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Spray pyrolytic deposition of barium hexaferrite thin films for magnetic recording applications

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Abstract

Barium hexaferrite films with particles in the 50–80 nm size range have been prepared by a simple spray pyrolytic method starting from a citrate complex precursor. High nucleation rates during thermal decomposition of citrate precursor along with low growth rates ensure the formation of nanoparticles. The particles have a predominantly perpendicular easy-axis orientation and a perpendicular coercivity of 5000 Oe. The angular-dependent coercivity measurements show a nearly monotonic angular dependence indicating weaker grain interaction and low media noise in these films, an extremely useful property for application in high-density recording media.

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Keywords: Barium ferrite; Spray pyrolysis; Thin films; Magnetic recording media; Nanoparticles; Grain interactions

1. Introduction

In high-density recording, reduction in the spacing between head and disk media to the extent of contact and semi-contact states has become unavoidable. CoCrTa and CoCrPt films, which are currently used in recording media, thus need a protective layer on them to prevent crashing. Increase of media noise at high density is a serious problem with them. Barium hexagonal ferrite (BaF) films with magnetoplumbite-type crystal structure are attractive candidates for high-density, overcoat-free, contact or semi-contact recording media [1]. On account of their superior chemical stability, mechanical hardness, excellent corrosion and wear resistance and low level of media noise, they could be applied for rigid-disk media without protective and lubricant layers. Due to the large magnetocrystalline anisotropy and strong dependence of the orientation of easy axis on the microstructure, they have potential for application in both perpendicular and longitudinal magnetic recordings [2–4].

One factor that limits the performance of recording media at high areal densities is the media noise, which results from coupling between the magnetic grains. Barium ferrite films, show lower level of media noise in comparison with Co-based alloy media. However, incoherent rotation, which results from grain interaction, has been identified as

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a main source of media noise in barium ferrite particulate media and films [5]. It is generally believed that the grain interactions should become less significant in films with very small grain size. In order to exploit the complete potential of barium ferrite films in ultrahigh density recording, magnetic grains < 50 nm are desirable to realize reasonable signal-to-noise ratio (SNR) [6]. An important objective of this study is to obtain magnetic barium hexaferrite films with crystallite size below 100 nm displaying less grain interaction and low media noise by using a simple and economical chemical deposition method.

To deposit barium ferrite thin films, a variety of methods such as sputtering, arc discharge evaporation and laser ablation have been used [7–15]. However, desirable magnetic properties are often achieved only after annealing the films at high temperatures, $\sim 900°C$ [16]. This step in turn leads to the dead layer problem [5] due to the diffusion of substrate material onto the film. Moreover, the particles grow over 100 nm in size due to high growth rates at these high annealing temperatures. Limited success has been achieved in controlling the nucleation rates and reducing the particle size by increasing the barium content of the film [17] and by changing the film thickness and structure of the underlayer [18]. However, barium ferrite films with the lowest grain size but still displaying good magnetic properties are yet to be realized.

We have prepared barium ferrite films by a chemical spray process involving pyrolytic decomposition of a citrate precursor solution. These films were crystallized at relatively low (700°C) temperatures with small grain size (< 80 nm). Detailed magnetic properties of barium hexaferrite films deposited this way have been investigated which show a dominant easy-axis orientation perpendicular to the film plane with high coercivities of ~ 5 kOe. This method is advantageous for commercial production because it does not require any vacuum and it facilitates precise control of chemical composition of the film by employing relatively inexpensive starting solutions. In this paper, we report on the microstructure and magnetic properties of the films in order to elucidate the role of grain size and grain interactions on incoherent rotation.

2. Experimental

The films are prepared by spray pyrolytic deposition using a citrate complex precursor. The preparation essentially consists of two stages, namely, the preparation of the citrate complex precursor and spray deposition of the films using the precursor solution. At first aqueous solutions of stoichiometric amounts of nitrates of Ba and Fe were prepared. These solutions were reacted with 1 : 1 molar ratio of citric acid under controlled pH conditions. The reaction takes place in a slightly alkaline solution. Ammonia solution was added drop by drop to the reaction mixture with constant stirring until the desired pH is obtained. This solution was then refluxed for 6 h under controlled pH condition for completion of the reaction to form the citrate complex precursor. The preparation of the citrate complex is a crucial step in obtaining homogeneous single-phase films. Once the right complex was formed, ternary oxide phase could be obtained at relatively low temperatures by thermal decomposition of the complex at appropriate temperatures as indicated by thermal analysis as reported earlier [19].

