MAGNETIC AND MAGNETO-OPTICAL PROPERTIES OF SPUTTERED Fe-B-F FILMS

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ABSTRACT

The Fe-B-F amorphous films were prepared by a high deposition rate sputtering apparatus with two opposing targets. The structure of these films can be easily changed from amorphous phase to fluoride mixed amorphous phase by changing the quantity of the fluorine element. High magneto-optical properties were obtained for (B+F)-rich composition films. These films had both ferromagnetism and transparent characteristics. The values of Faraday coefficient were between $3 \times 10^4$ and $1 \times 10^5$ deg/cm at 633 nm. In some cases the apparent Polar Kerr rotation angles were around 0.7 degree at 700 ~ 800 nm without an additional reflecting layer. The absorption coefficient decreases monotonically from $8 \times 10^4$ to $3 \times 10^4$ cm$^{-1}$ in the wavelength region of 300 ~ 800 nm.

1. INTRODUCTION

In the last decade a number of studies have been made on the magnetic and magneto-optical properties of various kinds of rare earth-iron garnet films. Bismuth substituted iron garnet films made by the liquid phase epitaxy (LPE) method are useful materials for magneto-optical devices such as optical isolators in the wavelength range of 0.8 μm and 1.3 ~ 1.6 μm. [1] Many efforts have been made to decrease the optical absorption coefficient $\alpha$ in these films. On the other hand, the sputtered films of Bi-substituted garnet having high coercivity is very attractive for use in magneto-optical recording media. [2] In general, however, these films require annealing at high temperatures for crystallization and show a medium noise due to grain boundaries. Therefore, it is necessary to increase $\alpha$ and to make very small grains or to eliminate the grain boundaries for magneto-optical recording media. The required properties for ideal magneto-optical material are as follows: high Curie temperature, low birefringence effects and high Faraday rotation associated with a low absorption coefficient in the visible spectrum and low saturation magnetization. Some of these properties (i.e. high Curie temperature and low absorption coefficient) are virtually the opposite of the requirements for magneto-optical recording.

Recently we have reported on the magneto-optical properties of Fe-B-F systems. [3] This ferromagnetic material has amorphous or fluoride mixed amorphous structures, and is transparent in the visible wavelength region. Magnetic and magneto-optical properties of Fe-B-F films are quite different from those of FeF$_2$ and FeF$_3$. The FeF$_2$ and FeF$_3$ compounds are antiferromagnetic and paramagnetic, respectively, and show good transparency. One approach was to research materials, typified by FeBO$_3$ [4] and FeF$_3$ [5], which have low values of $\alpha$ in the visible spectrum while maintaining higher values of $\Theta F$. However, there are two serious drawbacks concerning the use of FeF$_3$: unacceptable optical losses, and birefringence effects. In this study we have investigated the micro-structure, electronic structure, and the role of fluorine on the magnetic and magneto-optical properties of Fe-B-F systems.

2. EXPERIMENTAL PROCEDURE

All samples were prepared by a dc magnetron sputtering method. Figure 1 is a sketch of the sputtering apparatus used in the present work. Iron and boron atoms were sputtered from two dc magnetron opposing targets placed in the top section of the chamber. Reactive fluorine gas was provided by rf sputtering from an FeF$_3$ target placed on the bottom section of the chamber. The FeF$_3$ powder (~80 mesh) target, compressed under the pressure of 100 kg/cm$^2$, was heated up to 100 °C in vacuum for more than 24 hrs in order to remove the containing water. The Fe-B targets, containing 1 to 40 at.%B, were prepared by arc melting of Fe and B.
The Fe/B ratio in the films was controlled by varying the Fe-B target composition. F content was controlled by varying the power supplied to the dc and rf sputtering targets. Glass was employed as a substrate. Film thickness was in the range of 0.3 to 0.7 μm. The sputtering chamber was initially evacuated to approximately 5x10⁻⁷ Torr before pre-sputtering. After the presputtering of 2~6 hrs, Fe-B-F film was deposited onto the substrate. During sputtering, dc and rf powers were kept constant. Argon partial pressure was set to 1x10⁻² Torr. The chemical composition of the films was determined using an EPMA (electron probe micro analyzer) with a ZAF correction unit. Magnetic hysteresis loop at room temperature was measured with a vibrating sample magnetometer in applied fields up to 9 kOe. The temperature dependence of saturation magnetization was measured in the range from 77 to 1000 K using a magnetic balance.

