

Preparation of Fe-N films by r.f. sputtering

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Fe-N films over a wide compositional range have been prepared by the reactive sputtering method. Fe-N sputtered films were composed of a single or two phases such as ζ -Fe₂N, ε -Fe_{3.02}N, γ' -Fe_{3.82}N, γ' -Fe₄N and α -Fe; however, an unknown phase was observed at a higher nitrogen pressure. A remarkable preferred orientation of the ε -Fe_{3.02}N (1 1 0) plane parallel to the film surface was observed. The Curie temperature of the sputtered γ' -Fe_{3.82}N sample was 490°C, which was almost the same as that of γ' -Fe₄N prepared by metal nitriding. The saturation magnetization, σ_s , of the sputtered Fe-N samples decreased from 151.8 to 42.4 e.m.u. g⁻¹ with increasing nitrogen content from 7.94 to 24.87 at%, and its coercive force, H_c was found to lie in the range 150 to 600 Oe in the powder form at room temperature.

1. Introduction

In the Fe-N system, iron nitrides (Fe₁₆N₂, γ' -Fe₄N, ε -Fe_{2.3}N) have received much attention due to their use as superior magnetic recording materials, because they show higher saturation magnetization and favourable values of coercive force at room temperature. Many methods have been applied to prepare iron nitrides, such as iron metal nitriding [1], sputtering [2, 3], ion plating [4] and ion implantation [5]. Of all the iron nitrides, Fe₁₆N₂ shows an extremely high saturation magnetization of 298 e.m.u. g⁻¹ [6], a value which far exceeds that of α -Fe. However, pure Fe₁₆N₂ has not yet been synthesized and is usually formed coexisting with α -Fe or γ' -Fe₄N [2, 5, 6, 7]. For magnetic recording materials, not only the magnetic properties but also chemical stability, morphology and ease of production are important factors. It has been reported that γ' -Fe₄N shows a relatively higher chemical stability [1, 8]. It seems that Fe₁₆N₂ is not always the best phase, because it is difficult to obtain Fe₁₆N₂ as a single phase. γ' -Fe₄N shows a relatively higher saturation magnetization of 190 e.m.u. g⁻¹ [9], a value which is higher than that of Co-doped γ -Fe₂O₃.

Having succeeded with the Co-N system [10], we applied an r.f. sputtering method to the preparation of iron nitride over a wide compositional range through reactive sputtering. The chemical composition of Fe-N compounds was controlled by the sputtering gas composition, and the preparation conditions of iron nitride were determined. The Fe-N samples were characterized by X-ray diffraction, SEM observation and chemical analysis. The magnetic properties of iron nitrides were studied in relation to the chemical composition.

2. Experimental details

Fe-N films were prepared using an ULVAC SBR-1104

type r.f. sputtering apparatus. The reactive sputtering process was employed in order to control the composition of Fe-N films. The target used for the reactive sputtering was an α -Fe metal disc (99.9%, 100 mm diameter \times 1 mm thick). The α -Fe metal target was placed on the lower electrode and a substrate was attached to the centre of the upper electrode. A mixed gas of argon (99.99%) and nitrogen (99.995%) in varying ratios was used to control the Fe-N film composition.

Glass slides and polyimide films were used as substrates. After deposition of Fe-N on the polyimide film substrate, samples for chemical analysis and measurement of saturation magnetization and coercive force were separated mechanically from the polyimide film substrate. The Fe-N film samples for SEM observation and X-ray diffraction were prepared by sputtering deposition on glass slide substrates. Sputtering conditions are shown in Table I. The chemical composition of the Fe-N films was determined by means of JIS-M-8212 for iron and the Kjeldahl method for nitrogen [11]. Observation of the morphology was carried out by scanning electron microscopy. An ordinary X-ray diffractometer with a graphite monochromator was used to identify crystal phases. Measurement of the magnetic properties was carried out using a vibrating sample magnetometer at room temperature, and the temperature dependence of saturation magnetization was measured using a magnetic balance under a nitrogen gas flow between room temperature and 550°C.

