Soft magnetic properties and microstructure of nanocrystalline Fe-Hf-N sputtered films

著者	牧野　彰宏
journal or publication title	IEEE Transactions on Magnetics
volume	31
number	6
page range	3874-3876
year	1995
URL	http://hdl.handle.net/10097/47233

doi: 10.1109/20.489801

Soft Magnetic Properties and Microstructure of Nanocrystalline Fe-Hf-N Sputtered Films

Akihiro Makino and Yasuo Hayakawa

Nagaoka Branch, Central Research Laboratory, ALPS Electric Co., Ltd., Nagaoka 940, Japan

Abstract---- Magnetic properties, structure and electrical resistivity (ρ) of Fe-Hf-N films with a compositional range of 10-17 at.% Hf and 9-28 at.% N were investigated. In an as-deposited state, the high permeability (μ') above 700 at 10MHz is obtained in the compositional range of about 12-14 at.% Hf and about 9-19 at.% N. The highest μ' of 1200 is achieved for $Fe_{72}Hf_{13}N_{15}$ film consisting of the nanoscale bcc grains and the amorphous phase with the high Curie temperature (T_c) due to higher contents of Hf and N than those in the bcc phase. The soft magnetic properties are presumably caused by the reduced effective anisotropy resulting from the effect of the nanoscale bcc grains and the rather high magnetization of the amorphous phase at room temperature which does not inhibit the exchange coupling between the grains. $Fe_{65}Hf_{11}N_{24}$ film with the mixed structure exhibits the saturation magnetic flux density (B_s) of 1.2 T and the flat μ' characteristics of 1000 up to 100 MHz after annealing at 673K for 3 hrs under an uniaxial field. This excellent μ' characteristics originates in the rather large magnetic anisotropy field (H_k) of 510 A/m and the high ρ of 2.7 $\mu\Omega$m which comes from the Hf and N-riched amorphous phase.

I. Introduction

We have been studying on Fe-M-(O, N) films with high permeability at high frequency above 100 MHz for the application to thin-film transformers, inductors and others. It has been reported [1][2] that the Fe-M-O (M=Zr, Hf, Y, Ce) films composed of the nanoscale bcc grains and the amorphous phase with considerably high concentrations of M and O elements exhibit the high frequency permeability due to their higher ρ than those of other soft magnetic alloy films. These soft magnetic properties are presumably caused by the effects of the nanoscale bcc grain size and the considerably higher T_c of the amorphous phase than room temperature. This high T_c results from higher concentrations of M and O in the amorphous phase than those in the bcc phase. The mechanism of the achievement of the soft magnetic properties of the films is considered to be similar to that of the Fe-M-B (M= Zr, Hf and Nb) nanocrystalline alloys [3][4][5] produced by crystallization of the amorphous phases prepared by melt-spun and sputtering technique.

In this paper, microstructure, magnetic properties and the relation between them for Fe-Hf-N films with a large content of 10 -17 at.% Hf and 9 -28 at.% N are presented.

II. Experimental procedure

Fe-Hf-N films with about 2 μm in thickness were deposited onto partially crystallized glass substrates by rf reactive sputtering technique in mixed atmosphere of pure Ar and N. The substrates were indirectly water-cooled during deposition. The Fe and Hf contents are determined by the inductively coupled rf plasma atomic emission spectrometry (ICP) and electron probe micro analysis. The N content was estimated by the auger electron spectroscopy. Any considerable change in the film composition was not observed with the annealing. The films were annealed at 673K for 3hrs under an uniaxial field (Uniaxial Field Annealing ; UFA) of 160 kA/m in vacuum better than 10^{-3} Pa to induce the uniaxial anisotropy.

The film structure was observed by X-ray diffractometry using Co-Kα radiation and field-emission-type 200 kV transmission electron microscopy (JEM-2010F) combined with nano-beam electron diffraction and energy dispersive X-ray spectroscopy (EDX) using a beam diameter of 1nm. Saturation magnetic flux density (B_s) and coercivity (H_c) were measured with a vibrating sample magnetometer (VSM) under an external field of 800 kA/m and a B-H loop tracer under an applied field of 1.6 kA/m, respectively. Magnetic anisotropy field (H_k) and saturation magnetostriction (λ_s) were determined with a 50Hz B-H tracer and by the optical cantilever method under an applied field of 4 kA/m, respectively. The parallel line technique [6] was used to measure μ' and μ" up to 500 MHz. Electrical resistivity (ρ) was measured by conventional four probe method. All the measurements were carried out at room temperature.

