Microstructural Origin of the Perpendicular Anisotropy in M-type Barium Hexaferrite Thin Films Deposited by rf Magnetron Sputtering

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Abstract- **Barium hexaferrite thin films deposited by rf magnetron sputtering have been made which exhibit saturation magnetization 90% of that of bulk single crystals, whereas the perpendicular uniaxial anisotropy is only 60% of that of the bulk. X-ray diffraction spectra suggest good c-axis orientation perpendicular to the film plane. However, M-H hysteresis loops show a fairly large in-plane hysteresis. Scanning electron microscopy and transmission electron microscopy show that the films are made of a mixture of platelet-shaped grains and acicular grains. Microdiffraction studies in a transmission electron microscope indicate that the platelets have their c-axis oriented perpendicular to the plane and that the acicular grains have c-axis orientation in the plane. Preferential grain growth in the basal plane of the crystal is believed to be responsible for these grain geometries. Because the platelets occupy a much larger volume of the film than the acicular particles, there is a preferential c-axis orientation perpendicular to the film plane.**

I. INTRODUCTION

Because of its excellent chemical stability and large uniaxial anisotropy, barium hexaferrite thin films are of interest for both magnetic recording and microwave/millimeter wave devices. To deposit barium hexaferrite thin films, researchers have previously used target facing type of sputtering (TFTS) systems [1], [2] and conventional rf or dc diode sputtering [3]-[5] with 'in-situ' heating or post-deposition annealing. To grow thicker films, liquid phase epitaxy on well-textured barium ferrite sputtered films has been tried [6]. It is generally believed that TFTS produces the best film quality because of the smaller degree of ion bombardment on the substrate surface during film deposition [2]. The strength of perpendicular c-axis orientation, magnetic properties and recording performance in terms of the sputtering conditions have been carefully studied [3]-[5], [7]-[8]. The effects of different substrates and underlayers on the c-axis perpendicular orientation have also been investigated [8], [9]. However, detailed microstructural studies on such films have not yet been attempted. In this work, efforts have been made to correlate the film microstructure to the measured magnetic properties in order to achieve a better understanding of the origin of the magnetic anisotropy. A simple model of grain growth dynamics is proposed to explain the observed preferential c-axis orientation and reduction in perpendicular anisotropy from bulk values.

II. EXPERIMENTAL PROCEDURE

The films were deposited on thermally oxidized silicon substrates by rf magnetron sputtering in a Leybold Z-400 sputtering system. The target used was a three inch diameter sintered target of the constituent oxides with the composition of $Ba_{1.25}Fe_{12}O_{19}$. The sputtered amorphous films were then crystallized by annealing in a tube furnace at 800°C for about three hours in air. X-ray diffraction was used to characterize the film crystal structure. The composition of the film was determined with a Tracor x-ray spectrace 5000 energy dispersive x-ray fluorescence spectrometer (EDXRF). The perpendicular anisotropy, coercivity and saturation magnetization were measured using a DMS-1660 torque/vibrating sample magnetometer. The film thickness was measured with a Tencor alpha-step 200 profilometer. The film microstructure was studied by using both scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

III. RESULTS AND DISCUSSIONS

The sputtering conditions used to deposit the films are listed in Table I. Films had the stoichiometric composition, and their thickness was about 1200Å. The as-deposited films were amorphous. They were crystallized at 800°C in air. The reason that 800°C was chosen as the annealing temperature can be seen in Fig. 1. The x-ray diffraction patterns were measured at a range of temperatures by using a hot-stage x-ray diffractometer. At temperatures below 700°C, the sputtered film was in the amorphous state. However, at 800°C, the film was well crystallized with good c-axis orientation perpendicular to the film plane. The magnetic properties of the resulting film are listed in the bottom half of Table I. M_s is fairly close to the bulk value (380 emu/cc). However, the K_u measured by a torque magnetometer is

Table I

Power	20 watts
Ar pressure	5 mTorr
Background pressure	$< 8\times10^{-7}$ torr
Deposition rate	~22 Å/min
Saturation magnetization M_s	350 emu/cc
Coercivity H_c	1755 Oe
Anisotropy K_u	2.0×10^{6} erg/cc

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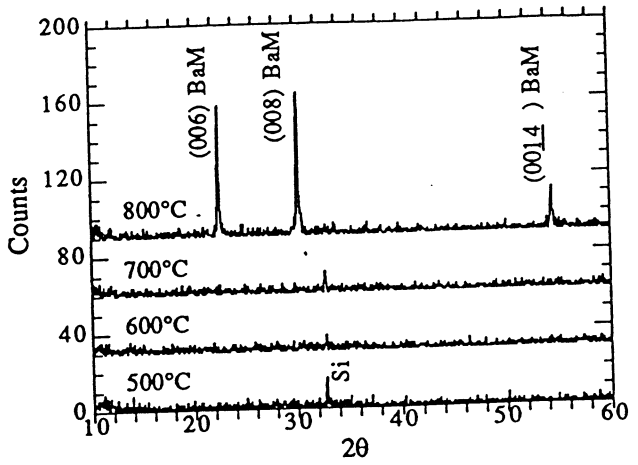

Fig.1: Hot stage x-ray diffraction data at four different temperatures.

about 60% of the value for a single crystal ($3.3x10^6$ erg/cc). Since the x-ray spectrum in Fig. 1 only shows a c-axis perpendicular orientation, this reduction in K_u is somewhat surprising. To understand this phenomenon, in-plane hysteresis loop measurements and microstructural studies were performed.

