape anisotropy affects the magnetization curve and thus the magnetic recording on a media.

2. Experimental procedure

CoPtC thin films were deposited in vacuum by using co-deposition ion-beam sputtering. Details of the apparatus are given in Refs. [2,3]. The base

* Corresponding author. Tel.: + 81-46-240-3110; fax : + 81-46-270-2320.

E-mail address: jean@aecl.ntt.co.jp (J.-J. Delaunay).
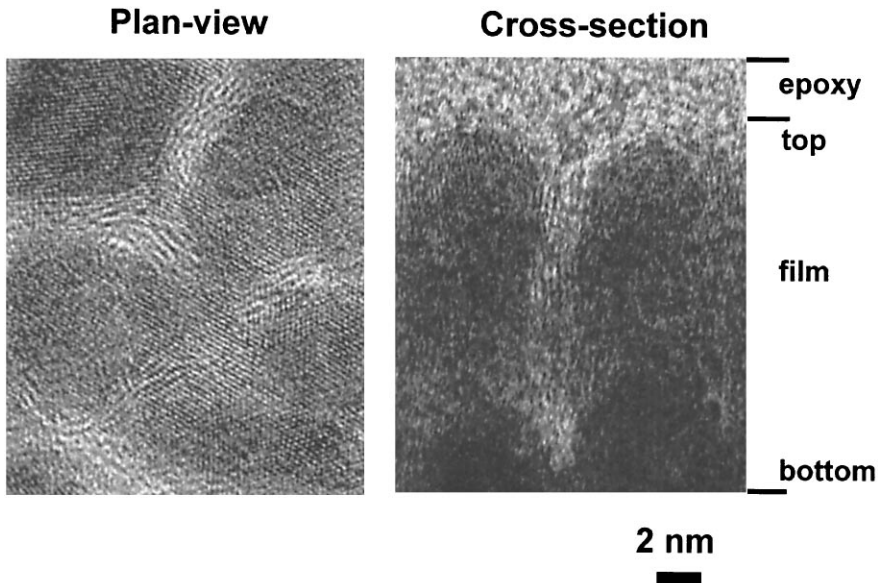
Plan-view   **Cross-section**

Fig. 1. TEM planview and cross-section images of the same CoPtC film. CoPt crystallites with an ellipsoidal shape and their long axes perpendicular to the film plane are observed in the cross-section view.

pressure of the deposition chamber was in the range of 10^{-8} Torr, and the argon pressure during deposition was 0.2 mTorr. The films were deposited onto silicon substrates at a substrate temperature of 250°C. A C underlayer was deposited onto the silicon substrates before the deposition of the CoPtC thin film. This C underlayer was 10 nm thick and amorphous. A Si/C/CoPtC series, in which the thickness of CoPtC film varies, was fabricated under the same experimental conditions and with the same chemical composition of $Co_xPt_yC_z$. All the films were annealed in a vacuum (pressure less than 10^{-6} Torr) at a temperature of 350°C.

The chemical composition of the films was determined using X-ray fluorescence analysis for the amount of Pt in the $(CoPt)_{100}$ and Auger electron spectroscopy for the estimated C content. Due to an unfortunate measurement error, our previous reports [4,5] on the determination of the Pt/(Co + Pt) ratio was incorrect: the previous Pt (at%) in $(CoPt)_{100}$ should be decreased by a factor of 0.5. All the films studied here had a chemical composition of $Co_{51}Pt_9C_{40}$. The variations in the chemical compositions were kept within 2 at%.

Cross-sectional TEM was performed on the Si/C/CoPtC films by using a Hitachi H9000 micro-

scope operating at an acceleration voltage of 300 kV. The cross sections of the samples were prepared using conventional ion milling; liquid nitrogen was used to cool the samples during the milling process. The film thicknesses were estimated using a thickness profilometer (Dektak); the results were corroborated by the thicknesses estimated from the TEM cross-sectional images.

Magnetic hysteresis loops were measured with a vibrating sample magnetometer at room temperature. The loops were measured with the applied field in the plane of the films and perpendicular to it. The magnetic properties in the plane of the films, the saturation magnetization $M_{s=}$, the coercivity $H_{c=}$, and the squareness $S_=$ were derived from the in-plane hysteresis loops, while $M_{s\perp}$, $H_{c\perp}$, and $S_\perp$ were derived from the loops perpendicular to the film plane.