III. Results and Discussion

A. Structure and Electrical resistivity

Figure 1 shows the compositional dependence of the structure determined by X-ray diffractometry and ρ for as-deposited Fe-Hf-N films. A mixed structure composed of bcc and an amorphous phases are formed in the compositional range below 15 at.% Hf and 23 at.% N, which indicated by the gray region. Above these contents, a mostly single amorphous phase is obtained. The detailed structure observed by high-resolution electron microscopy (HR-TEM) with nano-beam analysis is shown in Fig. 2, as exemplified for as-deposited $Fe_{72}Hf_{13}N_{15}$ and $Fe_{65}Hf_{11}N_{24}$. The mixed structure consisting of bcc grains with about 10 nm in diameter and an amorphous phase is revealed in Fig. 2 (a). The amorphous phase contains the larger amounts of Hf and

0018-9464/95$04.00 © 1995 IEEE

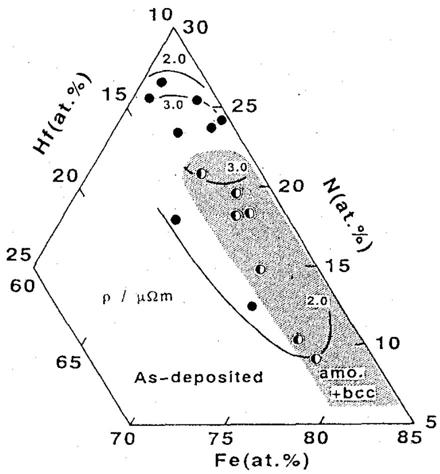

Fig. 1 Compositional dependence of the structure and the ρ for as-deposited Fe-Hf-N films.

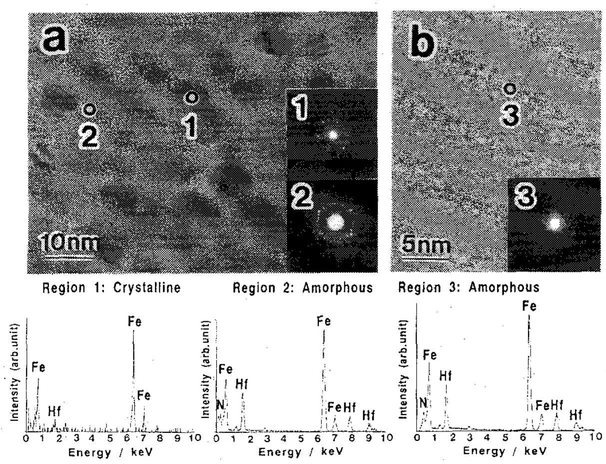

Fig. 2 HR-TEM images of as-deposited $Fe_{72}Hf_{13}N_{15}$ (a) and $Fe_{65}Hf_{11}N_{24}$ (b) films together with nano-beam electron diffraction patterns and EDX spectra.

N than those of the bcc phase. Fig. 2 (b) indicates the amorphous structure.

The ρ has a tendency to increase with increase in N content and reaches the highest value of 4.5 $\mu\Omega$ m for $Fe_{65}Hf_{11}N_{24}$ film which has the amorphous structure, as shown in Fig. 2 (b). With further increase in N content, the ρ decreases. The highest ρ value is considerably higher than those of ordinary Fe based amorphous alloys but much less than that of $Fe_{46}Hf_{18}O_{36}$ film we have already reported [1].

B. Magnetic Properties

The compositional dependence of B_s and T_c of the amorphous phase for as-deposited Fe-Hf-N films is shown in Fig. 3. In the compositional range above 15 at. % Hf where the amorphous structure is formed, the films show the lower B_s values than those in the range below the Hf content,

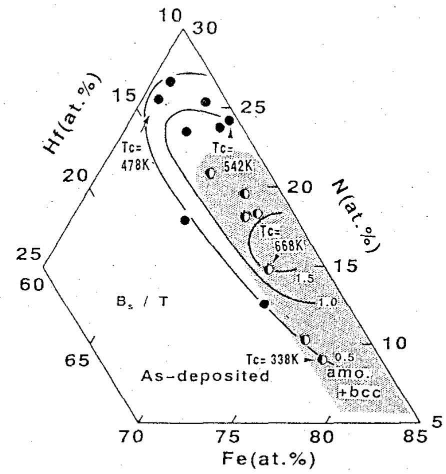

Fig. 3 Compositional dependence of the Bs and the Tc of amorphous phase for as-deposited Fe-Hf-N films.