Both perpendicular and in-plane hysteresis loops are plotted together in Fig. 2. A fairly wide in-plane loop is observed, indicating the existence of a significant amount of in-plane c-axis orientation, which was not revealed by the x-ray spectrum. To understand the cause of the in-plane hysteresis, the film microstructure was studied by SEM and TEM. A SEM picture of an etched film is shown in Fig. 3(a). This micrograph shows that the grains can be classified into two major categories: those with acicular shape and those which are platelets. Another SEM picture (Fig. 3(b)) with a higher magnification shows an area with many acicular grains. In order to investigate the detailed crystal structure difference between these two types of grains, TEM microdiffraction was used. A TEM bright field image showing a grain configuration similar to that observed by SEM is shown in Fig. 4(a). By focusing the electron beam onto the black long grain in the middle of Fig. 4(a), the microdiffraction pattern shown in Fig. 4(b) was obtained. It clearly shows the barium hexaferrite structure with the c-axis perpendicular to the long axis of the grain. Since the TEM

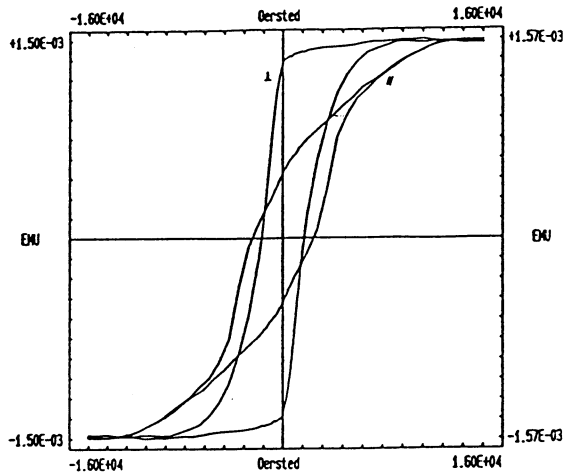

Fig.2: Perpendicular and in-plane hysteresis loops.

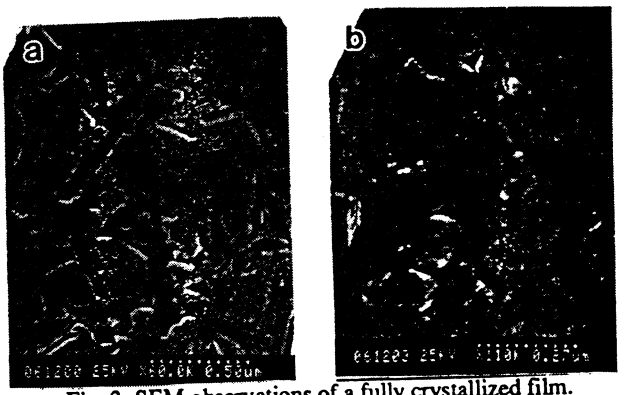

Fig. 3: SEM observations of a fully crystallized film.

microdiffraction pattern is in the reciprocal space, the spacing between the (0001) crystal planes, which is large in real space, appears to be short in the microdiffraction pattern. Another set of TEM pictures is shown in Figs. 5(a) and (b). Here, the electron beam was focused on the dark platelet-shaped grain in the center of the picture. The microdiffraction pattern in Fig. 5(b) shows a six fold symmetry indicating that the grain has its c-axis perpendicular to the film plane. From such TEM results, it was concluded that long grains have their c-axis in the film plane and perpendicular to their long axis, while platelets have their c-axis perpendicular to the film plane.

To see the natural grain geometry more clearly, another SEM picture is shown in Fig. 6 taken on an etched film which was annealed at 700°C for about 5 hrs. At this temperature, the crystal nucleation rate was low; therefore, a large grain size can be expected. Since the grain growth rate is also low at this temperature, it was possible to stop the grain growth before complete crystallization. The two distinctive grain shapes are clearly illustrated in this picture.

