SOFT MAGNETIC PROPERTIES OF COMPOSITIONALLY MODULATED Fe-(Nb,Zr,Ta,Ti)-N FILMS

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Abstracts--- Magnetic head materials are required to have high saturation magnetization and the thermal stability of soft magnetic properties. We have developed compositionally modulated nitride films (CMNF). The CMNF composed of Fe-(Nb,Zr,Ta,Ti)-N have high saturation magnetization and Fe-Zr-N shows especially the high thermal stability of soft magnetic properties. Nb and Ta addition to Fe-Zr-N is so effective in preventing it from surface oxidization during annealing that the CMNF composed of Fe-(Nb,Ta)-Zr-N have been studied. Fe-Nb-Zr-N have high saturation magnetization M_s ($M_s \geq 1.7T$), high initial permeability μ' ($\mu' \geq 3000$) and small saturation magnetostriction λ_s ($|\lambda_s| < 1 \times 10^{-6}$) after 600°C annealing in a magnetic field. The CMNF composed of Fe-(Nb,Ta)-Zr-N are good for practical use of magnetic recording heads.

INTRODUCTION

It is necessary to improve the performance of magnetic recording heads in order to achieve high density recording. Magnetic head materials are required to have high saturation magnetization to cope with high density recording by using high coercivity media and narrow gap recording heads. The saturation magnetization of Co-based amorphous alloys and Fe-Al-Si (Sendust), which are representative of magnetic head materials, is about 1 T. The upper limit of saturation magnetization in amorphous alloys is based on a thermal stability of soft magnetic properties, because amorphous alloys having high saturation magnetization (>1 T) lose soft magnetic properties at high temperature annealing and the manufacturing of magnetic heads requires a glass bonding at considerably high temperature process. It is necessary that magnetic head materials show good soft magnetic properties after high temperature annealing.

We reported compositionally modulated nitride alloy films^{[1]-[4]} (CMNF), which are multilayer films composed of nitride layers and non-nitride layers. CMNF have high saturation magnetization and high thermal stability of soft magnetic properties, suited for manufacturing magnetic heads. There are Co-based and Fe-based systems in CMNF, which include a variety of metal elements and metalloid elements that have a strong chemical affinity with nitrogen. The CMNF composed of Fe-M-N ($M=Zr,Nb,Ta,Ti$) have especially high saturation magnetization in CMNF.

In these Fe-M-N systems the CMNF composed of Fe-(Nb,Ta)-Zr-N have not only good magnetic properties but also good practical properties such as the high thermal stability and high corrosion resistance. We report magnetic properties of the CMNF composed of Fe-(Nb,Ta)-Zr-N in this paper.

EXPERIMENT

The films were prepared by RF sputtering using alloy targets. The CMNF laminated with nitride layers and non-nitride layers were formed by mixing nitrogen gas periodically into Argon gas during sputtering. The total sputtering gas pressure were kept at 1.6 Pa during the formation of nitride layers. The ratio of nitrogen gas in the sputtering gas is defined by the nitrogen gas partial pressure ratio $P_n(\%)$, which is expressed by a percentile as the ratio of the nitrogen gas versus the total sputtering gas. The thickness of a couple of a nitride layer and a non-nitride layer in CMNF is expressed by the wavelength of compositional modulation λ (nm). In this paper the thickness of a nitride layer is equal to that of a non-nitride layer and the wavelength of compositional modulation λ is about 20nm. The CMNF composed of Fe-M-N show good soft magnetic properties when $\lambda \leq 100(\text{nm})$. The film thickness of each alloy film was 1~8 μm . The annealing of the films was carried out in a vacuum of 3mPa or less and in a static magnetic field of 40 kA/m. The annealing time was 1 hour.

Saturation magnetization of the films were measured with VSM. The coercivity were measured with an ac B-H loop tracer at 60Hz. The initial permeability μ' of the films was measured by using a shunt core method at 5MHz. Saturation magnetostriction was measured with an optical cantilever method or estimated from the difference of anisotropy field in applying bending stress to the films, using Young modulus of 150GPa. Depth profiles of the films were studied with Auger electron spectroscopy (AES). X-ray diffraction and a transmission electron microscope (TEM) were also used to study the film structure.

FILM COMPOSITION

Average film composition were measured with ICP and Rutherford backscattering spectrometry (RBS) using carbon substrates.

Fig.1 shows the nitrogen gas partial pressure ratio dependence of the nitrogen content in the films. The CMNF represent compositionally modulated nitride films and the SLNF represent single layer nitride films, which are composed of Fe-Nb-Zr-N. The nitrogen content in the films increases with Pn and tends to saturate with increase of Pn. The nitrogen content in CMNF is about a half of that in SLNF. Precisely speaking, the nitrogen content of the films

Fig.1 Nitrogen gas partial pressure ratio dependence of the content of nitrogen.

depends on the content of Nb and Zr as well as on Pn, but the difference of the nitrogen content in films prepared with the same Pn was found to be small.

