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Preparation of Co–N films by rf-sputtering

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Co–N films in the wide compositional range can be prepared by reactive sputtering. Co–N sputtered films consist of one or two phases, such as CoN, Co_2N, Co_3N, Co_4N and α-Co. Co_4N phase with a cubic unit cell is observed, and its lattice constant is a = 0.3586 nm. The preferred orientation is observed on the Co–N films, CoN (2 0 0) plane, Co_4N (1 1 1) plane and α-Co (0 0 2) plane parallel to the film surface, respectively. Saturation magnetization σ_s of Co–N sputtered film decreases from 160 to 1.7 e.m.u. g^{-1} with increasing content of N from 0 to 21.7 at %, and coercive force $_IH_c$ is the range of 43 to 500 Oe at room temperature.

1. Introduction

3d transition metal nitrides have been studied by many workers, many of them exhibiting antiferromagnetism or paramagnetism. Only some iron nitrides showed ferromagnetism at room temperature [1, 2]. Since the magnetic properties of $Fe_{16}N_2$ were observed by Takahashi *et al.* [3, 4], iron nitrides ($Fe_{16}N_2$, Fe_4N, $Fe_{2-3}N$) have attracted attention as superior magnetic recording materials, because they show considerably large saturation magnetization and relatively high chemical stability compared to ferrites or metals for magnetic recording media [5–8]. Therefore, 3d transition metal nitrides seem to be favourable to magnetic recording materials, and may be intermediate between ferrites and metals in their magnetic and chemical properties.

With regard to the structural characteristics of 3d transition metal nitrides, it can be recognized that the larger metal atoms constitute the fundamental structure and the smaller nitrogen atoms are located at interstitial sites [1, 9–12]. Generally, stoichiometric compounds of metal nitrides are not always obtained, because the metal nitrogen system gives the interstitial compounds. But the above nature is favourable to the control of chemical composition, since magnetic properties strongly depend upon its chemical composition.

In the present work, the authors applied the Rf-sputtering method to the preparation of cobalt nitride in the wide compositional range through the reactive sputtering process. The chemical composition of Co–N compounds was controlled by the sputtering gas pressure and composition, and the preparation conditions of cobalt nitride were determined. X-ray diffractometry, SEM observation and chemical analysis were carried out, and the structural relation of preferred orientation between α-Co and Co_4N was examined. Furthermore, the magnetic properties of cobalt nitride were related to the chemical composition.

2. Experimental details

Co–N films were prepared using an ALVAC SBR-1104 (Alvac Co. Ltd., Tokyo) type Rf-sputtering apparatus. The reactive sputtering process was employed in order to control the composition of Co–N films. A target used for the reactive sputtering was a cobalt disc (99.9%, 100^{ϕ} × 1^{t}mm). The cobalt metal target was placed on the lower electrode and the substrate was attached on the centre of the upper electrode. Mixed gas of argon and N_2 (99.995%) was used as sputtering gas, and the Co–N film composition was controlled by the sputtering gas composition and the total sputtering gas pressure.

Glass slides and polyimide films were used as substrate. After Co–N films were sputtered onto the polyimide film substrates, samples for chemical analysis and the measurements of saturation magnetization and coercive force were obtained by mechanical separation from the polyimide film substrates. Co–N film samples for SEM observation and X-ray diffractometry were sputtered onto the glass slide substrates. Sputtering conditions are shown in Table I. The chemical composition of Co–N films were determined by means of the method of JIS-G-1222 for cobalt and the Kjeldahl method for nitrogen [13], respectively. The observation of morphology was carried out by a scanning electron microscope. An ordinary X-ray diffractometer with a graphite monochrometer was used to identify crystal phases. The measurement of magnetic properties was carried out by a vibrating sample magnetometer, and temperature dependence of saturation magnetization was measured using a magnetic balance under N_2 flowing between room temperature and 550° C.

3. Results and discussion

3.1. Characterization of Co–N films

All samples (films 8–10 μm thick) were prepared by sputtering for 6 h. The deposition rate was 22–28 nm min^{-1}.