From both Fig. 3 and Fig. 6, it is seen that the platelet grains occupy a much larger area than the acicular grains. We believe this is caused by the different crystal growth rates in the basal plane and c-axis directions. For barium hexaferrite, crystals grow preferentially in the basal plane and much less rapidly in the direction of the c-axis [10]. This is why barium hexaferrite particles always tend to be platelets. In our case, nucleation commences somewhere between 700°C and 800°C as revealed by the hot stage x-ray diffraction data (Fig. 1). If the initial nucleus has its c-axis perpendicular to the film plane, it can grow fast laterally without restriction because the basal plane is parallel to the substrate surface and thus the film thickness does not limit the crystal growth.

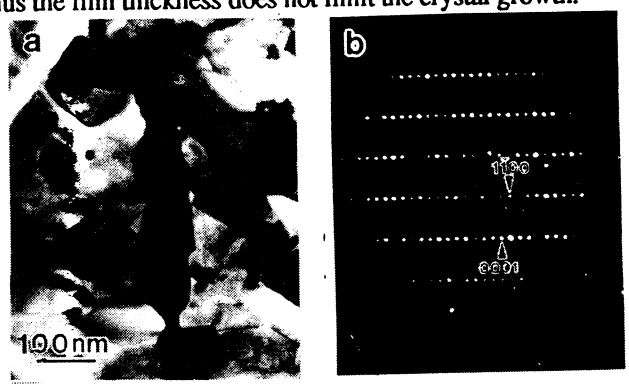

Fig.4: (a) Bright field image showing an acicular grain.
(b) Microdiffraction pattern on the acicular grain.

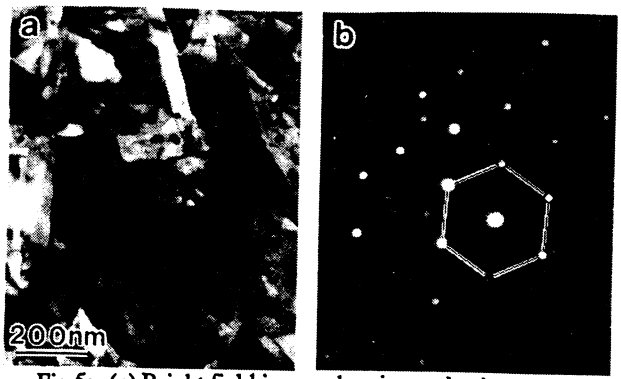

Fig.5: (a) Bright field image showing a platelet grain.
(b) Microdiffraction pattern on the platelet.

However, if the nucleus has its c-axis in the plane, the crystal can only grow fast in one direction which is perpendicular to both the c-axis and the film surface normal. In the direction of the c-axis, it can not grow large because its growth rate is small in that direction. In the direction of the film normal, it does grow fast, but it can not grow more than the film thickness. This is actually the mechanism of the formation of the acicular grains as shown in the SEM pictures. This also explains why platelets occupy a much larger volume than acicular grains. Although the exact reason is not clear at present, it does appear that there is a dual preference in the crystal orientation: one with the c-axis in the film plane and the other with the c-axis perpendicular to the film plane, rather than simply a random orientation.

SEM pictures clearly show many in-plane oriented grains, which have acicular shape. However, x-ray diffraction doesn't detect them. We believe there are two reasons. First, since the c-axis in-plane oriented grains have no preferred orientation in their basal plane, there is no specific set of crystal planes which must be parallel to the film plane. Second, as shown previously, the platelets occupy a much larger volume than acicular grains; therefore, the major contribution to the x-ray diffraction is from the large platelets.

Similarly, the reduction in overall perpendicular crystal anisotropy is due to the large volume fraction difference between platelets and acicular grains. Not only do acicular grains dilute the volume of the platelets, but they also have negative perpendicular anisotropy which cancels part of the positive perpendicular anisotropy from the platelets. Therefore, in order to obtain perfect c-axis perpendicular orientation the orientation of the initial crystal nuclei has to be well controlled.

Fig.6: SEM observation of a partially crystallized film.

IV. CONCLUSIONS

In-plane hysteresis loop measurements show some in-plane c-axis orientation in rf magnetron sputtered and air annealed barium hexaferrite thin films. SEM observations on the film microstructure illustrate grains tend to be either platelets or acicular in shape. TEM microdiffraction shows that the acicular shaped grains have their c-axis oriented in the plane while the platelets have their c-axis perpendicularly oriented. The large difference between the crystal growth rate in the basal plane and along the c-axis causes a large volume fraction difference between the two kinds of grains. This results in a net positive uniaxial perpendicular anisotropy. Since c-axis in-plane oriented grains occupy a small volume fraction and no preferred orientation in their basal plane, x-ray diffraction is unable to detect the grains with in-plane c-axis orientation. However, a SEM clearly shows their elongated shape, and microdiffraction in a TEM shows them to have their c-axis in plane. In order to obtain perfect orientation of the c-axis perpendicular to the plane, means must be found to control the orientation of crystal nuclei so that the needle like grains do not form.

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