presumably because of their low T_c of the phase owing to the inver effect [7]. The T_c of the amorphous phase have a tendency to be high as N content is large, and reaches the maximum value of 668K. The increase in T_c causes the increase in the magnetization at room temperature for the amorphous phase. It is assumed that the volume fraction (V_f) of the bcc phase that have higher magnetization than that of the amorphous phase decreases with increase in N content for the films with the mixed structure. Therefore, it is considered that the compositional dependence of B_s can be explained by the dependence the T_c of the amorphous phase and the V_f of the bcc phase.

Figure 4 shows the compositional dependence of λ_s and μ' at 10 MHz for as-deposited Fe-Hf-N films. The relatively large λ_s is obtained in the compositional range of the N content above 23 at. % where the single amorphous phase

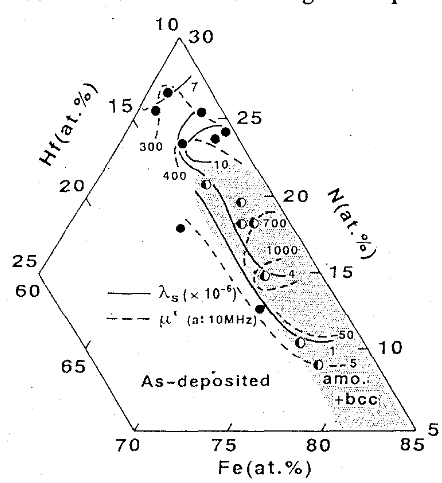

Fig. 4 Compositional dependence of λ s and μ' at 10MHz for as-deposited Fe-Hf-N films.

structure is formed. The high μ' above 700 and the highest value of 1200 for $Fe_{72}Hf_{13}N_{15}$ are obtained with the mixed structure composed of the nanoscale bcc grains and the high T_c amorphous phase, as shown in Fig. 2 (a). Comparing the μ' and the λ_s, the low λ_s does not necessarily bring about the high μ'. It has been reported that the mixed structure of the nanoscale bcc grains and the amorphous phase with the rather high T_c exhibits soft magnetic properties in the nanocrystalline Fe-M-B (M= Zr, Hf, Nb) alloys and the Fe-M-O (M= Hf, Zr, Y, Ce) alloy films, because of the reduced effective anisotropy [8] caused by the combined effect of the nanoscale bcc grains and the amorphous phase with rather high T_c which does not inhibit the exchange coupling between the grains. Therefore, it is supposed that the reason for the soft magnetic properties in the Fe-Hf-N films is similar to that in the above-mentioned nanocrystalline alloys.

In order to improve the soft magnetic properties, the UFA treatment was carried out. Figure 5 shows the frequency dependence of μ', μ'', B_s, H_c, H_k, λ_s, and ρ of annealed $Fe_{72}Hf_{13}N_{15}$ and $Fe_{65}Hf_{11}N_{24}$ films which have the mixed structure and the amorphous structure in the as-deposited state, respectively. After the annealing at 673 K for 3 hrs under an uniaxial field of 160 kA/m, the grain size of the bcc phase increases by about several times compared with as-deposited state for $Fe_{72}Hf_{13}N_{15}$, and a small amount of bcc phase with grain size of 1-2 nm appear in $Fe_{65}Hf_{11}N_{24}$. The B_s of 1.5 T, the H_c of 28 A/m, the μ' of 3500 at 10MHz and 1700 at 100MHz are obtained for $Fe_{72}Hf_{13}N_{15}$. The $Fe_{65}Hf_{11}N_{24}$ film exhibits the flat μ' characteristics of 1000 and reduced μ'' up to 100MHz. This results from the higher ρ of 2.7 $\mu\Omega$m and H_k of 510 A/m than those of $Fe_{72}Hf_{13}N_{15}$. These high ρ value is inferred to be responsible for the amorphous phase occupying the major part of that film. It is to be noticed that the Fe-Hf-N films have higher μ' in the high frequency range above 50 MHz. Therefore, they are thought to be useful for high frequency applications.