3. Results and discussion

3.1. Characterization of Fe-N films

All samples were prepared by the sputtering technique under the conditions as shown in Table I. The thickness of those films was 7 to 8 μ m after 6 h sputtering,

TABLE I Sputtering conditions

Target	Fe disc (99.9%, 100 mm diameter × 1 mm thick)
Gas	Ar (99.99%) + N ₂ (99.995%)
Pressure	3 × 10 ⁻² mm Hg
Substrate temperature	160°C
Sputtering power	100 W
Sputtering time	6 h

with a deposition rate of 19 to 22 nm min⁻¹. The sputtering conditions, observed phases and results of chemical analysis are summarized in Table II. Crystal phases were identified with reference to the pioneer study [12]. At a high partial pressure of nitrogen (P_{N_2}), i.e. $P_{Total} = 3 \times 10^{-2}$ mm Hg ($N_2 = 100\%$), ζ -Fe₂N phase and an unidentified crystal phase were observed. Assuming that the unidentified crystal phase was FeN with a cubic unit cell like CoN [13], the observed X-ray diffraction lines could not be indexed well, because the number of observed X-ray diffraction lines was not large enough to index sufficiently, or may be because FeN seems to have another structure. When P_{N_2} was relatively lower ($P_{Total} = 3 \times 10^{-2}$ mm Hg, $N_2 = 30.9\%$), the film was composed of a single phase ζ -Fe₂N. At $N_2 = 10.22\%$, a single-phase ϵ -Fe_{3.02}N was deposited with the preferred orientation of the (110) plane parallel to the film surface. At $N_2 = 4.86\%$, a single-phase γ' -Fe_{3.82}N was also formed. The X-ray diffraction patterns of sputtered ϵ -Fe_{3.02}N and γ' -Fe_{3.82}N films are shown in Fig. 1. At $N_2 = 2.52\%$ and 1%, both films were composed of the mixture of γ' -Fe₄N phase and α -Fe. Naturally, α -Fe was formed under conditions of pure argon (100%). It is concluded from the results of X-ray diffraction and chemical analysis that the nitrogen content in Fe-N films decreases with decreasing P_{N_2} , and Fe-N films can be prepared over a wide compositional range by the control of the sputtering gas composition. Under the present experimental conditions, Fe₁₆N₂ could not be obtained by reactive sputtering, but from the results of magnetic measurements it was found that a small amount of Fe₁₆N₂ was prepared using a high-rate reactive sputtering apparatus, coexisting with α -Fe or γ' -Fe₄N [2]. Fe₁₆N₂ could also be prepared by ion implantation [5] and reactive electron beam deposition [6], and its existence was confirmed by X-ray diffraction and electron beam diffraction, respectively. In either case, Fe₁₆N₂ has not been obtained previously as a single phase and usually coexisted with other phases, i.e. α -Fe and/or γ' -Fe₄N. Furthermore, even a small amount of Fe₁₆N₂ had not been obtained