3. Results and discussion

First, we analyzed the microstructure of a film, 25 nm thick, by using the TEM planview and TEM cross-section images. Fig. 1 shows an example of high-resolution TEM planview and
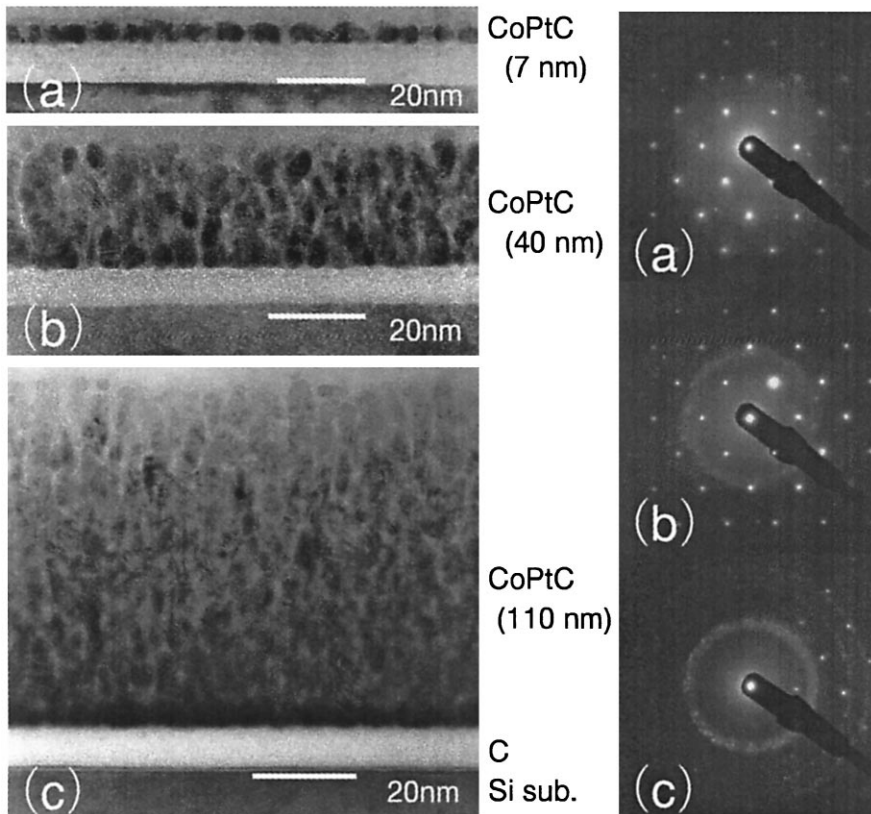
Fig. 2. TEM cross-sections for film thicknesses of (a) 7-, (b) 40- and (c) 110-nm, together with their SAD patterns. The spotty diffraction pattern of the Si substrate is superimposed onto the SAD patterns.

TEM cross-section images of the same film. The film had a nanogranular microstructure, as described in previous publications [2–4]. CoPt crystallites, about 10 nm in size as seen from the plan-view, were embedded in graphite-like C. The crystal structure of the CoPt grains was hexagonal close-packed structure with stacking faults. The c-axis of this hexagonal structure was randomly oriented (three dimensions) within the film, as was inferred from X-ray diffraction and electron diffraction patterns, which were measured in two different geometries. The cross-section view reveals new information about the shape of the CoPt crystallites perpendicular to the plane of the film growth. The CoPt crystallites were not spherical but ellipsoidal, with their long semiaxes oriented perpendicular to the film plane. The planview shows that (00.2) graphite C plane, which had a d-spacing of about

3.5 Å was oriented most frequently parallel to the surface of the CoPt crystallites. The same orientation is seen in the cross-section image. Therefore, it can be concluded that the films consisted mainly of ellipsoidal CoPt crystallites wrapped in (00.2) graphite C planes. It can also be seen from the cross-section image that the microstructure of the film bottom (i.e., close to the substrate) was less granular. This would imply that the microstructure depends on the film thickness in that the granularity of the film is improving.

We analyzed a series of films with thicknesses of 7, 18, 40, and 110 nm. The TEM cross-section views of the films with a thickness of 7, 40, and 110 nm are shown in Fig. 2, together with their selected area diffraction (SAD) patterns. The SAD patterns for the 40- and 110-nm-thick films (the SAD pattern for the 7-nm-thick film is too faint to clearly see its

features) gave the same results as the SAD pattern taken in the plane view, except for a lower accuracy due to the small amount of materials analyzed. Rings corresponding to the d-spacings of (10.0) CoPt at 2.23 Å, (00.2) CoPt at 2.11 Å, and (10.1) CoPt at 2.22 Å are seen. The elongated shapes of the CoPt crystallites at thicknesses larger than 15 nm are also seen in the cross-section images. Furthermore, the orientation of the long axes of the CoPt crystallites along the perpendicular direction of the film plane (film-growth direction) is clearly observed. In some places, the elongated particles appear to form chains in the perpendicular direction of the film plane. The shape and size of the CoPt crystallites did not change significantly with the film thickness (at thicknesses less than 110 nm). It is worth noting that no significant grain growth with increasing thickness is apparent. However, the bottom layer of the film grown on the amorphous C layer had a darker contrast, and the CoPt crystallites were not well distinguished, as also seen in Fig. 1. This bottom layer was about 10 nm thick.