Diluted precursor solution was sprayed onto the cleaned quartz plates previously heated to 350–400°C, using a sprayer and dry nitrogen as carrier gas. A highly adherent and homogeneous film of barium ferrite was formed by pyrolytic decomposition of sprayed precursor. For crystallization the films were annealed in a tubular furnace at a temperature (T_a) $\approx 700°C$ for about 3 h in air. Crystal structure of the film was determined by X-ray diffraction in a Siemens D-500 Powder X-ray Diffractometer using Cu K_α radiation. The microstructure was examined by a JEOL JSM 840 scanning electron microscope. The magnetic properties were measured using a DMS 880 vibrating sample magnetometer.

3. Results

Fig. 1 depicts the XRD pattern of the as-deposited and 700°C annealed films. The as-deposited film at 350°C showed no peaks in the XRD pattern indicating amorphous-like nature of the barium

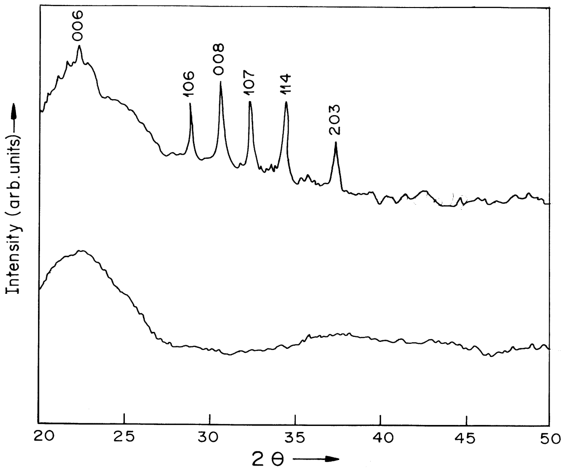

Fig. 1. XRD patterns of (a) as-deposited BaF film and (b) film annealed at 700°C.

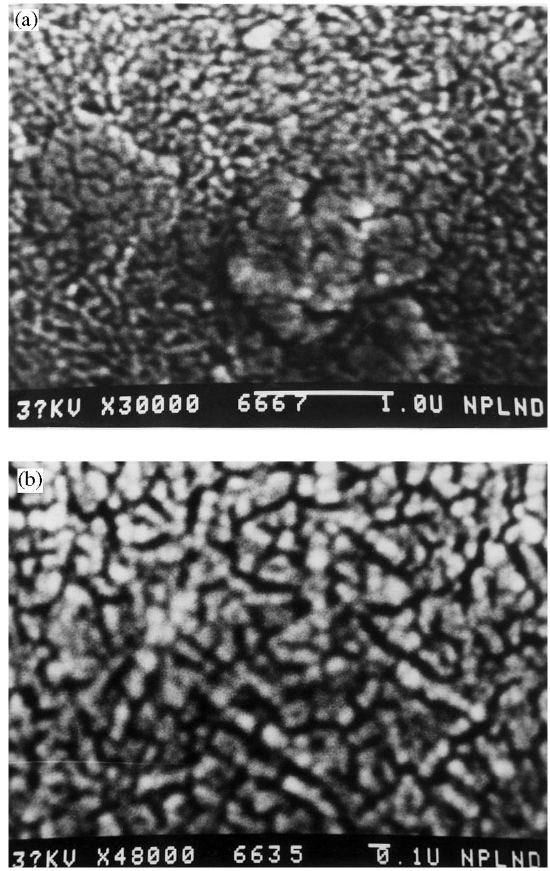

Fig. 2. (a) SEM micrograph of the BaF film annealed at 700°C, (b) magnified view.

ferrite growth. The XRD patterns do not show any discernible peaks or features even when films are annealed up to 650°C. These films show polycrystalline diffraction pattern on annealing at 700°C. The (0 0 8) and (0 0 6) peaks of high relative intensity are observed. The other diffraction peaks have been identified as belonging to (1 0 7) and (1 1 4) planes. The crystallization on annealing at 700°C leads to the evolution of a microstructure consisting of grains each of average nominal size of 50–60 nm attached to each other as a chain-like structure as shown in Fig. 2(a). A magnified view shown in Fig. 2(b) describes the structural features with more clarity. These crystallites have platelet-like shape and are densely packed.