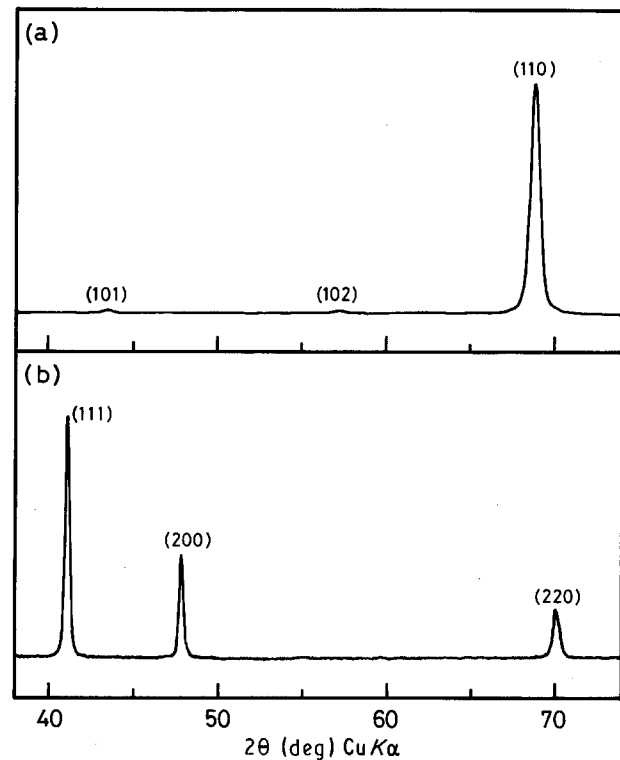


Figure 1 X-ray diffraction patterns of Fe-N sputtered films. (a) ϵ -Fe_{3.02}N (at $N_2 = 10.22\%$); (b) γ' -Fe_{3.82}N (at $N_2 = 4.86\%$).

by the r.f. sputtering as in the present results [3]. It may be considered that Fe₁₆N₂ exists in the non-equilibrium state in the iron-rich region and is formed in the distorted α -Fe lattice by interstitial substitution of nitrogen atoms [2, 5, 6, 7]. On the other hand, it is obvious that a single-phase γ' -Fe₄N can be prepared easily by the reactive sputtering method.

The scanning electron micrographs of the fracture and film surfaces of Fe-N sputtered films are shown in Figs 2 and 3. The fracture surface of the film sample sputtered at $N_2 = 10.22\%$, which consists of a single-phase ϵ -Fe_{3.02}N, exhibits columnar structure (Fig. 2a). It is found that the film surface consists of an assembly of rhombuses, 0.2 × 0.4 μ m in size (Fig. 2b). The fracture surface of the film sample sputtered at $N_2 = 4.86\%$, which consists of a single-phase γ' -Fe_{3.82}N, exhibits intermediate structure between columnar and polyhedral particles (Fig. 3a). γ' -Fe_{3.82}N triangular pyramids, 0.2 to 1 μ m wide are observed on the film surface (Fig. 3b).

3.2. Magnetic properties of Fe-N films

The temperature dependence of saturation magnetization, σ_s , of the sample sputtered at $N_2 = 4.86\%$ is

TABLE II Sputtering conditions, observed phases and chemical composition of sputtered Fe-N samples

P_{Total} (mm Hg)	P_{N_2}/P_{Total} (%)	Phase	Nitrogen content N (at %)
3 × 10 ⁻²	100	ζ -Fe ₂ N + ?	-
	30.9	ζ -Fe ₂ N	-
	10.22	ϵ -Fe _{3.02} N (110)**	24.87
	4.86	γ' -Fe _{3.82} N	20.75
	2.52	γ' -Fe ₄ N + α -Fe	12.64
	1.00	γ' -Fe ₄ N + α -Fe	7.94
	0.00	α -Fe	0.00