We investigated the differences in chemical composition with the film thickness for Co, Pt, and C by using energy-dispersive X-ray spectroscopy. No significant change in the chemical composition with the film thickness was found for Co and Pt. The analysis for C failed due to the presence of the C underlayer immediately under the analyzed CoPtC thin film; the spatial resolution of our EDX analysis, about 10 nm, was not sufficient to correctly determine the C concentration in CoPtC film immediately above a C layer. The darker contrast observed at the smaller film thickness may be due to a difference in thickness in the observed direction: a sample would appear to be thicker when it is observed close to the substrate than when it is observed far from the substrate. A difference in thickness could originate from difference in etching rates between the C underlayer and the CoPtC film (C has a very low etching rate) during the sample preparation for which ion milling is used to thin the sample. However, cross sections of an Ni/C multilayer, which were prepared under the same conditions, did not show a contrast difference in the Ni layer. Most likely, the contrast differences in the cross-section images between the bottom layer and the thicker layer can be attributed to a difference in
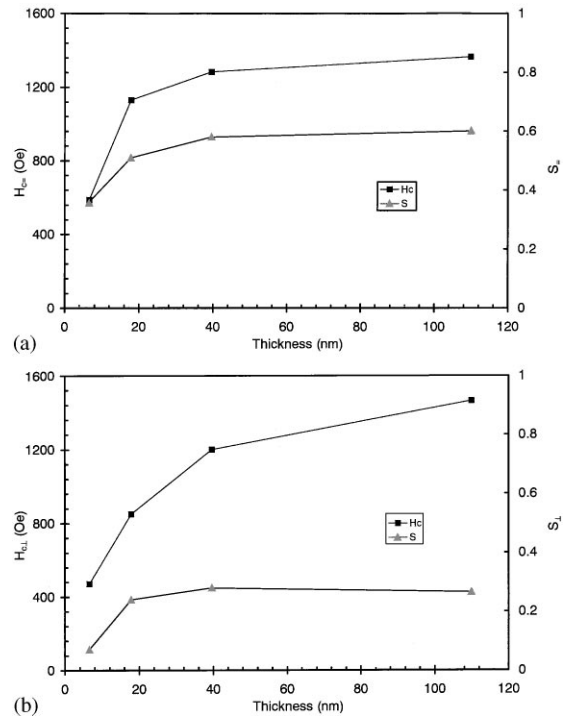

Fig. 3. Changes in film coercivity and squareness at room temperature as a function of film thickness: (a) in the film plane and (b) perpendicular to the film plane.

the microstructure of the bottom layer (crystallite grains were not well separated from each other by C at the initial layer).

Results presented for Cu–C system obtained using the grazing-incidence small-angle scattering method also showed the formation of elongated Cu particles with their long axes oriented perpendicular to the film plane [6]. Thus the formation of elongated particles may be a general characteristic of thin films of metal-C systems, in which the two materials are nonmiscible.

The measured magnetic properties for the same film thickness series (7, 18, 40 and 110 nm) are shown in Fig. 3. The saturation magnetization of the film was 700 emu/cm³, as determined for thick samples. As shown in Fig. 3(a), the in-plane coercivity increased with the film thickness, then saturated at a thickness of about 40 nm. The squareness followed a very similar pattern, saturating at $S_=$ of about 0.6. In a plane perpendicular to the film plane, the coercivity increased with the film

thickness all the way to 110 nm (the thicker thickness considered here). The squareness saturated at a thickness of 20 nm at a value of 0.3. These results show that the plane of easy magnetization lies in the film plane. However, there is a magnetization component out of the film plane.

The effect of the ellipsoidal shape of the CoPt crystallites in CoPtC thin films could be quantified by simulating the magnetization curve of a particle assembly composed of ellipsoidal particles with a long semiaxis (10 nm) and a short semiaxis (5 nm) separated by a C layer (2 nm). The long semiaxis should be oriented perpendicular to the film plane, and the particles should be made of hexagonal CoPt crystals having a uniaxial magnetocrystalline anisotropy (Ku) and oriented randomly. These CoPt particles would magnetically interact through the C layer. Such a simulation is beyond the scope of this paper.

