JOURNAL OF MATERIALS SCIENCE 28 (1993) 2715–2720

Synthesis and properties of Fe_3C film by r.f. magnetron sputtering

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Fe_3C film, which is a promising new magnetic recording material, can be synthesized by r.f. magnetron sputtering. Several graphite plates were attached to an iron plate to adjust the area of a composite target for the control of film composition. The crystalline phases in a film changed from Fe–C solid solution to Fe_3C with increasing substrate temperature from 350 °C and above. Sputtering at an argon pressure of 5 Pa was favourable for the formation of crystalline Fe_3C film. All Fe_3C films showed in-plane magnetization. The saturation magnetization of the film was around 100–120 e.m.u. g^{-1} regardless of the deposition conditions. The coercivity of the films increased from 1 Oe to 250 Oe with increasing substrate temperature, and the coercivity remained constant at 250 Oe at 350 °C, regardless of argon pressure.

1. Introduction

A new type of magnetic film was investigated for a magnetic recording medium application, which can substitute for the conventional particulate recording media. The particulate recording media with binder, which are used in discs and tapes, have lower effective saturation magnetization, σ_s, than bulk or sintered bodies. Therefore, magnetic films without binders are expected to have higher σ_s than particulate media, which should provide the higher storage density.

Metal films, such as α-Fe and Co, were investigated as a new type of magnetic recording medium, because the films have large σ_s. However, the metal films have low chemical stability and hardness. Therefore, metal alloy (Fe–Si), boride, carbide and nitride films are expected to be promising because of their higher hardness and higher oxidation resistance when compared with the metal films. These films have been prepared by sputtering, electroless plating or by chemical vapour deposition.

Iron carbides (Fe_3C, Fe_5C_2 and Fe_7C_3) have recently been investigated for application to magnetic recording media. They have higher saturation magnetization ($\sigma_s > 100$ e.m.u. g^{-1}) than γ-Fe_2O_3 (70 e.m.u. g^{-1}) [1], higher chemical stability when compared to iron metal, and relatively high hardness. However, it is difficult to synthesize the desired iron carbide particles as a single phase, because most iron carbides are metastable under atmospheric pressure [2]. We have already reported the synthesis and magnetic properties of Fe_3C, Fe_5C_2 and Fe_7C_3 particles produced by the reaction of iron sources with carbon monoxide (CO) [3–7]. Only a few papers, however, have reported the synthesis and magnetic properties of Fe_3C film or Fe–C solid solution film [8–11].

In the present work, the synthesis and properties of stoichiometric iron carbide films by radio frequency (r.f.) magnetron sputtering using an Fe–C composite target were investigated in detail to elucidate the magnetic characteristics.

2. Experimental procedure

Films of iron carbides were prepared by an r.f. magnetron sputtering apparatus. Highly pure argon gas (99.9995%) was employed as a sputtering gas. Quartz glass (SiO_2 glass) was used as a substrate, which had a square shape of 10×10 mm^2 and thickness of 1 mm. Several high-purity graphite plates (nuclear furnace grade) were attached to an iron plate as a target. The target composition could be adjusted by the area ratio of iron to carbon on the target.

Sputtering was carried out by the normal procedure; the sputtering conditions are shown in Table I. The film thickness and the deposition rate were calculated from the film area, film weight, film density and deposition time. The density of Fe_3C was assumed to be a single-crystal value of 7.5 g cm^{-3}, because the actual density of the film itself could not be measured.

The substrate temperature was controlled by the heater temperature and sputtering power, which was

TABLE I Sputtering conditions

Target	Fe disc, 3 in ($\sim$ 7.62 cm) diameter + several C plates ($7 \times 7 \times 1$ mm^3) Area ratio of C/Fe = 20/80–30/70
Substrate	SiO_2 glass ($10 \times 10 \times 1$ mm^3)
Sputtering gas	Argon (99.9995%)
Pressure	1–30 Pa
Power	100–400 W
Time	15–60 min
Substrate temperature	200–400 °C

calibrated beforehand according to the temperature measured with a thermocouple.

