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Phase transformations, magnetic and magnetoresistive properties of FeCoNi–N thin films

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Abstract

The saturation magnetization, coercive force, magnetic anisotropy field, resistivity, magnetoresistance and phase transformations of sputtered Fe15Co20Ni65–N thin films have been investigated. The considerable changes in these properties including formation of a non-magnetic state have been found for films deposited at high nitrogen pressure in Ar + N_2 plasma. It is found that vacuum annealing can cause partial recovery of film properties. Both the film thickness and the presence of the protective covering also affect this process. The change in the film properties may be explained by the structure and the phase transformations taking place in these films.

Keywords: Thin films; Magnetic properties

1. Introduction

It is well known that nitrogenation is a very efficient way to change the properties of magnetic materials [1]. The most consistent investigation in this field has been made for an Fe–N system. One of the latest considerable achievements is the preparation of $Fe_{16}N_2$ single-crystal films exhibiting a giant magnetic moment [2]. The nitrogen contamination of permalloy films has been studied by a number of researchers [3–6]. However, this effect for ternary alloy (FeCoNi) films having a large anisotropy of magnetoresistivity (AMR) has been investigated insufficiently. In this paper we report the results of a study of the effect of nitrogen on magnetic and magnetoresistive properties and phase composition of the Fe15Co20Ni65 thin polycrystal films. These non-magnetostriction films have relatively large induced magnetic anisotropy, low coercive force and high AMR [7–9]. This collection of the properties arouses great interest in these films for technical application [10].

2. Experimental

The films studied were prepared by r.f. diode sputtering of an Fe15Co20Ni65 target in an Ar–N_2 atmosphere. The system base pressure was 10^{-6} Torr. The partial nitrogen pressure P_{N_2} was varied by nitrogen flow rate at a fixed gas mixture pressure of 10^{-3} Torr. The films were deposited on single-crystal silicon plates heated to 200 °C and covered by an SiO_2 layer. The deposition rate was 0.21 nm s^{-1} and the thickness L_m of the films was 40–50 nm. The preparation and the 1 h vacuum annealing (T_a = 350 °C) of the films were carried out in the external magnetic field of 100 Oe applied parallel to the substrate.

The measurements of coercive force H_c, magnetic anisotropy field H_a and saturation magnetization M_s were performed by a magnetic hysteresis loop tracer, vibrating sample magnetometer and torquemeter respectively. The magnetoresistive characteristics were measured by a two-probe method on the stripe-form samples in magnetic fields up to 200 Oe. The phase composition and the structure of the films were analysed with a JEM 200 CX electron microscope.

3. Results and discussion

Fig. 1 shows the saturation magnetization of films as-sputtered and annealed at 350 °C as a function of the nitrogen partial pressure in the gas mixture. It is

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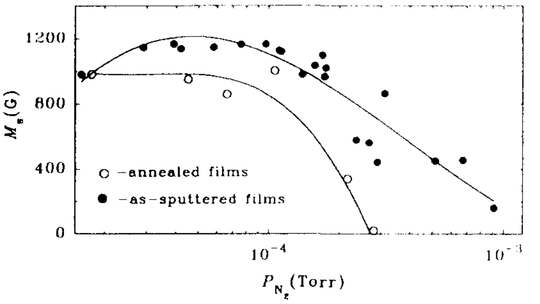

Fig. 1. Dependence of saturation magnetization on nitrogen partial pressure for as-sputtered and annealed films.

seen that the magnetization of as-sputtered film changes slightly if prepared at low P_{N_2}. However, M_s decreases drastically when P_{N_2} exceeds a critical value of 10^{-4} Torr. Finally, these films become non-magnetic with increasing P_{N_2}. A similar trend in this behaviour has been noted previously for Fe20Ni80 films [6].

The magnetization of annealed films behaves differently. First, the tendency of M_s to change non-monotonically should be noted when nitrogen pressure increases at low P_{N_2}. A slight maximum in the $M_s(P_{N_2})$ dependence is expressed. However, the existing increase in magnetization is more than the measurement error that is about 100 G. Second, the reduction in magnetization begins at larger values of P_{N_2} and proceeds in a less drastic way as compared with the as-sputtered films. As a result, we have the situation where as-sputtered films become non-magnetic but after annealing their magnetization is partially restored at $P_{N_2} > 2.3 \times 10^{-4}$ Torr.

Transmission electron microscopy has shown that only one f.c.c. phase appears in both as-sputtered and annealed films prepared at $P_{N_2} < 10^{-4}$ Torr. Its parameters, determined from the corresponding electron diffraction pattern shown in Fig. 2(a), are very close to those of the γ phase of Fe15Co20Ni65. The presence of other phases that might be responsible for the increase in M_s in the annealed films has not been detected. The possible change in electron structure of the material due to the introduction of nitrogen has not been a subject of analysis.

