Microstructural investigations of Bi doped Fe garnet thin films for magneto-optical recording

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$Gd_{1.6}Bi_{1.4}Fe_{3.8}Ga_{1.2}O_{12}$ garnet films for short wavelength magneto-optical recording are investigated. These films have high Faraday rotation (up to 1.3 °/μm), good corrosion resistance and good magnetic properties ($H_c > 1$ kOe with hysteresis loop squareness of 1) but poor noise performance. This paper shows that the noise is a result of the grain size being of the order of the recorded domain size and that the grain size and distribution are determined by the initial density of garnet nuclei. In the course of this study, it was discovered that these films contain a high density of Bi globules which precipitate out of the garnet matrix. It is believed that these globules contribute to the high coercivity of sputtered garnet films.

Ferrimagnetic garnet thin films are currently under investigation for use as short wavelength magneto-optical recording media.[1,2] We have investigated a series of Bi-substituted Fe garnet films with high Faraday rotation (up to 1.3 °/μm) and good corrosion resistance.[3] These films have shown good magnetic properties (i.e., coercivities > 1 kOe and hysteresis loop squareness of 1) but have poor noise performance. "Large" grain size and "poor" morphology are believed to be the critical factors responsible for the high noise in these materials. Rapid thermal annealing (RTA) has been reported to improve the morphology and reduce the grain size of garnet films.[4] Smaller grain sizes have also been reported for films deposited on GGG substrates and crystallized during deposition.[5] We have studied the post-deposition crystallization of bismuth doped garnet films deposited on glass substrates. The goal was to understand the factors which cause the high noise levels and to determine whether they could be circumvented without the use of RTA.

Garnet films of composition $Gd_{1.6}Bi_{1.4}Fe_{3.8}Ga_{1.2}O_{12}$ and 300-nm thickness were produced by rf magnetron sputter deposition onto Corning 7059 glass substrates. The crystalline garnet phase was then formed by annealing in air at temperatures between 650 and 705 °C.

Magnetic properties were measured using a magneto-optic hysteresis loop tracer. Micromagnetic investigations were conducted using Faraday microscopy with an argon ion laser ($\lambda = 488$ nm) as the writing source and an applied field of 100 Oe.

Overall crystallographic structure was studied using x-ray diffraction (Cu Kα). The film composition was monitored using x-ray fluorescence. Microstructural investigations were conducted on ion milled planar specimens in the transmission electron microscope (TEM) and on unthinned specimens in the scanning electron microscope (SEM). These included high-resolution TEM in a JEOL 4000EX, energy dispersive x-ray microanalysis (EDX) in a Philips 420T and *in situ* annealing in a JEOL 120CX. Additionally, selected area diffraction (SAD), bright and dark field imaging were employed to complement these techniques.

Magnetic measurements, x-ray diffraction and differential thermal analysis indicate that annealing at temperatures ⩾650 °C is necessary to form the crystalline garnet phase. A TEM image of a film annealed at 670 °C for 3 h is shown in Fig. 1. This film has a polycrystalline microstructure with a grain size of the order of 1 μm. This is the typical grain size in our annealed samples. The grain boundary regions are very well defined and have many voids. SEM/EDX studies suggest that these "voids" may be due to dropout of Bi rich precipitates during TEM specimen preparation. Higher magnification reveals a disordered microstructure within the grains with many "globule" like features as shown in Fig. 2. The SAD pattern for this sample reveals the garnet, βBi_2O_3 and Bi phases.

Using EDX microanalysis, it was possible to measure the local elemental composition by exciting characteristic x rays from a particular feature in the microstructure using a 10-nm-diam focused electron probe. A number of spectra were collected for the film as a whole, for the grains, for the grain boundaries and for the globules. We used the ratio of the counts in the Fe Kα peak to the counts in the Kα peak of each of the other elements to give the relative abundance of each element. The results are shown in Fig. 3. While it can be seen that the Ga and Gd concentrations remain relatively uniform for all the regions of the specimen, it is clear that there is significant Bi enrichment (of the order of twice the mean for the film) in the globules and slight Bi depletion at the grain boundaries (approximately 10% less than the film mean).

To investigate the origin of the globules the film microstructure prior to annealing was studied. Both x-ray diffraction and SAD reveal an amorphous type diffraction pattern as shown in Fig. 4. High-resolution TEM images, however, reveal elongated Bi crystallites, approximately 10 nm across, distributed throughout the film with a spacing of about 20 nm as seen in Fig. 5. It is believed that the Bi-rich globules form from these Bi crystallites.

To study the grain formation and growth process *in-situ* annealing was performed in the TEM. For the film as a whole only Bi and βBi_2O_3 phases were observed up to 650 °C. At 650 °C, the garnet phase developed with grain centered nucleation sites spaced ~1 μm apart as seen in Fig. 6. The grains then grew rapidly until they met, forming the grain boundaries. Thus the final grain size and distribution is controlled by the density of garnet nuclei obtained before significant grain growth has occurred. The nucleation sites could not be associated with any particular

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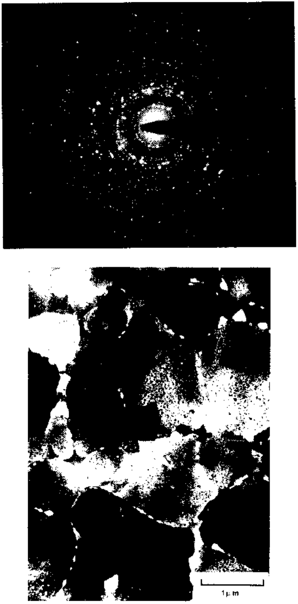

FIG. 1. (a) SAD pattern and (b) TEM image for garnet thin film.

feature in the microstructure prior to crystallization, and attempts to reduce the grain size by varying the annealing time and temperature were all unsuccessful.