The crystalline phases in the film were identified by X-ray diffractometry (XRD) using JCPDS cards. The Curie temperature, T_c, of the film was determined by a thermomagnetic curve measurement using a Faraday-type magnetic balance with an external electric furnace. The specimens were sealed in SiO_2 glass tubes under vacuum. Auger electron spectroscopy (AES) was used to analyse existing elements and their distribution in the film. A vibrating sample magnetometer (VSM) was used to measure the magnetic properties of the film, and the morphology of the film was observed by scanning electron microscopy (SEM). The amount of free carbon in the Fe–C films must be analysed to identify the saturation magnetization, σ_s of single-phase iron carbide films. However, it was difficult to measure the accurate amount of trace-free carbon. In this paper, σ_s of the films is given as the as-measured and uncorrected value.

3. Results and discussion

3.1. Synthesis of Fe_3C film

The deposition rate increased linearly with increase in the r.f. power, and the maximum deposition rate was obtained at an argon pressure of 10 Pa. Fig. 1 shows the effect of the target composition C/Fe on the deposition rate of Fe–C films under 5 Pa at 350 °C. The deposition rate decreased with increase in the area of the graphite plate on the target. In general, the sputtering yield of an alloy is an average of the rates of each element when the re-sputtering from the substrate can be neglected. The sputtering yield of carbon is smaller than that of iron. Thus, the deposition rate decreased as the area of carbon increased.

From above results, the sputtering time was adjusted in order to control the thickness of the Fe–C films, because the magnetic properties of the Fe–C films depend on the thickness, which should be kept constant (about 0.1 μm) in order to be able to compare magnetic properties.

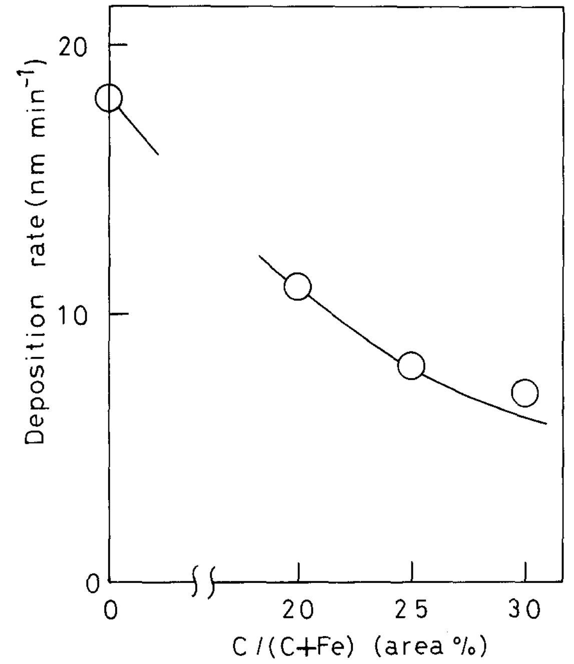

Figure 1 Effect of target composition on the deposition rate of Fe–C film at 350 °C under 5 Pa (r.f. power 200 W).

Fig. 2 shows the XRD profiles of the Fe–C films deposited on SiO_2 glass at various substrate temperatures under 20 Pa. Amorphous film was deposited at the substrate temperature of 250 °C, while crystalline film was produced at 400 °C. The deposited crystalline phases were confirmed to be α-Fe and Fe_3C.

Fig. 3 shows XRD profiles of the Fe–C films deposited on SiO_2 glass under various argon pressures at 350 °C. Under an argon pressure of 20 Pa, α-Fe film was deposited as the major phase together with Fe_3C, as shown in Fig. 2. Fe_3C was deposited as the major phase together with Fe_5C_2 and α-Fe under 10 Pa, while Fe_3C could be prepared as a single phase under 5 Pa. The diffraction intensity of Fe_3C deposited at 2 Pa changed due to the different orientation and/or crystallinity.