Fig. 2(b) shows a typical electron diffraction pattern of the films obtained at relatively high P_{N_2}. Its analysis indicates well that a γ' phase and, to a lesser extent, an ε phase which are similar to a Fe_4N and $Fe_{2-3}N$ [11] form and become dominant with the increase in nitrogen pressure. However, unlike the iron nitrides, these phases are obviously non-magnetic, since the decrease in magnetization in the films takes place with their appearance. The recovery of magnetization on annealing is accompanied by the restoration of a γ phase.

The change in phase composition affects not only the magnetic properties of the films but their electrical properties as well. Fig. 3(a) shows the dependences of electrical resistivity $\rho_0 = \frac{1}{3}\rho_\parallel + \frac{2}{3}\rho_\perp$ on the nitrogen partial pressure for as-sputtered and annealed films.

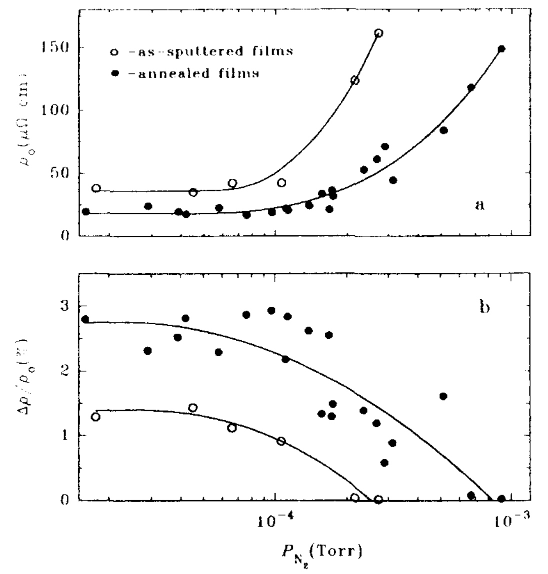

Fig. 3. Dependence of (a) electrical resistivity and (b) magnetoresistive ratio for as-sputtered and annealed films.

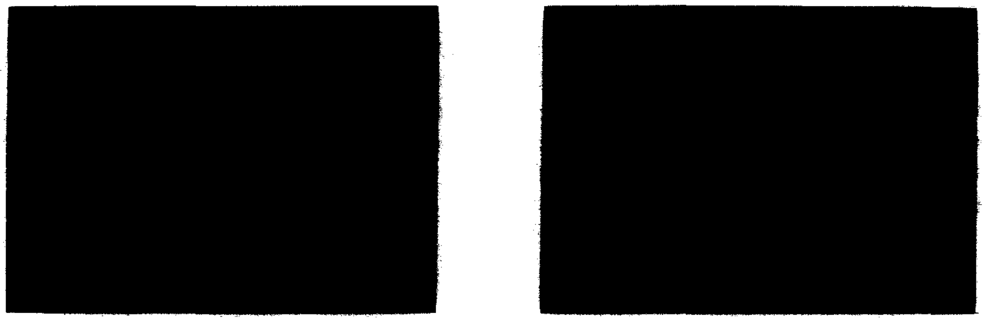
(a) (b)

Fig. 2. Typical electron diffraction patterns for annealed films obtained at (a) low (4×10^{-5} Torr) and (b) high (3×10^{-4} Torr) nitrogen partial pressure.

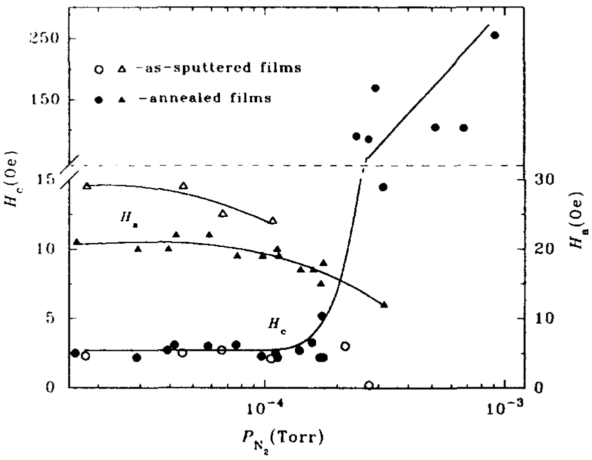

Fig. 4. Dependence of magnetic anisotropy field and coercive force for as-sputtered and annealed films.