The structure of the samples was examined by TEM (transmission electron microscopy) and by x-ray diffraction using Fe-Kα radiation. The Faraday rotation angle, θf, was measured at the wavelength of He-Ne laser light, and the polar Kerr rotation angle, θK, was measured by an automatic null type Kerr rotation spectrometer [8] in the wavelength region from 250 to 800 nm. Soft x-ray emission spectra, FeLα and FeLβ, and Er (Fermi edge level) were measured to provide information about the electronic structure of the samples.

3. RESULTS AND DISCUSSION

Figure 2 is an Fe-B-F ternary phase diagram showing the composition range of the various phases prepared. In the region bounded by solid lines and labelled "Am", the films were entirely amorphous judging from electron and x-ray diffraction results. In the composition region with more than about 20 at.%F, amorphous films with some crystalline phases (identified as FeF₂) were obtained. Compositions in low B content contained crystalline α-Fe, plus FeF₂ at higher F contents. Inclusion of F was accompanied by a spread of the amorphous phase to the area of lower B composition. Therefore, it is thought that F is an amorphous forming element under 20 at.%F.

Figure 3 shows transmission electron micrographs of (a) an amorphous sample (Fe₇₆B₂₅F₁₉), indicated by "X" in Fig. 2, and (b) a mixed-phase sample (Fe₇₆B₂₅F₁₉, indicated by "Y" in the figure). Although no crystalline phase is detectable in "X" by x-ray diffraction, some kinds of structures with the scale of about 50 Å are clearly observable in the transmission electron micrograph as seen in Fig. 3("X"). Similar structures have been observed in Fe-B-N [9] and Fe-B-O [9] sputtered films. These structures are attributed to the presence of two amorphous phases. However, at present, there is no way to determine the chemical composition of these phases. In region "Y", in contrast to "X", a large number of needlelike particles with lengths of a few hundred angstroms are seen in the TEM photograph, and crystalline peaks corresponding to FeF₂ are seen in the x-ray diffraction patterns as shown in Fig. 4. The Fe₇₆B₂₅F₁₉ film shows an amorphous phase pattern including two phases. However, the Fe₇₆B₂₅F₁₉ and Fe₇₆B₂₅F₁₉ films include a crystalline phase which coincides with the main peak of the FeF₂ standard sample.

The soft x-ray spectroscopy (SXS) is a useful method to obtain information about the partial densities of states (PDOS) associated with each constituent. Namely, this information might enable us to more precisely identify the Fe 3d-band. Fig. 5 shows FeLα and FeLβ x-ray emission spectra profiles of the Fe, FeF₂ and FeF₃ standard samples and FeF₂ Powder. The FeF₂ Powder
three kinds of Fe-B-F films. Here, all spectra are normalized with the maximum intensity. The peak of FeLα and the Fermi edge level (EF) of Fe-B-F films shift to the energy side lower than those of FeF2 and FeF3. The half width at maximum intensity of FeLα is also narrower compared with FeF2 and FeF3. However, the peak position and the half width (FeLα) of Fe-B-F films do not change from those of pure Fe. From these results, we can understand that the electronic structure of Fe-B-F films is fairly different from that of Fe-F crystalline compounds (FeF2, FeF3) and is similar to that of pure Fe.

The Curie temperature Tc was estimated from magnetization versus temperature curves in Fig. 6. As shown in Fig. 2, although Tc is highly dependent upon B content, there seems to be little relationship between Tc and F content. For instance, Tc values of amorphous Fe-B-F films containing about 10 at.%B are almost constant around 523K.