The effect of the argon pressure on formation of Fe_3C film could be explained as follows: the mean free path of the sputtered atoms (iron and carbon) increases with decreasing argon pressure. The kinetic energy of the sputtering atoms is dependent on the mean free path; therefore, the kinetic energy increases with decrease in the argon pressure. Thus, sputtering at low argon pressure would have a similar effect as substrate heating. It is apparent from these results that Fe_3C can be obtained by either high substrate temperature, or by sputtering at low argon pressure. On the other hand, while an argon pressure of 5 Pa was appropriate for synthesizing the single-phase Fe_3C film, the X-ray diffraction intensity ratio of the film sputtered at 2 Pa was not in good agreement with that of the JCPDS card. Not only was a high substrate temperature required but also an appropriate argon pressure, in order to synthesize single-phase Fe_3C films [8].

Fig. 4 shows XRD profiles of the Fe–C films deposited on SiO_2 glass from various target compositions at

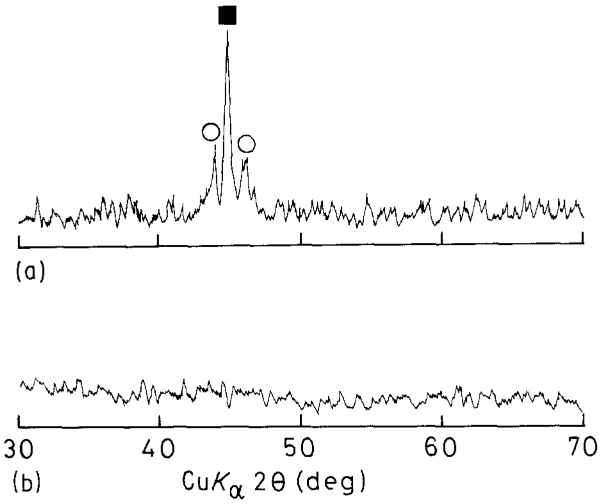

Figure 2 XRD profiles of Fe–C films deposited on SiO_2 glass at substrate temperatures of (a) 400 °C, (b) 250 °C under 20 Pa (target composition C/Fe = 20/80, r.f. power 400 W). (○) Fe_3C, (■) α-Fe.

