RAPID PUBLICATION

Structural Study of Amorphous Tb-Fe-Co Films by X-ray Diffraction

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Atomic structures of amorphous $\text{Tb}_{19}\text{Fe}_{81}$, $\text{Tb}_{20}\text{Fe}_{52}\text{Co}_{28}$, $\text{Tb}_{19}\text{Fe}_{26}\text{Co}_{55}$ and $\text{Tb}_{19}\text{Co}_{81}$ films of $1\text{ }\mu\text{m}$ thickness grown on quartz glass substrate have been studied by X-ray diffraction. Atomic distances and coordination numbers in these films were obtained and the essential structural features of these films appear to be unchanged by the variation of composition. It is found that the transition metals, Fe and Co are in direct contact with the surrounding atoms and preferentially surrounded by Tb. The structural change by annealing at 473 K in the amorphous $\text{Tb}_{20}\text{Fe}_{52}\text{Co}_{28}$ film was also investigated. The interference function of the annealed sample is slightly shifted to higher- Q and the peaks corresponding to the TM-TM and TM-Tb pairs (TM=Fe or Co) in the reduced radial distribution function are enhanced and their locations are shifted to lower- r with increase in annealing time. These results imply that the smaller size transition metals mainly change their position during low-temperature annealing while the variation in the position of Tb atoms having the larger size is not clearly detected.

(Received May 2, 1990)

Keywords: amorphous, thin film, X-ray diffraction, optical disk, radial distribution function, terbium-iron-cobalt, rare earth, transition metal

I. Introduction

Amorphous Tb-Fe-Co alloys prepared in thin film form by sputtering are the leading candidate as the magneto-optical recording media. Numerous studies for their magneto-optical characteristics have been carried out⁽¹⁾. However, the origin of the perpendicular uniaxial magnetic anisotropy has not been well understood yet although several mechanisms are proposed, such as pair-ordering⁽²⁾⁽³⁾, stress induced anisotropy⁽⁴⁾⁻⁽⁶⁾, bond-orientational anisotropy⁽⁷⁾, exchange anisotropy⁽⁸⁾, the single ion model⁽⁹⁾, and so on. In order to find out the presence of any structural anisotropy which may explain the magnetic anisotropy, only a few structural investigations were carried out on the binary Tb-Fe or Tb-Co system⁽¹⁰⁾ or the ternary Tb-Fe-Co system⁽¹¹⁾⁽¹²⁾ by X-ray diffraction. Thus, these facts prompt us to report our own X-ray diffraction results on the structures of as-grown amorphous Tb-Fe-Co alloys with different ratios of Fe to Co.

It is known that the performance of the magneto-optical disk gradually becomes worse after many read/write cycles by laser beam. This degradation is reported to be profoundly correlated with the structural relaxation and/or stress relief of the film by annealing⁽³⁾. Thus, the present paper includes the results of the structural variation with annealing at 473 K in the

$\text{Tb}_{20}\text{Fe}_{56}\text{Co}_{28}$ film for the practical use.

II. Experimental

Amorphous $\text{Tb}_{19}\text{Fe}_{81}$, $\text{Tb}_{20}\text{Fe}_{52}\text{Co}_{28}$, $\text{Tb}_{19}\text{Fe}_{26}\text{Co}_{55}$ and $\text{Tb}_{19}\text{Co}_{81}$ films of $1\text{ }\mu\text{m}$ thickness were prepared on a quartz glass substrate by DC magnetron sputtering with DC power of 500 W providing the deposition rate of about 1.51 nm/s (91 nm/min). The cathode target was of an Fe disk with a diameter of 203 mm, on which Tb and Co chips of 100 or 25 mm² were placed to obtain a desired composition. The background pressure was always less than 1×10^{-6} Torr prior to letting in Ar gas. Total gas pressure during the sputtering was 6.9 mTorr. In order to prevent the oxidation, the films were covered by a SiN_x film of about 90 nm thickness grown by reactive sputtering with DC power of 1 kW providing the deposition rate of about 1.5 nm/s, using Ar- N_2 gas of 6.0 mTorr and a Si target.