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TABLE I Sputtering conditions

Target	Co(99.9%, 1 × 100 mm$^{\phi}$)
Gas	Ar + N_2(99.995%)
Pressure	1 × 10^{-1}, 3 × 10^{-2} mm Hg
Substrate temperature	160° C
Power	100 W

The relation between observed phases and sputtering conditions, and the result of chemical analysis are summarized in Table II. When the total sputtering gas pressure was relatively high (P_{total} = 1 × 10^{-1} mm Hg, N_2 = 100%), CoN with the preferred orientation of (2 0 0) plane parallel to the film surface was formed. However, when the total sputtering gas pressure was lower (P_{total} = 3 × 10^{-2} mm Hg, N_2 = 100%), the film which consisted of Co_2N and Co_3N was formed. In the case of decreasing partial pressure P_{N_2}, the film which consisted of Co_3N and Co_2N was also formed (P_{total} = 3 × 10^{-2} mm Hg, N_2 = 30.9%). For the above conditions, it was found that the amount of Co_3N was larger than that of Co_2N from the measurement of the intensity of X-ray diffraction lines. At N_2 = 10.22%, Co_3N single phase was observed. Between N_2 = 4.86% and N_2 = 1%, a new phase was observed, which was identified to be Co_4N. As is well known, α-Co with the preferred orientation of (0 0 2) plane parallel to the film surface was observed on the sample sputtered under the condition of Ar = 100%. It is found from the results of X-ray diffractometry and chemical analysis that the content of nitrogen in Co–N films decreases with decreasing partial pressure P_{N_2}. Cobalt nitride films in the wide compositional range can be prepared by the control of both the total sputtering gas pressure (P_{total}) and the sputtering gas composition (P_{N_2}/P_{Ar}).

The phase diagram for the system Co–N has not yet been established, but some compounds were synthesized by the nitriding of cobalt metal and cobalt fluoride [14], and by the thermal decomposition of cobalt ammine azides [15], such as Co_3N, Co_2N and CoN. The synthesis of Co_4N has not yet reported.

X-ray diffraction patterns of Fe–N and Co–N sputtered film are shown in Fig. 1; these samples were prepared at the same sputtering conditions (P_{total} = 3 × 10^{-2} mm Hg, N_2 = 4.86%). It can be seen that the X-ray diffraction pattern of Co–N sputtered film is similar to that of Fe–N sputtered film (Fe_4N phase). The crystal structure of Fe_4N has been determined by

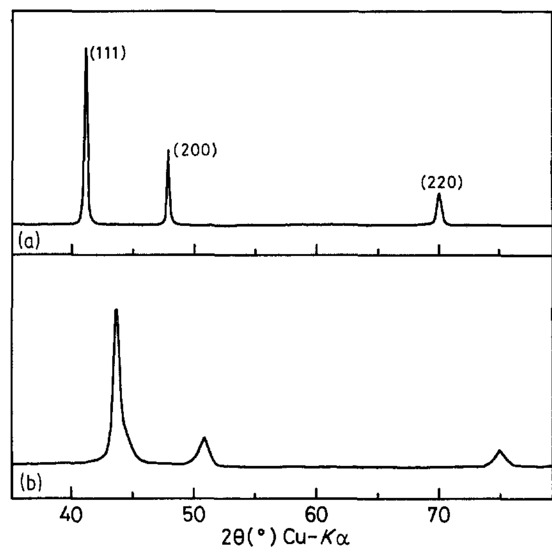

Figure 1 X-ray diffraction patterns of Fe–N and Co–N film sputtered at P_{total} = 3 × 10^{-2} mm Hg (P_{N_2}/P_{Ar} = 4.86/95.14). Phase (chemical composition) (a) $Fe_4N(Fe_{3.82}N)$; (b) $Co_4N(Co_{5.47}N)$.

Jack [10–12], and its lattice constant of cubic unit cell is a = 0.3795 nm. From the result of chemical analysis, the obtained Fe–N sputtered film ($Fe_{3.82}N$) contains little excess nitrogen compared to Fe_4N. On the contrary, obtained Co–N sputtered film ($Co_{5.47}N$) consists of nitrogen deficient Co_4N under the same sputtering conditions. By the assumption that Co_4N has a cubic unit cell, observed X-ray diffraction lines are well indexed and its lattice constant is a = 0.3586 nm. X-ray diffraction data of Co–N sputtered film are shown in Table III. The crystal structure of Co_4N is constructed by larger cobalt metal atoms packed in f c c and a smaller nitrogen atom situated in the centre of a unit cell of Co_4N as Fe_4N. A schematic illustration of Fe_4N and Co_4N crystal structures is shown in Fig. 2.