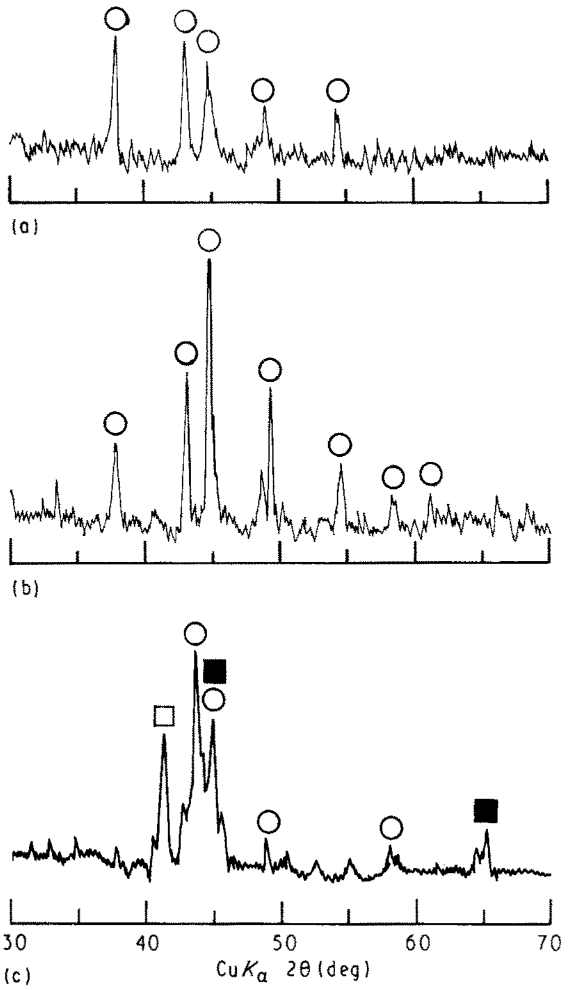

Figure 3 XRD profiles of Fe–C films deposited on SiO_2 glass at 350 °C under argon pressures of (a) 2 Pa, (b) 5 Pa, (c) 10 Pa (target composition C/Fe = 30/70, r.f. power 200 W). (○) Fe_3C, (■) α-Fe, (□) Fe_5C_2.

350 °C under 5 Pa. All diffraction peaks of XRD profiles could be assigned to Fe_3C. The difference in intensity ratio was derived from the difference in orientation, crystallinity and/or composition of the films. The target area ratio of C/Fe = 30/70 was appropriate in order to synthesize Fe_3C with high crystalline state. Because no iron carbide except Fe_3C was deposited, the target composition had no effect on the resultant phases. The following two reasons were considered.

1. Existence of free carbon: excess carbon might exist in the film as free carbon, although it could not be detected by XRD, especially in the case of lower Fe/C of target.

2. Self-controlling of the film composition: excess carbon and iron elements on the substrate were removed due to the vapourization and/or the resputtering by sputtered atoms, because Fe_3C might be kinetically more stable than iron and carbon under the deposition conditions. High kinetic energy of the sputtered atoms (corresponding to about 10 000 K) might contribute to the formation of Fe_3C rather than the formation of Fe_5C_2 and Fe_7C_3.

Fig. 5 shows scanning electron micrographs of Fe_3C films. The surface of the amorphous film at a substrate temperature of 150 °C is rather rough and exhibits a network pattern. The rough surface was caused by the difference in the thermal expansion coefficient between amorphous Fe–C film and the substrate (SiO_2). At a substrate temperature of 350 °C, the network structure changed to a granular film composed of Fe_3C fine particles with a grain size of around 0.1 μm. The film structure was smoother than that deposited at 150 °C, because the thermal expansion coefficient of Fe_3C is closer to SiO_2 glass than that of amorphous Fe–C. At 400 °C, the Fe_3C particle increased in size due to the high substrate temperature. The argon pressure (in the range 2–5 Pa) and the composition of the target hardly affected the microstructure of the film, because the substrate temperature mainly influenced the phases formed.