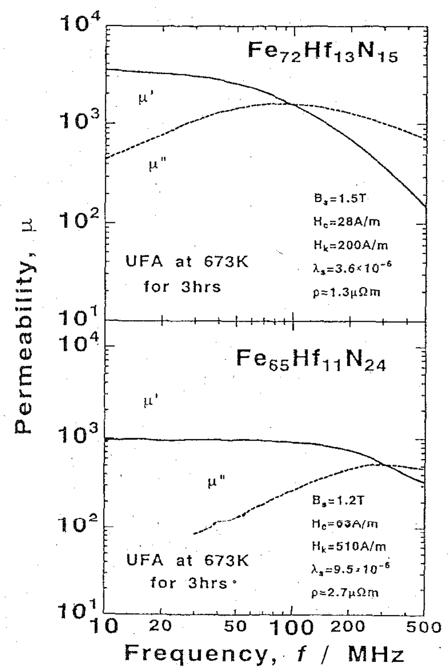

Fig. 5 Frequency characteristics of μ' and μ'' for $Fe_{72}Hf_{13}N_{15}$ and $Fe_{65}Hf_{11}N_{24}$ films annealed at 673K for 3hrs under applied field of 160kA/m.

IV. Conclusions

The microstructure, magnetic properties and ρ of Fe-Hf-N films were studied. The high μ' of 1200 at 10MHz is obtained in the as-deposited structure consisting of the nanoscale bcc grains and the Hf, N-riched amorphous phase with the high T_c. The good soft magnetic properties may be closely related to the mixed structure of the nanoscale bcc grains and the rather high magnetization of the amorphous phase at room temperature for the films. After annealing at 673 K for 3 hrs under an uniaxial field, the B_s of 1.5 T and 1.2 T, the H_c of 28 A/m and 63 A/m, the μ' of 1700 and 1000 at 100MHz , and the ρ of 1.3 $\mu\Omega$m and 2.7 $\mu\Omega$m are obtained for $Fe_{72}Hf_{13}N_{15}$ and $Fe_{65}Hf_{11}N_{24}$ films , respectively. In particular, the $Fe_{65}Hf_{11}N_{24}$ film shows the flat characteristics of μ' and reduced μ'' up to 100 MHz due to the high ρ and the high H_k.

References

[1] A. Makino and Y. Hayakawa, " Sputtered Fe-Hf-O films with high electrical resistivity and good soft magnetic properties", *Mater. Sci. Eng.*, Vol. A181/A182, pp. 1020-1024, 1993.

[2] Y. Hayakawa and A. Makino, " SOFT MAGNETIC PROPERTIES OF Fe-M-O (M= Hf, Zr, Y, Ce) FILMS WITH HIGH ELECTRICAL RESISTIVITY", *NanoStructured Materials*, in press.

[3] K. Suzuki, A. Makino, A. Inoue and T. Masumoto, "Low core losses of nanocrystalline Fe-M-B (M=Zr, Hf or Nb) alloys", *J. Appl. Phys.*, Vol. 74, pp. 3316-3322, 1993.

[4] A. Makino, A. Inoue and T. Masumoto, " Nanocrystalline Soft magnetic Fe-M-B (M= Zr, Hf, Nb) alloys Produced by Crystallization of Amorphous phase", *Mater. Trans. JIM.*, in press.

[5] A. Makino, K. Suzuki, A. Inoue and T. Masumoto, " Soft Magnetic Properties of bcc Fe-Zr-B Sputtered Films with Nanoscale Grain Size", *Mater. Trans. JIM.*, Vol. 33, pp. 80-86, 1992.

[6] T. Kimura, M. Mitera, S. Terasaka, M. Nose, F. Matsumoto, H. Matsuki, H. Fujimori and T. Masumoto, " System for Measuring Thin-Film Permeability by Using a Parallel Line", *J. Magn. Soc. Jpn.*, Vol. 17, pp. 497-502, 1993 (in Japanese).

[7] K. Fukamichi and H. Hiroyoshi, "Forming Ability, Thermal Expansion and Electrical Resistance Minimum of Fe-Metal Binary Amorphous Alloys", *Sci. Rep. RITU*, Vol. 32, pp. 154-167, 1985.

[8] G. Herzer, " GRAIN SIZE DEPENDENCE OF COERCIVITY AND PERMEABILITY IN NANOCRYSTALLINE FERROMAGNETS ", *IEEE Trans. Magn.*, Vol. 26, pp. 1397 - 1402, 1990.