**Preferred orientation of (hkl) plane parallel to the film surface.

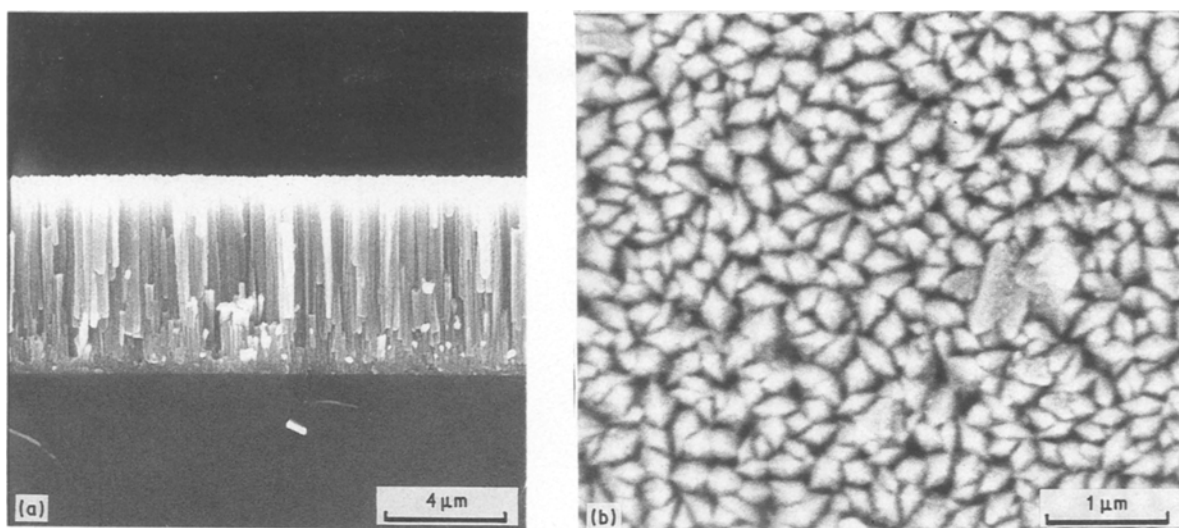


Figure 2 Scanning electron micrographs of $\epsilon\text{-Fe}_{3.02}\text{N}$ sputtered film. (a) Fracture surface, (b) film surface.

shown in Fig. 4. The sample obtained was identified as $\gamma'\text{-Fe}_{3.82}\text{N}$ by X-ray diffraction and chemical analysis. $\gamma'\text{-Fe}_{3.82}\text{N}$ shows $\sigma_s = 128.5 \text{ e.m.u. g}^{-1}$ at room temperature. The σ_s of $\gamma'\text{-Fe}_{3.82}\text{N}$ decreases gradually with increasing temperature from room temperature to 550°C . In the reverse process, the σ_s of $\gamma'\text{-Fe}_{3.82}\text{N}$ increases gradually with decreasing temperature from 550°C to room temperature. A sputtered $\gamma'\text{-Fe}_{3.82}\text{N}$ sample shows a Curie temperature of 490°C , which is almost the same as that of $\gamma'\text{-Fe}_4\text{N}$ prepared by metal nitriding [1]. It seems that the Curie temperature of $\gamma'\text{-Fe}_4\text{N}$ phase is not so sensitively dependent on the composition and preparation methods. However, a small difference in the $\sigma_s\text{-}T$ curves between the heating and cooling processes was observed for $\gamma'\text{-Fe}_{3.82}\text{N}$.

After measurement of σ_s , the sample was analysed by X-ray diffraction. Only a very weak diffraction line (d_{110} of $\alpha\text{-Fe}$) was observed for the sample, that is the strongest line of $\alpha\text{-Fe}$ (JCPDS; Powder Diffraction Data, 6-696). The sample showed the same appearance before and after measurements of $\sigma_s\text{-}T$. However, a trace of $\alpha\text{-Fe}$ was formed. Thus the increase of σ_s in the cooling process was caused by the formation of this trace of $\alpha\text{-Fe}$. Therefore, $\gamma'\text{-Fe}_{3.82}\text{N}$ shows higher thermal resistance than Co_4N [10].

A plot of σ_s of sputtered Fe-N samples against nitrogen content is shown in Fig. 5, summarizing the data for iron nitrides reported by other workers [1, 2, 3, 9, 15]. In the range 7.94 to 20.75 at % N, σ_s of the present sputtered Fe-N samples decreases gradually with increasing nitrogen content, where the sample consists of a mixture of two phases, $\gamma'\text{-Fe}_4\text{N}$ and $\alpha\text{-Fe}$, or a single-phase $\gamma'\text{-Fe}_{3.82}\text{N}$. The degree of decrease of the saturation magnetization of the present sputtered Fe-N sample is similar to that of Fe-N prepared by metal nitriding [1]. However, it decreases steeply in the range 20.75 to 24.87 at % N. Experimental values of σ_s of $\gamma'\text{-Fe}_4\text{N}$ are dispersed over a wide range from 190 to 110 e.m.u. g^{-1} (Fig. 5). Lo *et al.* [3] observed slightly different values on the $\gamma'\text{-Fe}_4\text{N}$ sputtered film in-plane and perpendicular to the applied magnetic field, and the average σ_s was 148 e.m.u. g^{-1} at room temperature [3]. In the present work, $\gamma'\text{-Fe}_{3.82}\text{N}$ showed $\sigma_s = 128.5 \text{ e.m.u. g}^{-1}$ at room temperature, a value which is comparable to the above value. The lower value of 110 e.m.u. g^{-1} may be due to the morphology of $\gamma'\text{-Fe}_4\text{N}$ prepared by the iron metal nitriding [1], in which the needle-like $\gamma'\text{-Fe}_4\text{N}$ ($0.5 \mu\text{m} \times 0.05 \mu\text{m}$ in size) seems to be composed of an assembly of small particles. On the other