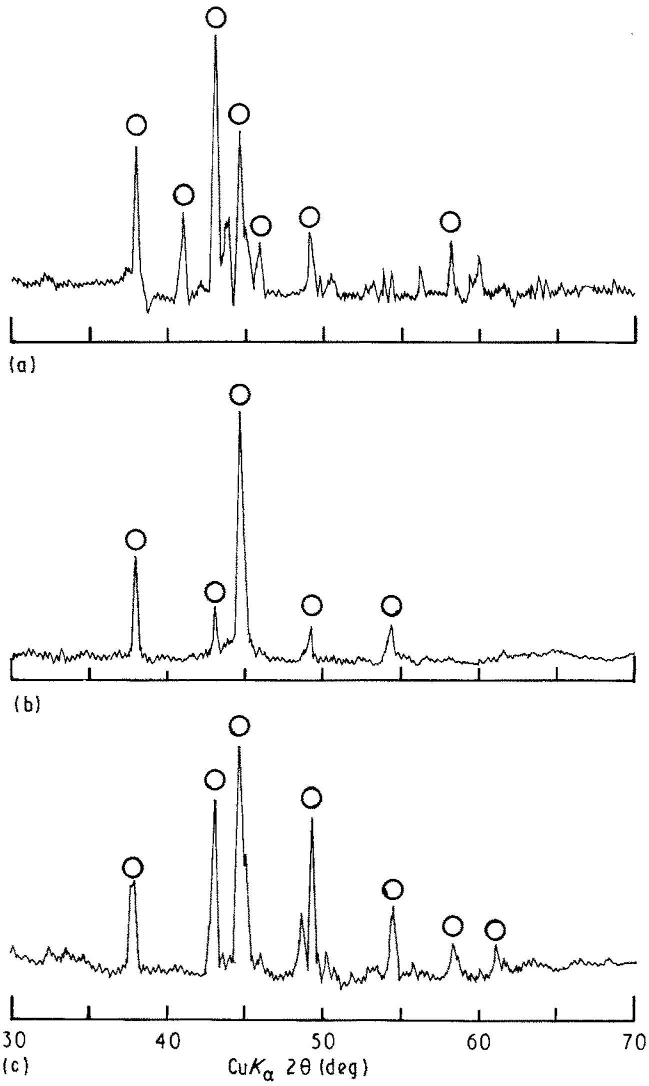

Figure 4 XRD profiles of Fe–C films deposited on SiO_2 glass at 350 °C from target compositions of (a) C/Fe = 20/80, (b) C/Fe = 25/75, (c) C/Fe = 30/70, under 5 Pa (r.f. power 200 W). (○) Fe_3C.

The Fe_3C film could be synthesized by the r.f. magnetron sputtering, but it was difficult to synthesize Fe_5C_2 or Fe_7C_3 film in this work.

3.2. Composition of Fe_3C film

Fig. 6 shows an Auger electron spectrum (AES) of the depositied Fe–C films. No elements other than iron and carbon were detected. Although AES depth profiles of the films revealed a homogeneous composition

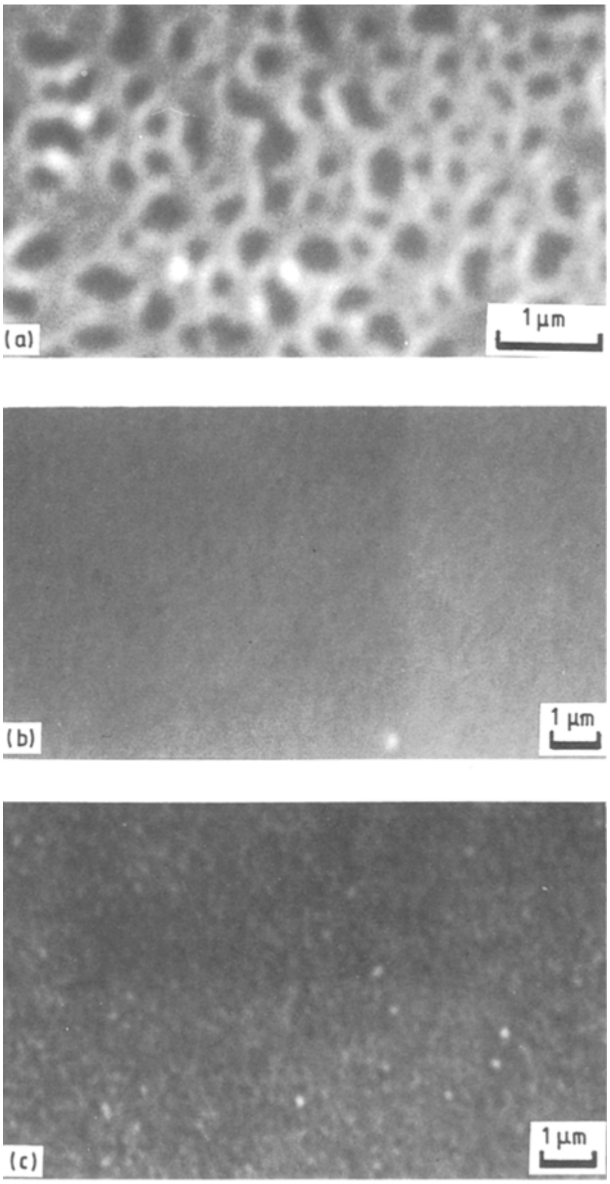

Figure 5 Scanning electron micrographs of Fe–C films deposited on SiO_2 glass at (a) 200 °C, 5 Pa, C/Fe = 30/70, (b) 350 °C, 5 Pa, C/Fe = 30/70, (c) 400 °C, 10 Pa, C/Fe = 30/70.

of iron and carbon, the quantitative ratio of iron to carbon in the film could not be determined accurately, because it is generally difficult to obtain highly accurate quantitative data by AES.