The structural relationship of the preferred orientation between α-Co and Co_4N is schematically demonstrated in Fig. 3. α-Co sputtered film shows the preferred orientation with (0 0 2) plane parallel to the film surface, where cobalt atoms are packed in h c p. However cobalt atoms in Co_4N are packed in f c c, which is caused by the introduction of nitrogen into f c c cobalt (high temperature form). From the result of X-ray diffractometry, the degree of the preferred orientation of the Co_4N phase increases with decreasing content of nitrogen, where (1 1 1)

TABLE II Sputtering conditions, observed phases by X-ray diffractometry and chemical composition of Co–N sputtered films

P_{total} (mm Hg)	P_{N_2}/P_{Ar}(%)	Phase	Composition	
			Co_xN	Nitrogen content (at %)
1 × 10^{-1}	100	CoN (2 0 0)*	–	–
3 × 10^{-2}	100	Co_2N + Co_3N	–	–
	30.9	Co_3N + Co_2N	–	–
	10.22	Co_3N	$Co_{3.61}N$	21.7
	4.86	Co_4N	$Co_{5.47}N$	15.5
	2.52	Co_4N	$Co_{11.6}N$	8.0
	1.00	Co_4N (1 1 1)*	$Co_{18.6}N$	5.1
	0.00	α-Co (0 0 2)*	Co	0.0

*Preferred orientation of (h k l) plane parallel to the film surface.

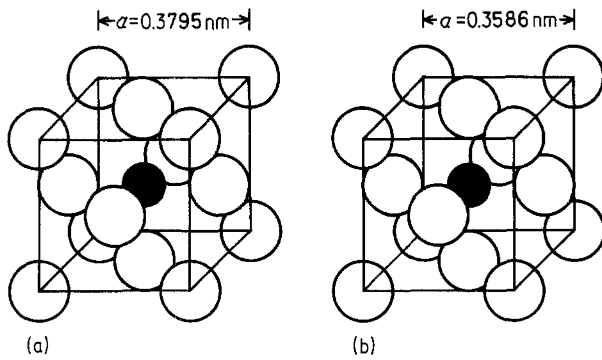

Figure 2 Similarity of crystal structure between (a) Fe_4N and (b) Co_4N. (a) ○, iron; ●, nitrogen; (b) ○, cobalt; ●, nitrogen.

reflection of Co_4N is converted gradually to (0 0 2) reflection of α-Co.

Scanning electron micrographs of fracture surface and film surface of Co–N sputtered films are shown in Fig. 4. Fracture surface of film sample sputtered under the condition of P_{N_2}/P_{Ar} = 10.22/89.78, which consists of Co_3N single phase, exhibits a columnar structure [Fig. 4a(i)]. It is observed that the film surface consists of an assembly of rhombuses with the size of ≈0.1 × 0.4 μm [(Fig. 4a(ii)]. The fracture surface of film sample sputtered under the condition of P_{N_2}/P_{Ar} = 4.86/95.14, which consists of Co_4N single phase, exhibits an intermediate structure between columnar and polyhedron particles [Fig. 4b(i)]. It is observed that the film surface consists of Co_4N polyhedron particles with the size of ≈0.1 μm in diameter [Fig. 4b(ii)]. The particle size of Co–N sputtered films tends to decrease with decreasing content of nitrogen.

3.2. Magnetic properties of Co–N films

Temperature dependence of saturation magnetization σ_s of sample sputtered under the condition of P_{N_2}/P_{Ar} = 4.86/95.14 is shown in Fig. 5. The phase of the obtained sample was identified to be Co_4N by X-ray diffractometry, and its chemical composition was $Co_{5.47}N$. $Co_{5.47}N$ shows saturation magnetization, σ_s, of 46.5 e.m.u. g^{-1} at room temperature. Saturation magnetization σ_s of $Co_{5.76}N$ decreases drastically on raising the temperature from room temperature to 270° C. Its saturation magnetization σ_s discontinuously increases at ~270° C, and again decreases very gradually with raising the temperature from 270 to 550° C. In the reversal process, the saturation magnetization σ_s increases very gradually with lowering the temperature from 550° C to room temperature. After the measurement of σ_s, the $Co_{5.47}N$ sample was analysed by X-ray diffractometry, and it was found that the sample was converted to both the large amount of cobalt metal and the very small amount of CoO. It can be considered that $Co_{5.47}N$ decomposes at ~270° C thermally and the lower thermal coefficient of σ_s is due to cobalt metal (T_c = 1395 K) [16]. The formation of very small amount of CoO is caused by the reaction between cobalt nitride and oxygen remaining in the magnetic measurement apparatus, since the measurement was carried out under the condition of flowing N_2. It is supposed that the lower decomposition temperature of $Co_{5.47}N$(Co_4N phase) obstructed the formation of Co_4N by the usual preparation method, such as metal nitriding or pyrolysis of cobalt organic compounds. In the same temperature range, the temperature dependence of σ_s of $Fe_{3.82}N$ was measured under the same conditions. However, the large difference of σ_s–T curves between the heating and cooling processes was not observed for $Fe_{3.82}N$. After the measurement, only a very weak diffraction line (d_{110} of α-Fe) was observed, which is the strongest line of all powder diffraction lines of α-Fe (JCPDS; Powder Diffraction Data, 6-696). Consequently, $Co_{5.47}N$(Co_4N phase) shows lower thermal resistance than $Fe_{3.82}N$ (Fe_4N phase).