They have certain correlation with the $M_S(P_{N_2})$ dependence and indicate an increase in ρ_0 with the increase in multiphase nature of the film. In addition, the AMR $\Delta\rho = \rho_{\parallel} - \rho_{\perp}$ changes. Its reduction together with the increase in resistivity lead to the rapid drop in the value of the magnetoresistive ratio $\Delta\rho/\rho_0$ and the complete disappearance of the magnetoresistance in the as-sputtered films at $P_{N_2} > 10^{-3}$ Torr (Fig. 3(b)). The similar change in $\Delta\rho/\rho_0$ is slower in the annealed films.

Fig. 4 shows two magnetic characteristics of films: magnetic anisotropy field H_a and coercive force H_c. It is important to point out that the uniaxial induced magnetic anisotropy characterized by H_a is well marked only in the single-phase films. When non-magnetic phases appear the measurement of H_a turns out to be difficult because of a large coercive force.

From the above data it follows that magnetic anisotropy is noticeably less in annealed samples. This fact is not unusual since annealing is conducive to the growth of grains and an increase in local anisotropy dispersion. The competition between the natural crystal and the induced anisotropy leads to the effective decrease in the induced anisotropy. In addition, the slight decrease in H_a with the increase in P_{N_2} should also be noted. This is typical for the films of both types and suggests that there may be fine structural changes that cannot be detected by the electron microscope.

The behaviour of the coercive force for the nitrogen-containing films is rather special. It is seen from Fig. 4 that nitrogenation practically does not affect H_c of the as-sputtered films, although at $P_{N_2} > 6 \times 10^{-4}$ Torr the non-magnetic phases appear and film magnetization decreases. On the contrary, in the annealed films the multiphase state is accompanied by a drastic increase in H_c. It might be suggested that a rise in coercive force is connected with both the presence of the film microstructure inhomogeneities and their sizes.

The measurements of microstructure parameters have shown that the grain size is 5–10 nm and 20–50 nm in the as-sputtered and annealed films respectively. If we assume that the size of phase precipitation correlates with the grain size, the increase in H_c could be connected with the domain wall pinning on such phase inhomogeneities. Also, the effectiveness of phase precipitation is determined by both the significant magnetization dispersion and their large sizes.

On the basis of the above results we can draw the conclusion that nitrides arising in the process of film preparation are unstable compounds and disintegrate under the heat treatment. This also suggests the formation of free nitrogen and its desorption from the film. This process must be dependent on the film thickness and the state of the film surface. Thus, the above-mentioned factors might influence the magnetic

Table 1
Magnetization, coercive force, resistivity and phase composition of the films prepared in a pure Ar and Ar + N_2 atmosphere (the thickness of the protective layer is 10 nm)

P_{N_2} ($\times 10^{-4}$ Torr)	L_m (nm)	T_a (°C)	Protective layer	M_s (G)	H_c (Oe)	ρ_0 (μΩ cm)	Phase composition[a]
0	40	—	—	980	1.8	38	γ
0	44	350	—	980	4.0	22	γ
2.7	44	—	—	Non-magnetic		160	$\gamma' + \varepsilon$
2.7	44	350	—	430	150	60	$\gamma + \gamma' + \varepsilon$
0	10	—	—	980	1.9	36	γ
0	10	350	—	980	6.2	19	γ
2.6	10	—	—	Non-magnetic		130	$\gamma + \gamma'$
2.7	10	350	—	720	3.1	45	γ
2.6	10	—	TiN	Non-magnetic		70	γ'
2.6	10	370	TiN	820	19	34	γ
2.5	10	360	SiO_2	470	25	107	$\gamma + \gamma'$

[a] γ, f.c.c. phase of Fe15Co20Ni65; γ', f.c.c. phase of Fe_4N type; ε, f.c.c. phase of $Fe_{2-3}N$ type.

and electrical properties of the nitrogen-containing films.

The results of the corresponding experiments are given in Table 1. This shows the properties and the phase compositions of the three film groups. The first group includes the thick films. They are similar to the films for which the above results have been obtained. The films of the second group are thinner (L_m = 10 nm). The third group includes the thin films with 10 nm protective layers of TiN and SiO_2.

Comparing the data for the first and second group samples it can be seen that the annealing of the thin nitrogenated films, having once being magnetized, restores their properties almost completely. Moreover, the coercive force of these films is less than in the corresponding films obtained without nitrogen. It is evidently connected with the smaller size grains whose growth is blocked by nitrogen. At the same time the magnetic properties of thick films are only partially restored, the coercive force being large. The protecting coating (particularly SiO_2) blocks the nitrogen desorption during the annealing of the film. This is reflected in the character of the film properties.

4. Conclusions

We found that both reversible and non-reversible changes in the properties and the phase transformation take place in the Fe15Co20Ni65 films on their nitrogenation. This depends on the nitrogen pressure, the annealing temperature and the presence of a protective covering. Similar regularities may be expected for the other magnetic 3d metal alloy films.

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