Fe-M-N (M=Zr,Nb,Ta,Ti)

Fig.2 shows the annealing temperature dependence of coercivity Hc in CMNF composed of Fe-M-N. In these systems good soft magnetic properties are obtained by high temperature annealing. The thermal stability of Fe-Zr-N system is especially superior and is maintained up to 700°C.

Fig.3 shows AES depth profile in the film surface of CMNF after 600 °C annealing. These CMNF have a clear modulation structure having $\lambda = 20(\text{nm})$. It is remarkable that a weak surface oxidation takes place in Fig.3(a) Fe-Zr-N system after annealing and the thickness of the oxidization layer is 30nm. On the other hand the oxide layer thickness of Fe-Ta-N system is less than 10 nm as shown in Fig.3 (b). Fe-Nb-N system also shows small oxidation as Fe-Ta-N system. The CMNF composed of Fe-(Nb,Ta)-Zr-N are found to show little surface oxidation during annealing and have a good corrosion resistance, which is proved by a dipping test in water. The CMNF composed of Fe-(Nb,Ta)-Zr-N systems are good for practical use of magnetic heads.

Fig. 2 Annealing temperature dependence of coercivity.

Fig.3 AES depth profile in the film surface of CMNF after 600°C annealing.

Fe-(Nb,Ta)-Zr-N

Magnetic properties

Fig.4 shows the nitrogen gas partial pressure ratio P_n dependence of coercivity H_c of the CMNF composed of Fe-Nb-Zr-N after 600°C annealing in a static magnetic field. High nitrogen gas partial pressure ratio P_n is required in Zr-less films to obtain low coercivity and good soft magnetic properties are obtained when P_n is 10%.

Fig.4 Nitrogen gas partial pressure ratio dependence of coercivity in Fe-Nb-Zr-N.

Fig.5 shows the composition dependence of coercivity H_c and initial permeability μ' of Fe-(Nb,Ta)-Zr-N systems. The films were prepared in $P_n=10(\%)$ and the film thickness was about $2\mu\text{m}$. These CMNF, which are annealed at 600°C in a static magnetic field, show low coercivity and high initial permeability; Fe-Nb-Zr-N systems shows $\mu' \geq 3000$ and $H_c \leq 20(\text{A/m})$ in Fe content $X \leq 95.5(\text{at.}\%)$. Fe-Nb-Zr-N systems also have the thermal stability maintained up to 700°C.

Fig.6 is an example showing the frequency dependence of initial permeability in the CMNF composed of $(\text{Fe}_{0.928}\text{Nb}_{0.03}\text{Zr}_{0.042})_{89}\text{N}_{11}$ with a variety of film thickness d . The films have high permeability, but the permeability in the thick film decreases in high frequency region because of the eddy current loss as shown in $d=8(\mu\text{m})$. The electric resistivity of these films is about $0.56\mu\Omega\cdot\text{m}$, which is lower than amorphous alloys.

Fig.7 shows the composition dependence of saturation magnetization M_s in CMNF, which are composed of above-mentioned Fe-(Nb,Ta)-Zr-N and Fe-Zr-N after 600°C annealing. The saturation magnetization M_s of these CMNF are more than 1.5T and much higher than that of Fe-Al-Si and Co-based amorphous alloys: the CMNF composed of $(\text{Fe}_{0.928}\text{Nb}_{0.03}\text{Zr}_{0.042})_{89}\text{N}_{11}$ have $M_s \geq 1.7(\text{T})$. It is also interesting that the saturation magnetization decrease due to Nb content increase is smaller than that due to Zr content increase.

Fig.5 Composition dependence of coercivity and initial permeability.

Fig. 6 Frequency dependence of initial permeability.

Fig. 7 Composition dependence of saturation magnetization.

The saturation magnetostriction λ_s , which is necessary to be small for practical use of magnetic recording heads, depends on the film composition and annealing condition. Fig.8 shows the composition dependence of saturation magnetostriction λ_s in CMNF composed of Fe-Zr-N and Fe-Nb-Zr-N which were prepared in Pn=10(%) and are annealed at 600°C.

The saturation magnetostriction of Fe-Zr-N and Fe-Nb-Zr-N annealed at the same temperature is small and shifts from a positive value toward a negative value with the increase of Fe content. $(\text{Fe}_x\text{Nb}_3\text{Zr}_{97-x})\text{-N}$ system and $(\text{Fe}_x\text{Nb}_{96-x}\text{Zr}_4)\text{-N}$ system show zero magnetostriction for around $X=92.5(\text{atomic}\%)$ and $X=91.5(\text{atomic}\%)$ as shown in Fig.8. The saturation magnetostriction of CMNF also depends on the annealing temperature. Fig.9 shows the annealing temperature dependence of saturation magnetostriction λ_s of CMNF composed of Fe-(Zr,Nb,Ta)-N.

Fig. 8 Composition dependence of saturation magnetostriction.

Fig. 9 Annealing temperature dependence of saturation magnetostriction.