The composition of the films were determined by inductively coupled plasma (ICP) spectrometer within an accuracy of ± 1 at.%. The $\text{Tb}_{20}\text{Fe}_{52}\text{Co}_{28}$ films covered by the SiN_x film were annealed for 2 and 24 h at 473 K. Densities of the $\text{Tb}_{19}\text{Fe}_{81}$, $\text{Tb}_{20}\text{Fe}_{52}\text{Co}_{28}$, $\text{Tb}_{19}\text{Fe}_{26}\text{Co}_{55}$ and $\text{Tb}_{19}\text{Co}_{81}$ films estimated from their thicknesses and weights are 8.17, 8.11, 8.36 and 8.60 Mg m^{-3} , respectively. Since the uncertainty of the thickness and weight of the films is about a couple of percent, the errors of these densities are estimated to be about a few percent. The change of the density in the annealed samples was ignored because it is, if any, less than 0.5% at most⁽¹³⁾ which is far less than the detectable limit of the densities

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for the present samples. It may be added, within the best knowledge of the present authors, that only the density of amorphous TbFe_2 ⁽¹⁴⁾ has been reported; 8.3 Mg m^{-3} . This value is close to the ones obtained in the present samples by taking account of the experimental errors.

X-ray scattering intensities were measured in the Seemann-Bohlin geometry with a fixed incidence of 1.3° . Monochromatic Mo $K\alpha$ radiation obtained by a flat Ge(111) single crystal in the incident beam was used with fine vertical soller slits in front of the scintillation counter to limit the horizontal divergence within 0.57° . Since the intensity of the sample (I_t) is a sum of the intensities from the film and the substrate, the scattering intensity from the film alone (I_f) was obtained by subtracting the intensity of the substrate (I_s) corrected for the absorption by the amorphous film from the intensity I_t ⁽¹⁵⁾, that is,

$$I_f = I_t - \exp \left\{ -2\mu t \frac{\sin \theta \cos (\theta - \alpha)}{\sin \alpha \sin (2\theta - \alpha)} \right\} I_s \quad (1)$$

where 2θ is the angle between the incident and diffracted beams, μ the linear absorption coefficient of the film, t the thickness of the film, and α the incidence angle.

The intensity I_f was corrected for the polarization and absorption, and converted to absolute units by the generalized Krogh-Moe-Norman method⁽¹⁶⁾ with the atomic scattering factors tabulated in ref. (17) including the anomalous dispersion terms⁽¹⁸⁾. Then, the coherent intensity in absolute units, $I_{\text{eu}}^{\text{coh}}(Q)$ was obtained by subtracting the theoretical values of the Compton scattering⁽¹⁹⁾ with the Breit-Dirac recoil factor. From the resultant coherent intensity $I_{\text{eu}}^{\text{coh}}(Q)$, the total structure factor $S(Q)$ of the film was evaluated⁽¹³⁾.

$$S(Q) = \{I_{\text{eu}}^{\text{coh}}(Q) - \langle f^2 \rangle + \langle f \rangle^2\} / \langle f \rangle^2 \quad (2)$$

$$\langle f \rangle = \sum_{j=1}^n c_j f_j \quad (3)$$

$$\langle f^2 \rangle = \sum_{j=1}^n c_j f_j^2 \quad (4)$$

where $Q = 4\pi \sin \theta / \lambda$, λ is the wavelength, c_j and f_j are the atomic fraction and the atomic scattering factor of the j th element, and n is the total number of the constituent elements. The values of $S(Q)$ less than 10 nm^{-1} have been smoothly extrapolated to $Q=0$. The effect of the extrapolation and the truncation up to the maximum Q -values (Q_{max}) of 153 nm^{-1} is known to give no critical contribution in the calculation of the radial distribution function (RDF) by the Fourier transformation.

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{Q_{\text{max}}} Q i(Q) \sin(Qr) dQ \quad (5)$$

where the function of $i(Q)$ is the interference function and defined by $i(Q) = S(Q) - 1$, $\rho(r)$ is the radial number density function and ρ_0 is the average number density of the film.

III. Results and Discussion

The reduced interference functions $Q i(Q)$ of the as-

Fig. 1 Interference functions $Q i(Q)$ in as-grown amorphous $\text{Tb}_{19}\text{Fe}_{81}$ (curve a), $\text{Tb}_{20}\text{Fe}_{52}\text{Co}_{28}$ (curve b), $\text{Tb}_{19}\text{Fe}_{26}\text{Co}_{55}$ (curve c), $\text{Tb}_{19}\text{Co}_{81}$ (curve d) films.

grown $\text{Tb}_{19}\text{Fe}_{81}$, $\text{Tb}_{20}\text{Fe}_{52}\text{Co}_{28}$, $\text{Tb}_{19}\text{Fe}_{26}\text{Co}_{55}$ and $\text{Tb}_{19}\text{Co}_{81}$ films are shown in Fig. 1. These profiles correspond to a typical non-crystalline structure and consist of a relatively sharp first peak followed by small diffuse peaks. The first peak is slightly shifted to higher Q with increase in Co concentration, which qualitatively interpreted by replacing Fe for the smaller radius of Co. It appears, however, the overall atomic structure is unchanged by finding good coincidence at the subsequent small peaks of each film up to high Q region.