Fig. 7 shows the reciprocal susceptibility, $1/\chi$, as a function of temperature for the Fe_3C film deposited at 350 °C and 5 Pa. T_c of the film was determined to be 220 °C from the inflection point of the $1/\chi$ versus T curve, which agrees with previously published data. No other magnetic phase, such as iron metal, was evident in the curve up to 800 °C.

Because σ_s of the film was 120 e.m.u. g^{-1} (see Fig. 10), the film might include a non-magnetic impurity phase up to a few per cent, such as a free carbon. The free carbon may not have the sp^2 bonding, because a Raman spectrum of the film indicated the absence of graphite.

These results strongly indicate that the film deposited at 350 °C under 5 Pa was composed only of Fe_3C without any other iron carbide. However, the accurate composition of the films could not be decided, because it is very difficult to determine the free carbon content by the ordinary methods.

3.3. Magnetic properties of Fe_3C film

All films deposited in this work showed a in-plane magnetization, on the basis of the fact that the magnetization perpendicular to the film did not show any hysteresis. All films were about 0.1 μm thick, as mentioned in Section 3.1.

Fig. 8 shows the effect of the substrate temperature on magnetic properties of the Fe–C films deposited on SiO_2 glass at 10 Pa. The σ_s of the films increased slightly from 100 e.m.u. g^{-1} to 120 e.m.u. g^{-1} with increase in the substrate temperature, because the crystallinity of the films increased with the temperature. The coercivity, H_c, of the film was around 1 Oe at the substrate temperature of 250 °C and increased rapidly from 1 Oe to 200 Oe with increase in the substrate temperature.

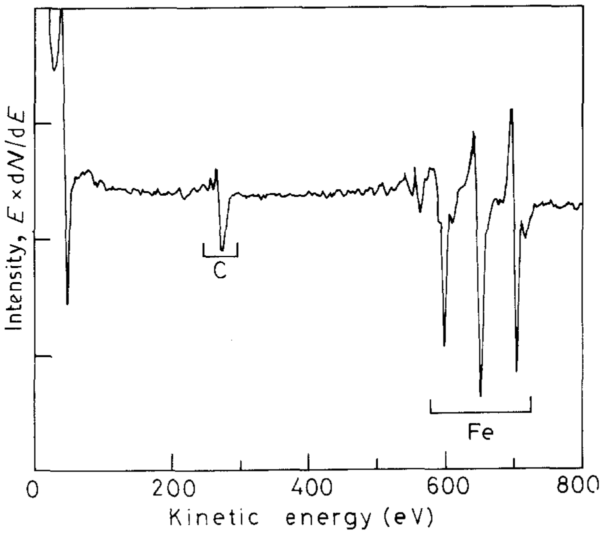

Figure 6 AES of Fe_3C film deposited on SiO_2 glass at 350 °C under 5 Pa (target composition C/Fe = 30/70, r.f. power 200 W).