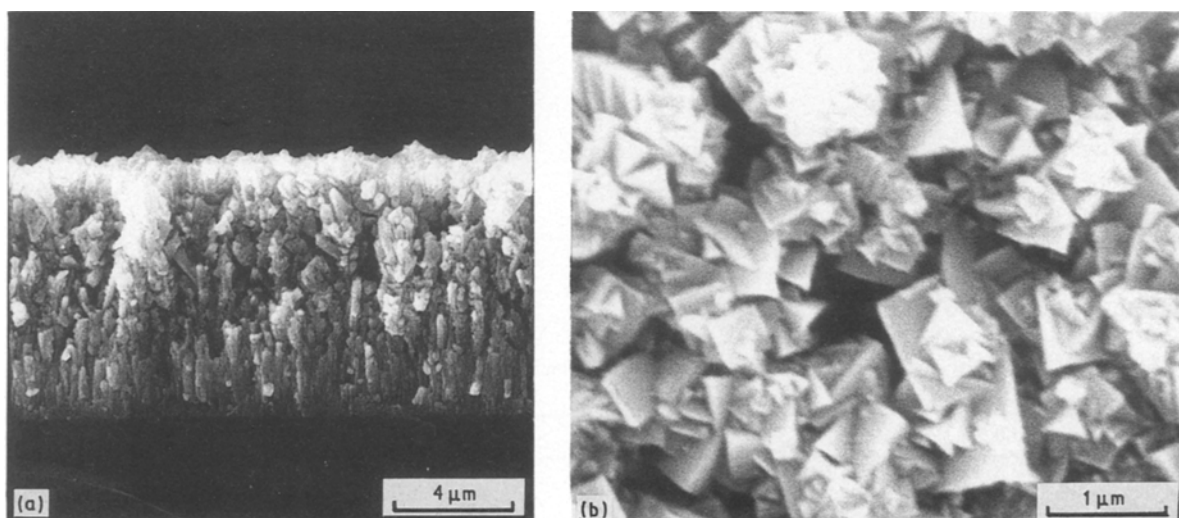


Figure 3 Scanning electron micrographs of $\gamma'\text{-Fe}_{3.82}\text{N}$ sputtered film. (a) Fracture surface, (b) film surface.

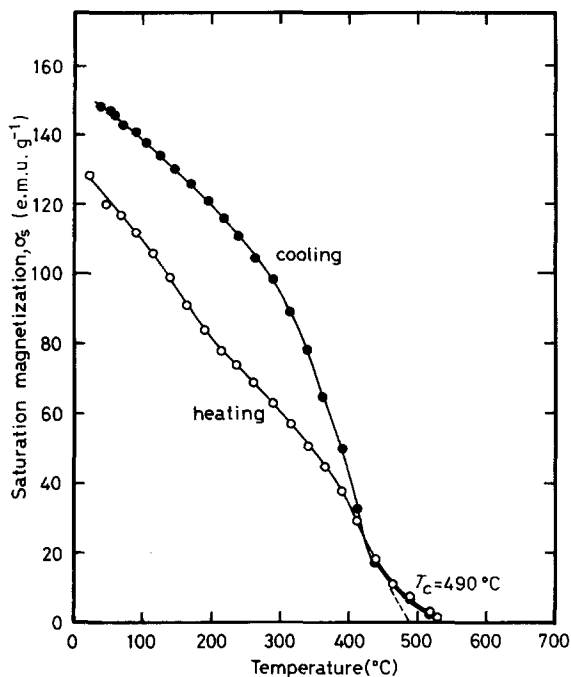


Figure 4 Temperature dependence of saturation magnetization, σ_s , of γ' -Fe_{3.82}N sputtered sample.