However in the case of the 7 nm thick film, the film morphology can be described as a monolayer of elongated particles (Fig. 2(a)), and therefore the anisotropy energy due to the shape of the CoPt particles can be estimated and compared to the anisotropy energy due to the shape of the film. The energy of the film shape anisotropy is $\frac{1}{2}4\pi M_s^2 V_{film}$, where V_{film} is the volume of the film. This energy level is usually large enough to force the magnetization to lie in the film plane, resulting in an easy axis of magnetization in the film plane. The energy of the shape anisotropy of very elongated prolate ellipsoids is $\frac{1}{2}2\pi M_{CoPt}^2 V_{CoPt}$, where M_{CoPt} is the saturation magnetization of pure CoPt and V_{CoPt} is the volume of the CoPt materials. The chemical composition of our film was $Co_{51}Pt_9C_{40}$, so C was 40 at%. This corresponds approximately to 30 vol% C, giving a ratio V_{CoPt}/V_{film} of $\frac{2}{3}$. M_{CoPt} can be approximated by $(1-x) \times M_{Co}$ if we assume that M_{CoPt} decreases linearly with the Pt atomic content x, which in our case is 0.15 ($Co_{1-x}Pt_x$). The value of M_{Co} is taken to be 1400 emu/cm^3. In the case of very elongated prolate ellipsoids, the shape anisotropy energy due to the film shape was of the same order as that due to the shape of the ellipsoid particles. If one considers elongated prolate ellipsoids with a ratio of 2 between the long and short axes as in the case of CoPtC thin films, then the energy due to the film shape becomes larger than that due to the particle shape, which agrees with our observation of an easy axis in the film plane.

For thicker films (> 7 nm), the effect of the chains in the perpendicular direction of the film plane has to be taken into account. An upper limit of the shape anisotropy of chains of elongated prolate ellipsoids can be taken as the very elongated prolate ellipsoid case, for which it was shown that the shape anisotropy energy was of the same order as that of the film shape anisotropy. This is in agreement with our observation of an easy axis in the film plane with a magnetization component out of the plane.

Thermal fluctuation in magnetic media has recently received considerable attention because a smaller magnetic grain size of the recording media is required to achieve higher recording densities [7,8]. For recording densities larger than 10 Gbit/in^2 to be achieved, the grains should be smaller than 10 nm. The time decay of the remanent magnetization observed when the grains become too small is governed by the ratio $K_u V/kT$, where V is the volume of the magnetic grains. For longitudinal media, elongated prolate ellipsoids of revolution, having their long axis perpendicular to the film plane, could offer a way to increase the volume of the magnetic grains while keeping the radius of the grains in the film plane small. The consequence of this would be the appearance of a magnetization component out of the film plane, while the easy plane of magnetization would be kept in the film plane. It is not clear whether this larger volume of magnetic grains combined with a magnetization component out of the film plane would offer advantages when recording at very high linear density.

4. Conclusion

The microstructure of granular CoPtC thin films has been investigated using TEM planview and cross-section images. The shape of the CoPt crystallite particles was found to be close to that of elongated prolate ellipsoids of revolution. The ellipsoidal CoPt crystallites were wrapped in (00.2) graphite-like C planes. Further, the long axes of the ellipsoid particles were oriented perpendicular to

the film plane. The shape anisotropy of the elongated particles resulted in a magnetization component out of the film plane. The shape anisotropy energy of the elongated prolate ellipsoids was not large enough to force the easy magnetization plane to be perpendicular to the film plane.

References

[1] S.H. Liou, L. Chien, Appl. Phys. Lett. 52 (1988) 512.

[2] T. Hayashi, S. Hirono, M. Tomita, S. Umemura, Nature 381 (1996) 772.

[3] J.-J. Delaunay, T. Hayashi, M. Tomita, S. Hirono, J. Appl. Phys. 82 (1997) 2200.

[4] J.-J. Delaunay, T. Hayashi, M. Tomita, S. Hirono, S. Umemura, Appl. Phys. Lett. 71 (1997) 3427.

[5] J.-J. Delaunay, T. Hayashi, M. Tomita, S. Hirono, IEEE Trans. Mag. 34 (1998) 1627.

[6] A. Naudon, D. Thiaudiere, J. Appl. Crystallogr. 30 (1997) 822.

[7] M.P. Sharrock, IEEE Trans. Mag. 26 (1990) 193.

[8] Pu-Ling Lu, Stanley H. Charap, J. Appl. Phys. 75 (1994) 5768.