The saturation magnetostriction of the CMNF shifts from a positive value toward a negative value with increasing annealing temperature. The annealing temperature dependence of the saturation magnetostriction of Fe-(Nb,Ta)-Zr-N was similar to those of these Fe-M-N systems. The magnetostriction in CMNF composed of Fe-(Nb,Ta)-Zr-N can be reduced to be small by appropriate choices of combination of the film composition and the annealing temperature.

The CMNF composed of Fe-(Nb,Ta)-Zr-N have high saturation magnetization M_s , high initial permeability μ' and small saturation magnetostriction λ_s : the CMNF composed of $(\text{Fe}_{0.928}\text{Nb}_{0.03}\text{Zr}_{0.042})_{89}\text{N}_{11}$ shows $M_s \geq 1.7(\text{T})$, $\mu' \geq 3000$ and $|\lambda_s| < 1 \times 10^{-6}$ after 600°C annealing in a static magnetic field.

Film structure

The CMNF composed of $(\text{Fe}_{0.928}\text{Nb}_{0.03}\text{Zr}_{0.042})_{89}\text{N}_{11}$ having $\lambda = 20(\text{nm})$ were prepared in Pn=10(%).

Fig.10 shows the AES depth profile in the CMNF composed of Fe-Nb-Zr-N. The compositionally modulated structure is clearly formed as shown in the as-prepared sample (a). The sample (b) annealed at 600°C has also weak modulation structure. Fig.11 shows the X-ray diffraction pattern of the Fe-Nb-Zr-N. The as-prepared sample (a) has extremely weak peak. Although it is not completely amorphous but crystal, the grain size is very fine. On the other hand, the annealed sample as shown in (b) displays the weak peak of α -Fe and unclear peaks in low angle region. The analysis using an electron beam diffraction showed that the unclear peaks were of nitrides. The grain sizes of α -Fe and nitrides are fine. Fig.12 shows the TEM image of Fe-Nb-Zr-N cross section after 600°C annealing. The Fe-Nb-Zr-N has the layered structure and fine grains of α -Fe. It seems that the layered structure suppressed the grain growth and contributed the thermal stability of the fine grain structure.

It is thought that the magnetic properties of CMNF are closely related to the above-mentioned film structure: the nucleation of α -Fe and the segregation of Fe-rich phase from other elements rich phase are related to the appearance of soft magnetic properties, the increase of saturation magnetization and the change of magnetostriction by annealing.

Fig. 10 AES depth profile of $(\text{Fe}_{0.928}\text{Nb}_{0.03}\text{Zr}_{0.042})_{89}\text{N}_{11}$.

Fig. 11 X-ray diffraction pattern of $(\text{Fe}_{0.928}\text{Nb}_{0.03}\text{Zr}_{0.042})_{89}\text{N}_{11}$.

Fig. 12 TEM image of cross section
in $(\text{Fe}_{0.928}\text{Nb}_{0.03}\text{Zr}_{0.042})_{89}\text{N}_{11}$
after 600°C 60min. annealing.

CONCLUSION

The compositionally modulated nitride films (CMNF) composed of Fe-M-N (M=Nb,Zr,Ta,Ti) were prepared and the following points were clarified.

(1)The CMNF composed of Fe-M-N show good soft magnetic properties by high temperature annealing and the thermal stability of Fe-Zr-N system is especially superior among them and is maintained up to 700°C.

(2)The weak surface oxidization takes place in Fe-Zr-N system after annealing, and Ta and Nb addition to Fe-Zr-N system is effective in preventing the CMNF from surface oxidization. The CMNF composed of Fe-(Nb,Ta)-Zr-N system show little surface oxidization during annealing and have the good corrosion resistance.

(3)The CMNF composed of Fe-(Nb,Ta)-Zr-N have high saturation magnetization M_s , high initial permeability μ' and small saturation magnetostriction λ_s : the CMNF composed of $(\text{Fe}_{0.928}\text{Nb}_{0.03}\text{Zr}_{0.042})_{89}\text{N}_{11}$ shows $M_s \geq 1.7(\text{T})$, $\mu' \geq 3000$ and $|\lambda_s| < 1 \times 10^{-6}$ after 600°C annealing in a static magnetic field.

(4)The CMNF composed of $(\text{Fe}_{0.928}\text{Nb}_{0.03}\text{Zr}_{0.042})_{89}\text{N}_{11}$ show clear modulation structure when they are prepared and show weak modulation structure after annealing. The as-prepared CMNF are not completely amorphous but crystal with fine grains. The films annealed at 600°C. have the fine grain structure of α -Fe and nitrides.

The CMNF composed of Fe-(Nb,Ta)-Zr-N have good magnetic properties and good practical properties such as high corrosion resistance and the high thermal stability of soft magnetic properties. The CMNF enable us to use bonding glass having high melting point in the manufacturing process of magnetic heads.

We have already reported that MIG heads using the CMNF composed of Fe-Nb-Zr-N showed good head performance in hard disc systems^[5]. We hope that the high performance magnetic heads using the compositionally modulated Fe-based nitride films are used for high density recording in the near future.

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