The radial distribution functions (RDFs) obtained by the Fourier transformation of the interference functions in Fig. 1 are shown in Fig. 2. Referring to Goldschmidt's radii⁽²⁰⁾ (Fe: 0.127 nm, Co: 0.126 nm, Tb: 0.177 nm), the first three peaks can be associated to the TM-TM, TM-Tb and Tb-Tb pairs, respectively, where TM denotes the transition metal Co or Fe. These peaks were fitted by assuming Gaussian for their peak shapes. An example of the result of this fitting procedure is shown in the three shaded Gaussian peaks for the curve (a) in Fig. 2. The atomic distances were estimated from the positions of the apexes of the fitted curves and the coordination numbers were calculated from the area under the fitted profiles. The results are summarized in Table 1. In this process, Fe and Co in the ternary alloys were not distinguished since their scattering powers for X-rays and atomic sizes resembles each other. Although there is no unique procedure for estimating the experimental errors of the coordination numbers, the errors of the coordination numbers due to counting statistics in the intensity measurements were estimated to be about $\pm 8\%$ at most in all samples along the way similar to the previous work⁽²¹⁾. An error for the atomic distance is about $\pm 0.002 \text{ nm}$. As it was expected for the interference functions of the as-grown films in Fig. 1, no significant difference in the coordination numbers and atomic distances of all the films is observed except for a slight decrease in the atomic

Fig. 2 Radial distribution functions (RDFs) in as-grown amorphous Tb₁₉Fe₈₁ (curve a), Tb₂₀Fe₅₂Co₂₈ (curve b), Tb₁₉Fe₂₆Co₅₅ (curve c), Tb₁₉Co₈₁ (curve d) films.

Table 1 Coordination numbers (*N*) and atomic distances (*r*) in as-grown amorphous Tb₁₉Fe₈₁, Tb₂₀Fe₅₂Co₂₈, Tb₁₉Fe₂₆Co₅₅ and Tb₁₉Co₈₁ films.

Samples	TM-TM <i>r</i> (nm)	<i>N</i>	TM-Tb <i>r</i> (nm)	<i>N</i>	Tb-TM <i>N</i>	Tb-Tb <i>r</i> (nm)	<i>N</i>
Tb ₁₉ Fe ₈₁	0.252	6.8	0.302	2.9	(12.3)	0.341	3.9
Tb ₂₀ Fe ₅₂ Co ₂₈	0.256	7.3	0.306	3.1	(12.3)	0.349	3.9
Tb ₁₉ Fe ₂₆ Co ₅₅	0.250	7.3	0.300	3.0	(12.7)	0.348	3.6
Tb ₁₉ Co ₈₁	0.248	7.3	0.295	2.9	(12.5)	0.336	3.6

distances for the TM-TM and TM-Tb pairs in the binary Tb₁₉Co₈₁ alloy in comparison with those in the binary Tb₁₉Fe₈₁ alloy. This is readily understood in the qualitative manner by the fact that the atomic size of Co is slightly smaller than that of Fe.

The atomic distance of the TM-TM pairs in the amorphous films is shorter than the distance of 0.260 nm between the near-neighboring Fe-Fe pairs in crystalline TbFe₂⁽²²⁾ and is close to the sum of the Goldschmidt radii of the transition metals. The atomic distance for the Tb-TM pairs in the amorphous films corresponds to the values of 0.305 nm in the crystalline TbFe₂ as well as the value of a sum of the Goldschmidt radii of the transition metals and Tb. This indicates that the transition metals, Fe and Co are in direct contact with the surrounding atoms. Thus, from the coordination numbers in Table 1, it is estimated that the transition metals are surrounded by about 10 atoms on average. Since the atomic fraction of Tb is about 20%, the Fe or Co atoms will have about 2 Tb atoms for statistical distribution of the constituent elements. However, the number of Tb atoms around the transition metal is about 3, which is 1.5 times larger than the value expected in the random mixture. This indicates

the tendency of compound formation, that is, the Tb-atoms are preferentially surrounded by Fe-atoms and vice versa. The distance between the Tb atoms in the amorphous films is appreciably larger than the distance of 0.318 nm in the crystalline TbFe₂.