A plot of saturation magnetization, σ_s, at room temperature against the nitrogen content in the Co–N film is shown in Fig. 6. The σ_s of Co–N sputtered film drastically decreases from 160 to 1.7 e.m.u. g^{-1} with increasing nitrogen content from 0 to 21.7 at %. It is found that Co–N sputtered films which consist of the Co_4N phase show σ_s of 46.5–85.1 e.m.u. g^{-1} at room temperature, which order is approximately comparable to that of ferrites. The degree σ_s found above is not

TABLE III X-ray diffraction data for $Co_{5.47}N$ sputtered film (cubic; a = 0.3586 nm; d = interplanar spacing)

2θ (deg) ($CuK\alpha$)	d_{obs} (nm)	(h k l)	I/I_0(%)	d_{calc} (nm)
43.75	0.2069	(1 1 1)	100	0.2070
50.90	0.1794	(2 0 0)	20	0.1793
75.00	0.1266	(2 2 0)	13	0.1268

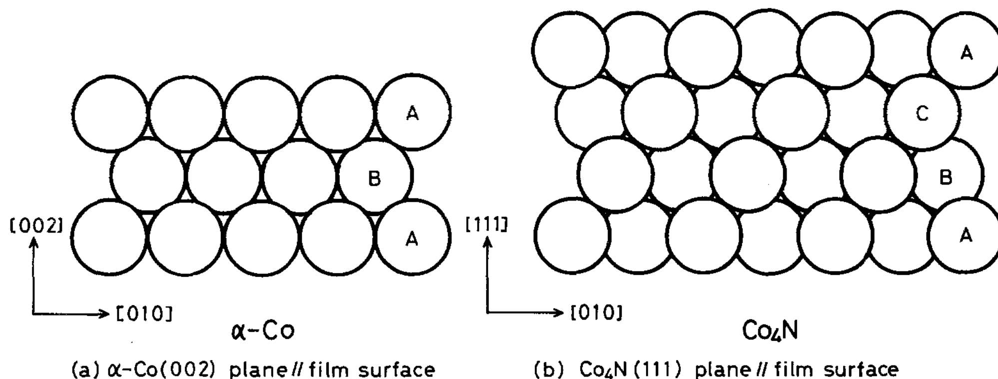

Figure 3 Preferred orientation of α-Co and Co_4N sputtered films. (a) α-Co (0 0 2) plane ∥ film surface; (b) Co_4N (1 1 1) plane ∥ film surface. ○, cobalt.