M–H curves of the as-deposited films generally do not show saturation of magnetization even upto fields of 10 kOe and there is no hysteresis. Such magnetization characteristics suggest superparamagnetic behavior of these films. This is attributed to the presence of nanocrystalline particles in the film. On annealing, the crystallite size increases. This leads to the enhancement in magnetization. Films annealed at 650°C for 3 h show a marginal improvement in magnetization values. A narrow hysteresis loop is observed (Fig. 3) with M_s and H_c values of 250 emu/cm^3 and 148 Oe, respectively. For films annealed at ~700°C considerably improved magnetic characteristics are observed. Figs. 4(a) and (b) compare the perpendicular M–H characteristics of film annealed at 700°C for 0.5 h and 3 h, respectively. Short-term annealed films show M_s and H_c values as 300 emu/cm^3 and 2025 Oe, respectively. Magnetization did not saturate even at 10 kOe field. The BaF films after 30 min anneals are in partially crystallized state. One expects smaller size of BaF platelet grains in these films. When 700°C annealing was done for extended time of 3 h, H_c values improved by 2.5 times to 5072 Oe. The corresponding increase in M_s value was however only 1.1 times. The broad loop in the perpendicular direction to the film plane is consistent with X-ray diffraction data suggesting a significant number of barium ferrite crystallites having normal *c*-axis orientation. The M_s and H_c values along perpendicular plane are comparable to the barium ferrite films prepared by sputtering process as reported by others [20]. The in-plane values of M_s and H_c are somewhat low at 325 emu/cm^3 and 3400 Oe, respectively. Typically, the ratio of H_c in the two directions ranges between 1.5 and 2. High-temperature crystallization annealing at 800 and 900°C was also carried out to bring out the effect of crystallite size on magnetic properties. Table 1 shows M_s and H_c (perpendicular) values obtained from the hysteresis data. It is seen that H_c values decrease on annealing at temperatures just above the crystallization threshold temperature for these films. The M_s values on the other hand show only a marginal change.

The angular dependence of coercivity was measured for barium ferrite films subjected to crystallization anneal at 700°C for 0.5 and 3 h. The

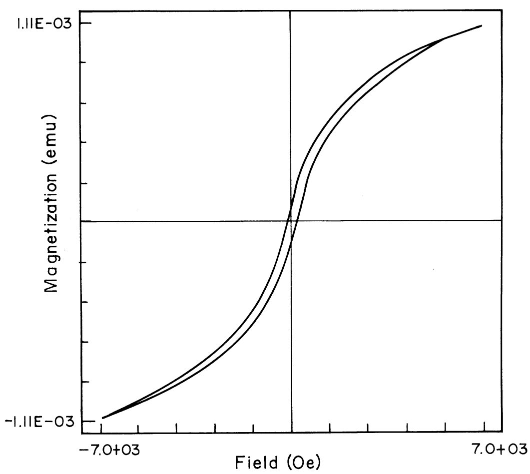

Fig. 3. Hysteresis curves for the BaF film annealed at 650°C for 3 h.

Table 1
Magnetic parameters of the BaF films annealed at different temperatures

Annealing temperature (°C)	Annealing time (h)	Coercivity (Oe)	Magnetization (emu/cm^3)
650	3.0	148	250
700	0.5	2025	300
700	3.0	5072	336
800	3.0	3405	330
900	3.0	3039	340