The amorphous Tb₂₀Fe₅₂Co₂₈ film for the practical use was chosen to investigate the annealing effect on its atomic structure. The structural change by annealing is known extremely delicate and a change of the scattering profile by annealing is not so distinct in the interference function $Q_i(Q)$. Therefore, taking the difference between the interference functions of the as-grown and the annealed film, the variations of the profile were investigated. In Fig. 3, the curves (b) and (c) were obtained by subtracting the interference function of the as-grown film (the curve (a) in Fig. 3) from those of the films annealed for 2 and 24 h at 473 K, respectively. It has generally been reported that the amplitude of the oscillations in the interference function of amorphous alloys is enhanced with the annealing time in the structural relaxation process due to low-temperature annealing⁽¹³⁾. However, as clearly seen in the first peaks of curves (b) and (c) which are denoted with arrows in Fig. 3, these ternary alloys show a different change. With increase in the annealing time, this peak becomes sharper and is shifted to higher- Q . Taking account of the experimental evidence that the first peak of the interference function $i(Q)$ is shifted to larger Q -values for increasing Fe concentration in amorphous Tb-Fe alloys⁽¹¹⁾, the difference of the interference functions observed higher Q -side of the first peak is attributed to any change of the partial structures including the transition metals of the smaller sizes, although the details of the actual structural variations can not be drawn only from the present results. In other words, the transition metals play a dominant role while the larger size Tb atoms stay still during low-temperature annealing.

Increase in the amplitude of the oscillations for $Q_i(Q)$ is also observed in those for $G(r)$ in several amorphous

Fig. 3 Changes $Q\Delta i(Q)$ (curves b and c) correspond to the difference between the interference functions $Q_i(Q)$ in amorphous Tb₂₀Fe₅₂Co₂₈ film annealed for 2 and 24 h at 473 K, and the as-grown film (curve a), respectively.

Fig. 4 Changes $\Delta G(r)$ (curves b and c) correspond to the difference between the reduced radial distribution functions $G(r)$ in amorphous $\text{Tb}_{20}\text{Fe}_{52}\text{Co}_{28}$ film annealed for 2 and 24 h at 473 K, and the as-grown film (curve a), respectively.

alloys during the low-temperature annealing⁽¹³⁾. However, the $G(r)$ in this ternary alloy shows a change different from the ordinary case as it was observed in the $Q_i(Q)$. Similarly, the $G(r)$ of the as-grown sample (curve (a) in Fig. 4) and the differences between the $G(r)$ of the samples annealed for 2 and 24 h at 473 K, and the as-grown sample are shown in curves (b) and (c) of Fig. 4. The difference is apparently seen in the first two peaks at about 0.250 and 0.300 nm designated with the arrows, which correspond to the TM-TM and TM-Tb pairs as indicated in the curve (a) at the top of Fig. 4. Thus, it is found that the near-neighbor structure around the transition metals is changed by annealing. This result is consistent with that deduced from the differences of the $Q_i(Q)$ in Fig. 3. The near-neighboring correlations of the TM-TM and TM-Tb pairs change although that for the Tb-Tb pairs does not show a significant difference. Also the positions of the TM-TM and TM-Tb pairs are shifted to lower- r . With increasing in the annealing time, the difference for the TM-TM pairs becomes prominent rather than that for the TM-Tb pairs. Since α ferrite precipitates are reported at higher temperature annealing in amorphous $\text{Tb}_{20}\text{Fe}_{80}$ ⁽²³⁾, the tendency of the TM-TM segregation might be observed even in lower-temperature annealing.

As the origin of the degradation of the magnetic anisotropy, the two major mechanisms are proposed⁽³⁾. One is the change in local ordering and another is the stress relief during the annealing process. These two ma-

jor effects do not separately appear in the present X-ray diffraction data. However, it can be worth mentioning from the present work that a certain structural change definitely occurs in the annealed sample and transition metals whose size is smaller than Tb appear to play a dominant role during the annealing process. In order to discuss the details of the structural change during annealing, further analysis is required, including the anomalous X-ray scattering or EXAFS studies to reveal the variation of the environmental structures around each constituent elements.

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