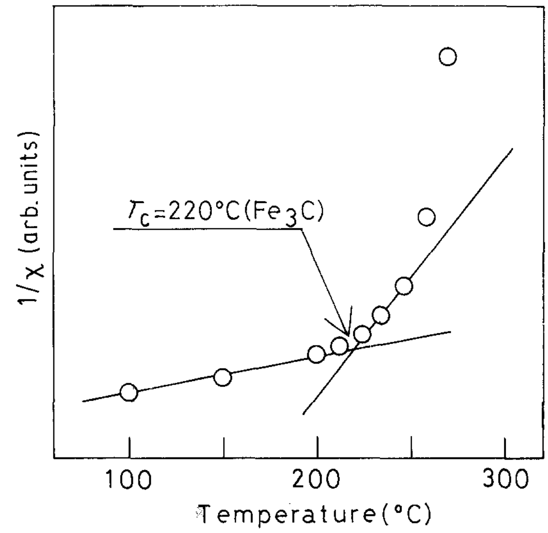

Figure 7 Reciprocal susceptibility versus temperature curve of Fe_3C film deposited on SiO_2 glass at 350 °C under 5 Pa (target composition C/Fe = 30/70, r.f. power 200 W).

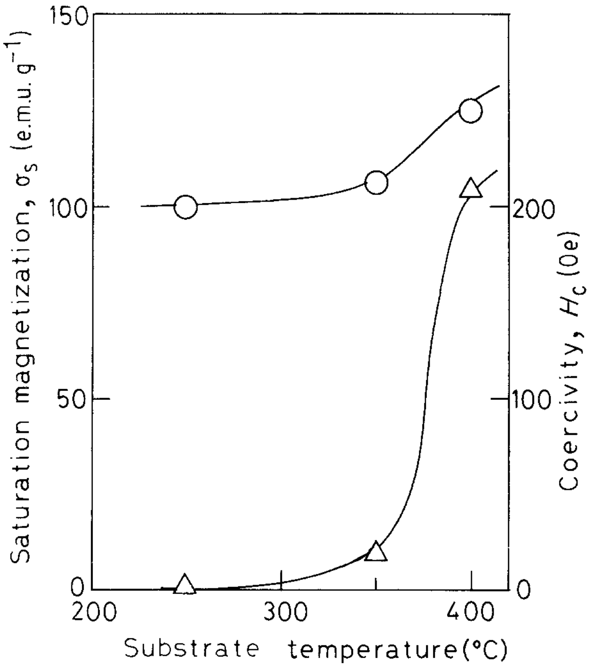

Figure 8 Effect of substrate temperature on magnetic properties of Fe–C films deposited on SiO_2 glass under 10 Pa (target composition C/Fe = 30/70, r.f. power 200 W). (○) σ_s, (△) H_c.

The result can be explained as follows: generally speaking, H_c of the film depends on the degree of magnetic domain wall motion. Therefore, an amorphous film is essentially soft, because the grain boundaries, which can hinder magnetic wall motion (pinning effect), are not incorporated in the film. Thus, the H_c of a polycrystalline film is larger than that of an amorphous film.

Fig. 9 shows the effect of the target composition on the magnetic properties of Fe–C films deposited on SiO_2 glass at 350 °C and 5 Pa. Both the σ_s and H_c of the films increased from 100 e.m.u. g^{-1} to 120 e.m.u. g^{-1} and from 190 Oe to 250 Oe, respectively, with increase in the area of graphite on the target. The major phase was Fe_3C under all these conditions. The increases in σ_s and H_c result from the differences in orientation, crystallinity or composition of the films.