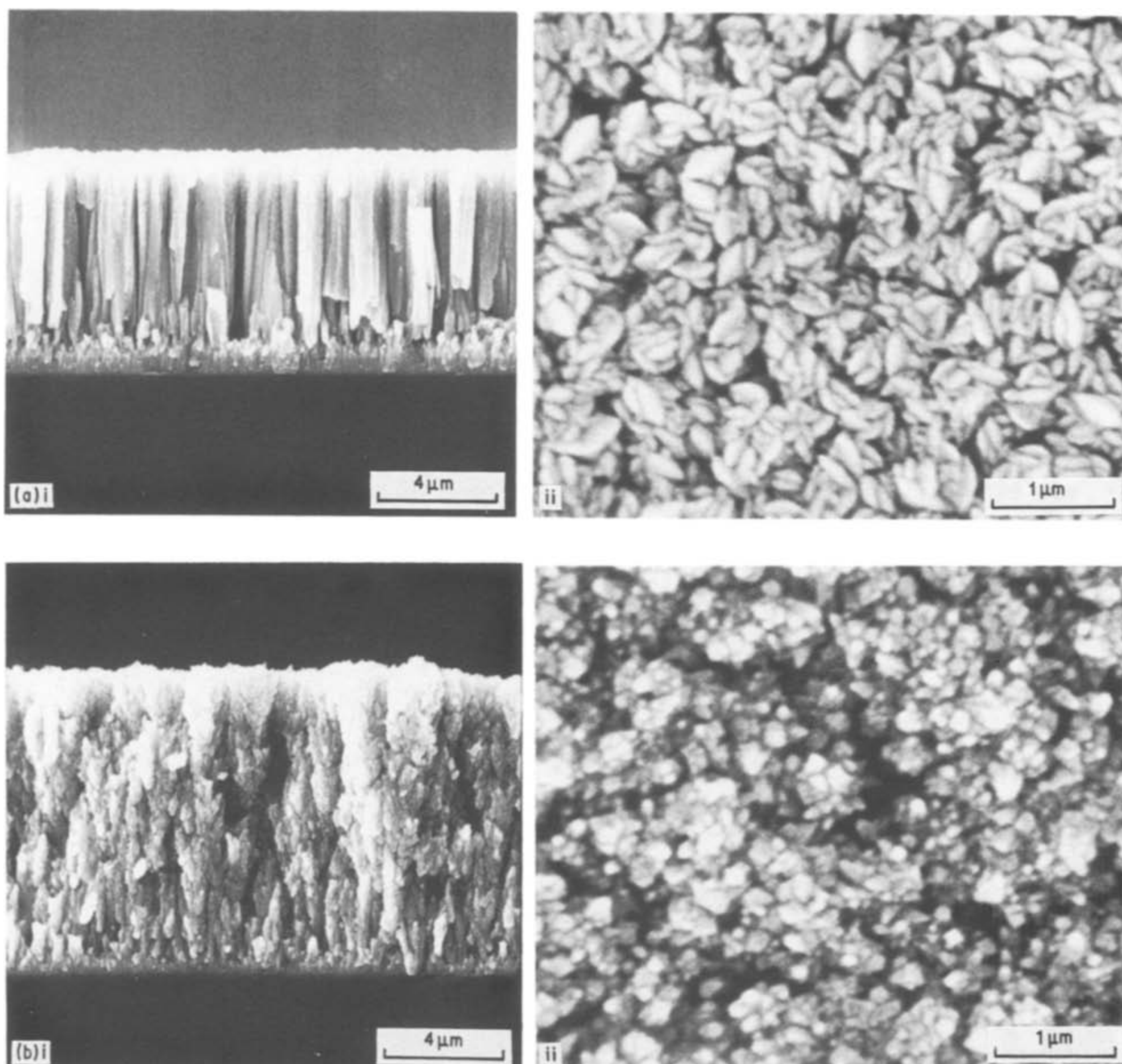

Figure 4 Scanning electron micrographs of Co–n sputtered films. (a) $Co_{3.61}N$; (b) $Co_{5.47}N$. (i) fracture surface, (ii) film surface.

surprising, and is comparable to that of Co–Cr sputtered film. Iwasaki and Ouchi observed that saturation magnetization σ_s of Co–Cr sputtered film decreased almost linearly from ~ 160 to ~ 20 e.m.u. g^{-1} with increasing content of chromium from 0 to 20 at % [17].

A plot of coercive force, ${}_IH_c$, at room temperature against nitrogen content in the Co–N film is also shown in Fig. 6. In the present work, the measurement of coercive force ${}_IH_c$ was carried out in the form of powder (< 1 mm), which was obtained by the mechanical separation of Co–N film from polyimide film substrate. Coercive force ${}_IH_c$ of α-Co sputtered film exhibits a value of 380 Oe. However, Co–N sputtered film attains to a maximum value of 500 Oe at 5.1 at % nitrogen and its coercive force ${}_IH_c$ decreases from 500 to 43 Oe with increasing content of nitrogen from 5.1 to 21.7 at %. It is found that the ${}_IH_c$ of Co–N sputtered films can be controlled by the introduction of nitrogen into cobalt metal through reactive sputtering. Generally, coercive force is strongly dependent upon particle size (morphology), orientation of particles and magneto-crystalline anisotropy energy K_1. With respect to the relation between coercive force ${}_IH_c$ and nitrogen content, it can be supposed that two factors have an effect on the change of coercive force ${}_IH_c$. One is the increase of particle size with increasing content of nitrogen seen by SEM observation, which causes the decrease of ${}_IH_c$. Another is the decrease of magneto-crystalline anisotropy energy K_1 which may be caused by the crystal structure, namely the change from h c p to f c c caused by the introduction of nitrogen into cobalt metal. Therefore, the change of coercive force ${}_IH_c$ may be derived from the superposition of the above two factors. So that the maximum is observed on the curve of ${}_IH_c$ against nitrogen content.