On the other hand, Ms varied mainly with Fe content from ~140 emu/g at 88 at.%Fe to ~60 emu/g at 44 at.%Fe. The magnetization Ms varies reversibly with heating and cooling under the crystallization temperature. On heating, the change of Ms in Fe69B29F3 and Fe44B4F52 occurs between 800 and 900K. This seems to be caused by precipitation of some Fe-F compound.

Figure 7 shows the field dependence of Faraday coefficients, θF, in two kinds of Fe-B-F films. As seen here, θF increases linearly with an applied field until reaching a field (saturation field) corresponding approximately to the demagnetizing field. The saturation fields for the Fe69B29F3 and Fe44B4F52 films are ~8 kOe and ~5.5 kOe, respectively, and the maximum values of θF at the saturation field are 3.9x10^4 and 3.5x10^4 deg/cm. The maximum values of θF in the films having the composition range of 5 at.% < F < 52 at.% and 45 at.% < Fe < 83 at.% changed between 3x10^4 and 1x10^5 deg/cm.

Figure 8 shows the wavelength dependence of the absorption coefficient, α, in three kinds of Fe-B-F films. The α tends to decrease with the increase of F content and the decrease of Fe content. From these results, we have calculated the figure of merit in these films. The values obtained are about 0.1 deg/dB in these films. The transparency of Fe-B-F films increases with increasing of the F content in the film.
Figure 9 shows the wavelength dependence of reflectivity, R, in several kinds of Fe-B-F films. As shown in this figure, R has a tendency to decrease with increasing F. However, in Fe₄ₓBₓF₄₋ₓ and Fe₄₄B₄ₓFs₂₂ films, there is a maximum R at about 600 nm and about 500 nm, respectively. These behaviors differ from those of rare earth-iron garnets. Reflectivity is very closely related to the wavelength dependence of the apparent $\theta \chi$.

Figure 10 shows the wavelength dependence of the apparent $\theta \chi$ in three Fe-B-F films. The $\theta \chi$ hysteresis loop at 633 nm in Fe₄₄B₄ₓFs₂₂ film is also shown in the inset figure. $\theta \chi$ of Fe₄₄B₄ₓFs₂₂ film exhibits negative value and its $\theta \chi$ spectrum is relatively simple. However, in the other two films containing much fluorine element, the $\theta \chi$ spectra vary considerably with wavelength, similar to that of the R spectra. In general, it is well known that the $\theta \chi$ is enhanced by multiple reflection in the transparent materials, that is, the value of $\theta \chi$ increases considerably at the wavelength where the reflectivity decreases. Although the enhancement peak of $\theta \chi$ does not correspond to the wavelength where R decreases in Fe₄₄B₄ₓFs₂₂ film, the $\theta \chi$ peak in Fe₄₄B₄ₓFs₂₂ corresponds closely to the minimum of R. From this result, it is possible that the peak of $\theta \chi$ might be caused by multiple reflection in the film itself.

4. CONCLUSION

Amorphous Fe-B-F films having various fluorine contents were prepared by reactive sputtering. It was found that these amorphous films include some crystalline phases, identified as FeF₂, in the composition region with more than about 20 at.% F. Furthermore, the films prepared are generally ferromagnetic with Curie temperatures above room temperature. These films show a relatively high saturation magnetization of 60 ~ 140 emu/g, and a relatively high Faraday rotation, $\theta F$, between 3x10⁴ and 1x10⁵ deg/cm at 633 nm. Optical interference occurs in high fluorine compositions of 46 or 52 at.% under $\alpha$: 8x10⁴ cm⁻¹. Consequently, in Fe₄₄B₄ₓFs₂₂ film, the apparent $\theta \chi$ of about 0.7 degree is obtained at about 800 nm. The absorption coefficient $\alpha$ of Fe₄₄B₄ₓFs₂₂ film is above 3x10⁴ cm⁻¹ in the wavelength range 300 to 800nm, and the figure of merit is the value of about 0.1 deg/dB.

From the results of soft X-ray spectra, it is thought that the electronic structure of the Fe-B-F films is very similar to that of pure metallic Fe, in spite of a high fluorine content.

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