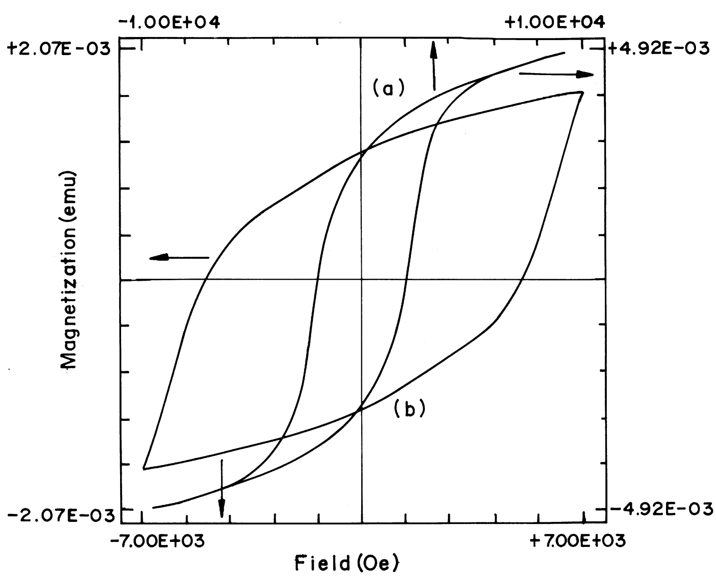

Fig. 4. Hysteresis curves of the BaF film annealed at 700°C (a) for 30 min (b) for 3 h.

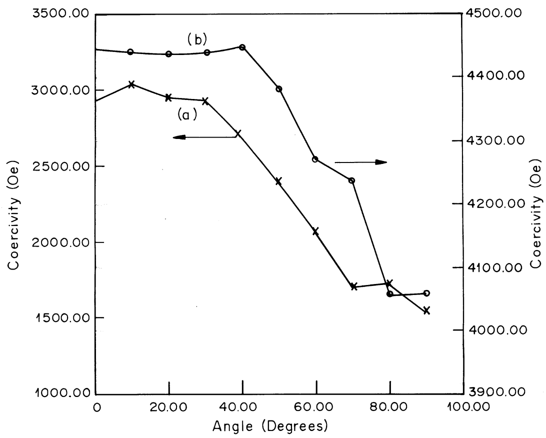

Fig. 5. Angular dependence of coercivity of BaF films annealed at 700°C (a) for 30 min and (b) for 3 h.

short-term annealed state of barium ferrite (BaF) film represents a partially crystallized state where the crystallites are still small. The results are shown in Figs. 5(a) and (b), respectively. H_c values decrease in both the cases. The decrease is very nearly monotonic with no peaks observed at any angle. Highest H_c value is observed when the magnetic field is perpendicular to the plane of the film. A large decrease in H_c for perpendicular to in-plane orientation suggests predominant uniaxial nature of anisotropy in short-term annealed film. In comparison, there is only about 10% decrease in H_c in the case of highly crystalline films.

4. Discussion

Crystallized barium hexaferrite phase shows a texture of grains with predominantly perpendicular orientation of *c*-axis from the film plane [20]. The existence of strong diffraction from (0 0 8) and (0 0 6) plane clearly indicates this. Although the presence of (1 0 7) and (1 1 4) diffraction peaks indicates the existence of crystallites, which have out-of-plane orientation of the *c*-axes, these are not aligned normal to the film plane. Here the *c*-axis is oriented at 64 and 40° out of plane, respectively. It is significant that no diffraction peaks corresponding to (1 1 0) and (2 2 0) diffraction planes are observed in crystalline barium ferrite films. Thus, crystallites with in-plane orientation of *c*-axis do not exist [15].

It is worth noting that the crystallization threshold at 700°C for spray-deposited films is lower in comparison with 800–900°C for sputter deposited BaF films [20]. Though sputter-deposited and annealed films tend to show uniaxial perpendicular *c*-axis orientation, the spray-deposited film does not reorient and continue to show only a preferential *c*-axis orientation. The as-deposited films have been interpreted as amorphous like as XRD do not show any peaks. However, crystallization behavior on annealing has no similarity to the usual amorphous to crystalline transformation. Differential thermal analysis (DTA) studies on bulk precursor have been carried out. Except for peaks around 400°C corresponding to decomposition of the precursor, no crystallization peaks were observed. The as-deposited barium ferrite films are more likely to be nanocrystalline, which are not revealed by the XRD data. Annealing process causes the grains to grow. Due to different growth rates corresponding to different crystallographic planes polycrystalline growth is thus seen. Microstructure studies further provide support to this inference.