The Bi-rich globules discovered in this study are believed to significantly increase the domain wall motion coercivity of sputtered post-deposition annealed garnet films. The diameter of the globules is comparable to the domain wall width and they are therefore expected to act as local pinning sites to domain wall motion. It is likely that these globules increase the coercivity of sputtered garnet films relative to that of films grown by liquid phase epitaxy.

To help in understanding the influence of the microstructure on the recording, we wrote domains in these films with an Ar ion laser. A Faraday microscope image of a typical domain recorded by a circular laser spot is shown in Fig. 7. The recorded domain has an irregular shape in

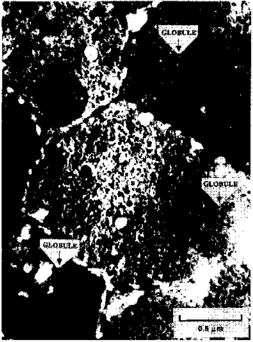

FIG. 2. TEM micrograph showing Bi-rich "globules" in garnet microstructure.

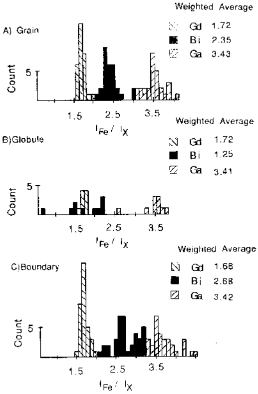

FIG. 3. Histograms showing changes in relative abundance of elements for EDX spectra collected (a) within the grains, (b) on the globules, and (c) at the grain boundaries.

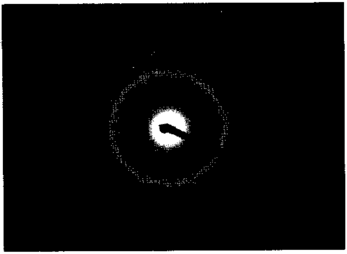

FIG. 4. SAD pattern for sample of unannealed film suggesting an amorphous structure.

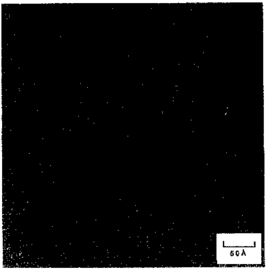

FIG. 5. HRTEM image of unannealed sample showing crystalline Bi particles.

FIG. 6. TEM image showing nucleation of the garnet phase at the grain center.

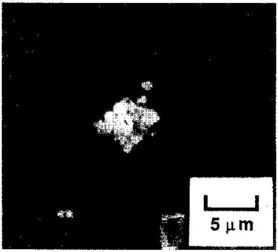

FIG. 7. Faraday microscope image showing a magnetic domain recorded with a circular laser spot.

which domain walls are clearly located along grain boundaries. The density of the Bi-rich globules seen in Fig. 2 is too high for them to be the dominant pinning mechanism since the resultant domain regularity would be much better. It is believed that the grain boundaries are responsible for the domain wall pinning. Therefore, the grain size and shape control the domain shape and to reduce the noise, it is essential to reduce the grain size.

It has been shown that Bi-doped sputtered garnets films which are post-deposition annealed contain a high density of Bi-rich globules which form from Bi crystallites present in the amorphous matrix before annealing. This suggests that the solubility limit for Bi in these films is less than that in the bulk material.[6] Although it is believed that these globules contribute to domain wall motion coercivity, they do not appear to be the main cause of the high noise level in these films. Rather, the high noise level is believed to be due to the domain irregularity, which is caused by the grain size being similar to the recorded domain size, combined with the fact that the domain walls follow the grain boundaries. The grain size achieved using conventional post-deposition annealing is determined by the density of nucleation sites, and attempts to increase the number of nucleation sites by varying the annealing time and temperature were all unsuccessful. It appears that a reduction in the noise level in sputtered garnets films will require the use of RTA like that employed by Suzuki[4] or the introduction of a higher density of nucleation sites, either by introducing a second phase or a suitable underlayer.

[1] P. Hansen and J. P. Krumme, Thin Solid Films **114**, 69 (1984).

[2] F. Inoue, A. Itoh, and K. Kawanishi, Jpn. J. Appl. Phys. **19**, 2105 (1980).

[3] W. Eppler and M. H. Kryder, IEEE Trans. Magn. **MAG 25** (5), 374 (1989).

[4] T. Suzuki, J. Appl. Phys. **69**, 4756 (1991).

[5] K. Shono, H. Kano, N. Koshino, and S. Ogawa, J. Appl. Phys. **63**, 3639 (1988).

[6] K. Shinagawa and S. Taniguchi, Jpn. J. Appl. Phys. **13**, 21 (1974).