From the above results, the saturation magnetization, σ_s, of Co–N sputtered film changes sensitively with the content of nitrogen, and relatively high saturation magnetization σ_s of 46.5–85.1 e.m.u. g^{-1} is observed on Co_4N phase, and coercive force ${}_IH_c$ of 43 to 500 Oe is the order of magnetic recording materials.

4. Conclusions

1. Co–N films in the wide compositional range can be prepared by reactive sputtering. These films consist of

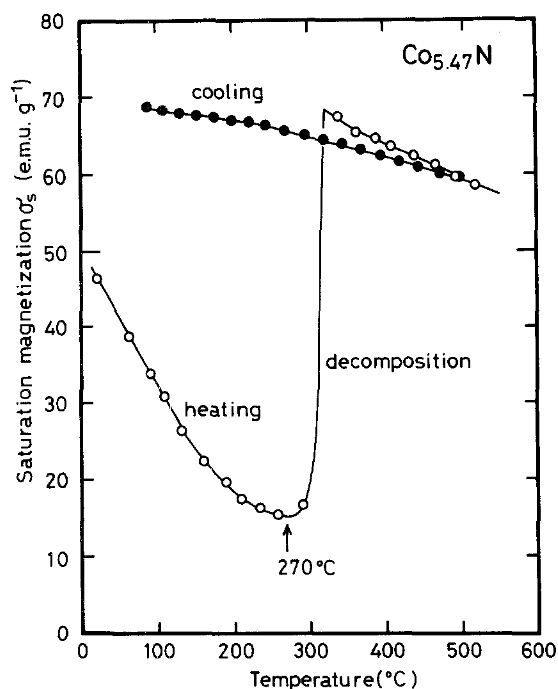

Figure 5 Temperature dependence of saturation magnetization, σ_s, of Co–N sputtered film.

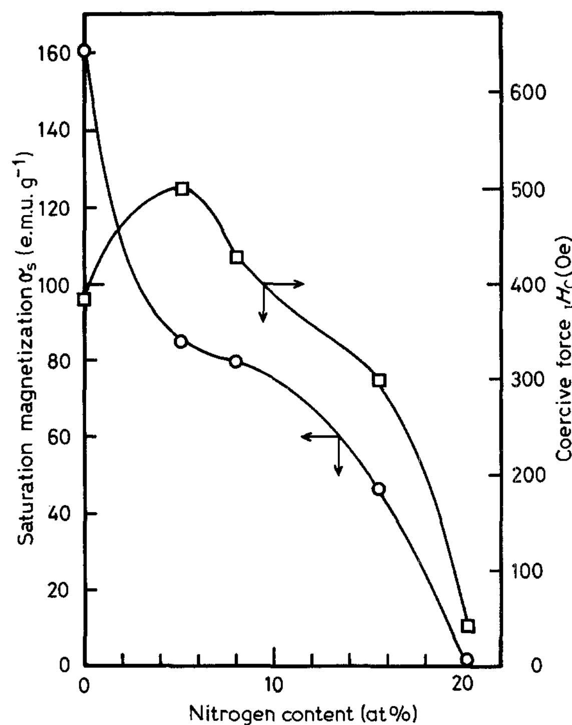

Figure 6 Plots of saturation magnetization, σ_s, and coercive force against nitrogen content in the Co–N film.

single or two phases, such as CoN, Co_2N, Co_3N, Co_4N and α-Co. The film composition can be controlled by the sputtering gas composition of argon and N_2, and the total sputtering gas pressure.

2. A new phase is observed in the system Co–N, such as Co_4N with a cubic unit cell, and its lattice constant is $a = 0.3586$ nm. The preferred orientation is observed on Co–N films, CoN (2 0 0) plane, Co_4N (1 1 1) plane and α-Co (0 0 2) plane parallel to the film surface.

3. Saturation magnetization σ_s of Co–N sputtered film decreases from 160 to 1.7 e.m.u. g^{-1} with increasing content of nitrogen from 0 to 21.7 at %. Co–n sputtered films show the value of coercive force ${}_iH_c$ of 43 to 500 Oe in the form of powder, which order is comparable to that of magnetic recording materials.

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