The microstructure of crystalline barium ferrite films showed both rod-like as well as a significant density of spherical/platelet-shaped grains. The rod-like grains have width $\sim$50–60 nm, similar to the diameter of the platelet grains. These are essentially platelets, which are joined as a chain to give rod-like (acicular) shape. We have not observed any diffraction peaks corresponding to (1 1 0) or (2 2 0) planes, which also suggest that acircular grains do not exist. It is known that in BaF, the crystal growth occurs preferentially in the basal plane and at much smaller rates in the direction of *c*-axis [21]. In the spray-deposited BaF, these initially formed nanosize crystallites in the as-deposited state having normal *c*-axis orientation, on crystallization grow along the film plane unhindered as platelets. Magnetic data of Fig. 4(a) and Table 1 also show that initially formed BaF crystallites have *c*-axis-aligned normal to the film plane. At an early stage of crystallization, platelet growth of BaF crystals yields the observed magnetic properties. Reorientation of crystallites due to growth along other crystal planes causes some loss in anisotropy nature and c-axis orientation. If for the initially formed BaF crystals the c-axes were to lie in the film plane, on crystallization these still grow in the direction of the film plane. Their growth in the other direction shall be restricted by the limited film thickness. Morphology of these crystallites would be rod like which is not seen in our case. High density of the platelet-like grains of average size < 50 nm observed in the present case are responsible for the dominant c-axis orientation of these spray-formed as-crystallized BaF films.

The microstructure of the spray-deposited BaF films is different from the films deposited by sputtering. A high density of spherical/platelet particles of the average size of 50–60 nm indicates high degree of nucleation in the thermal decomposition process [22]. The formation of nanocrystalline barium ferrite compound phase in the spray pyrolytic method takes place via the thermal decomposition of the citrate precursor. In sputtering the deposition from stoichiometric barium ferrite target leads to an amorphous barium ferrite film which crystallizes on annealing to form the granular microstructure. The differences in the microstructure in turn are reflected in the observed magnetic properties.

Angular dependence of coercivity, H_c, provides knowledge of grain interactions and rotation mechanism in BaF nanoparticles [2]. Significant deviations from Stoner–Wohlfarth coherent rotation model have been reported in barium ferrite particulate media and thin films. The model predicts an H_c value, which is equal to the anisotropy field in the easy-axis direction which monotonically, decreases to zero in the hard-axis direction with a relatively flat region between angles 30 and 50°. For an assembly of noninteracting particles the SW model holds well. It may be noted from the figure that H_c values for both the samples show a very nearly monotonic angular dependence, quite unlike the observation in easy-axis in-plane-oriented films prepared by sputtering [2], in spite of the densely packed crystalline microstructure. No peaks are observed in the angular-dependent curves at any angle and H_c falls gradually and monotonically to its minimum value at 90°. The monotonic angular dependence is a clear indication of weaker grain interaction among the nanosize crystallites in these spray pyrolytically deposited films. It is generally believed that incoherent rotation should become less significant in films with smaller grain size with nanoparticles. The monotonic angular dependence in both the samples confirms that the grain interaction and incoherent rotation does become less important in particles of smaller grain size.

Essentially, there are two types of interactions between magnetic grains in the recording media, the exchange coupling and magnetostatic coupling. Exchange coupling between grains gives rise to a cooperative type of switching mechanism of the magnetic grains, which is responsible for the high media noise. The magnetostatic interaction, on the other hand, is usually negative, deterring cooperative switching between the grains and reducing transition noise [23]. Exchange coupling among the grains in spray-deposited barium ferrite films is quite unlikely. Super-exchange interaction, which depends sensitively on the oxygen sublattice in barium ferrite, is hardly likely to extend across the grains. Therefore, the monotonic angular dependence of H_c which is a signature of weaker grain interactions is understandable. Such films are required for recording media applications to minimize noise, in spite of the fact that the small grain BaF films show lower H_c and M_s values. Clearly, spray-deposited films are well suited for recording applications due to the early formation of BaF compound, due to low crystallization threshold and consequent platelet crystalline microstructure with < 50 nm size and appropriate magnetic parameters.

5. Conclusions

Spray pyrolytic deposition starting from a citrate complex precursor yields thin films of barium hexaferrite with particles of average 50 nm size. The method leads to nanoparticles because of the high nucleation and low growth rates involved in the thermal decomposition of the citrate precursor. The predominantly perpendicular orientation of the easy axes with perpendicular coercivity of 5000 Oe could make them useful for application in high-density perpendicular magnetic recording. The weaker grain interaction as indicated by the monotonic angular dependence of coercivity would mean low media noise which again is very important from the viewpoint of such applications.

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