hand, high values, of σ_s were observed by Guiland and Creveaux [9], and by Eickel and Pistch [15]; however, its morphology was not revealed. It is supposed that γ' -Fe₄N with high σ_s had a larger particle size even though its precise features are not clear. The disparity in the values for γ' -Fe₄N may be associated with the particle size and the surface oxidation of particles, because the smaller particles become more reactive to oxygen and moisture. Its saturation magnetization is probably independent of the preparation methods. In any case, it is clear that the γ' -Fe₄N phase shows higher σ_s than other oxide magnetic materials.

The magnetic data obtained are summarized in Table III. A coercive force H_c of sputtered Fe-N samples lies in the range 150 to 600 Oe, values which are comparable to that of magnetic recording materials. However, the compositional dependence of coercive force of the sputtered Fe-N sample is not clearly observed in the present work, because coercive force is strongly dependent upon the particle size, shape anisotropy and magneto-crystalline anisotropy of the materials.

4. Conclusions

1. Fe-N films over a wide compositional range can be prepared by the reactive sputtering process. The films were composed of a single or two phases such as ζ -Fe₂N, ϵ -Fe_{3.02}N, γ' -Fe_{3.82}N, γ' -Fe₄N and α -Fe. The film composition can be controlled by the composition of the sputtering gas of argon and nitrogen.

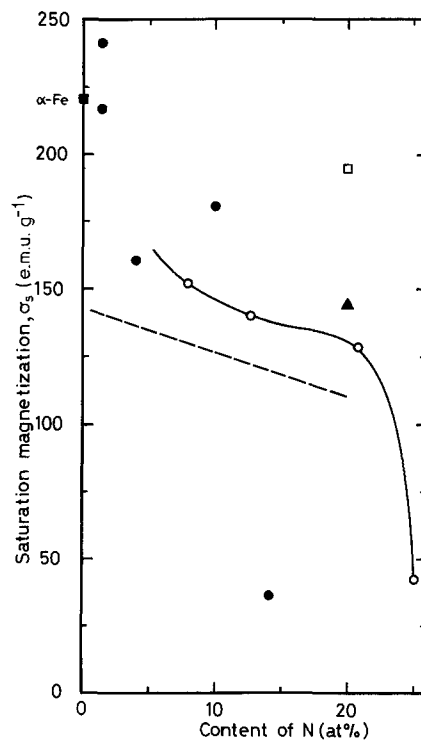


Figure 5 Plot of saturation magnetization, σ_s , of iron nitrides against nitrogen content. (O) sputtering (present work), (---) metal nitriding [1], (●) sputtering [2], (▲) sputtering [3], (□) metal nitriding [9, 15].

2. A remarkable preferred orientation of the ϵ -Fe_{3.02}N (110) plane parallel to the film surface was observed.

3. The saturation magnetization, σ_s , of sputtered Fe-N samples decreases from 151.8 to 42.4 e.m.u. g⁻¹ with increasing nitrogen content from 7.94 to 24.87 at%. Sputtered Fe-N films show values of coercive force, H_c , of 150 to 600 Oe in the powder form, values which are comparable to that of magnetic recording materials.

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TABLE III Chemical composition, observed phases, saturation magnetization, σ_s , and coercive force, H_c , of sputtered Fe-N samples

Nitrogen content (at%)	Phase	σ_s (e.m.u. g ⁻¹)	H_c (Oe)
24.87	ϵ -Fe _{3.02} N	42.4	207
20.75	γ' -Fe _{3.82} N	128.5	157
12.64	γ' -Fe ₄ N + α -Fe	139.9	598
7.94	γ' -Fe ₄ N + α -Fe	151.8	359

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