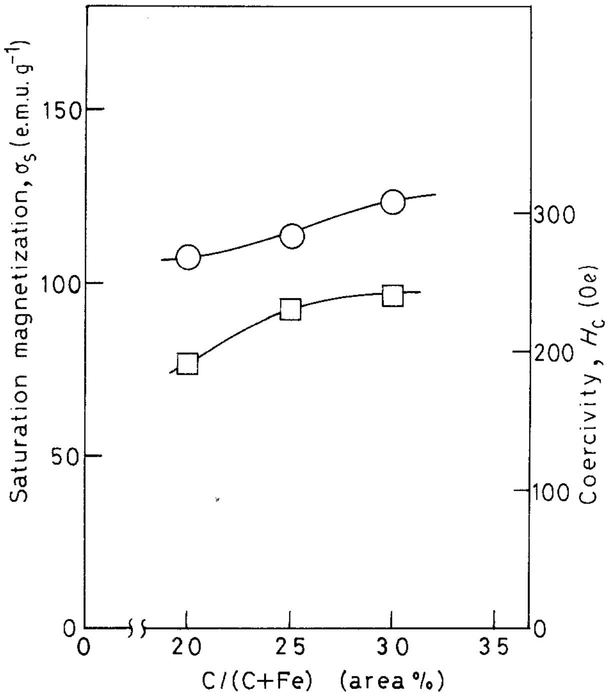

Figure 9 Effect of target composition on magnetic properties of Fe_3C films deposited on SiO_2 glass at 350 °C under 5 Pa (r.f. power 200 W). (○) σ_s, (□) H_c.

Fig. 10 illustrates the effect of the argon pressure on the magnetic properties of the Fe–C films deposited on SiO_2 glass at 350 °C. The σ_s of the films ranged from 100–120 e.m.u. g^{-1}, and passed a maximum value of 120 e.m.u. g^{-1} at 5 Pa. As described above, the film deposited under 5 Pa was composed only of Fe_3C. The maximum σ_s is attributable to the fact that the Fe_3C film had good crystallinity at 5 Pa. The H_c of the films was constant at 250 Oe, regardless of the argon pressure. Because H_c depends strongly on the microstructure, the result reveals that the films sputtered at different argon pressures had similar microstructure.

Fig. 11 shows the hysteresis loops of the Fe_3C films deposited on SiO_2 glass at 350 °C, at 5 and 10 Pa (in-plane magnetization). The film deposited under 10 Pa had a complex loop, because the film was comprised of a mixture of Fe_3C, Fe_5C_2 and α-Fe. On the other hand, the film deposited at 5 Pa has a square loop, which indicates that the film is composed only of Fe_3C. The H_c and σ_r/σ_s were 250 Oe and > 0.7, respectively.

The magnetocrystalline anisotropy constant, K_1, of Fe_3C could be calculated from the fact that the deposited film can be magnetized longitudinally. The following conditions are required for the perpendicular magnetization when the effects of shape anisotropy and magnetostriction [9] on the H_c are neglected

$$H_k = 2K_1/\sigma_s > 4\pi\sigma_s = H_{demag} \quad (1)$$

where H_k is the anisotropy field, and H_{demag} is the

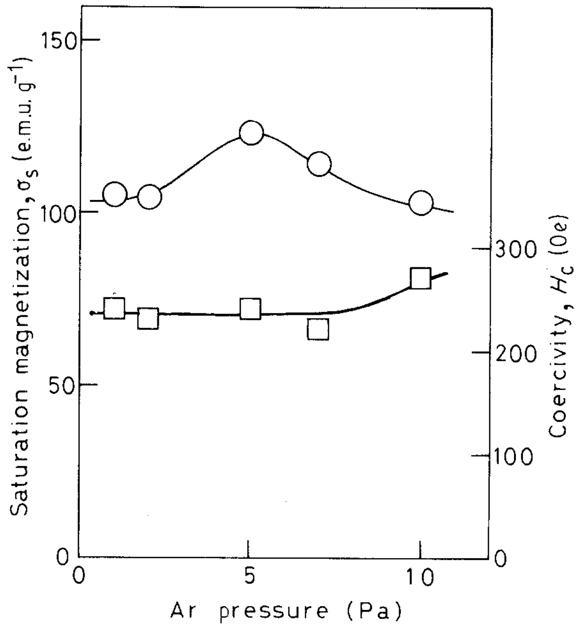

Figure 10 Effect of argon pressure on magnetic properties of Fe_3C films deposited on SiO_2 glass at 350 °C (target composition C/Fe = 30/70, r.f. power 200 W). (○) σ_s, (□) H_c.

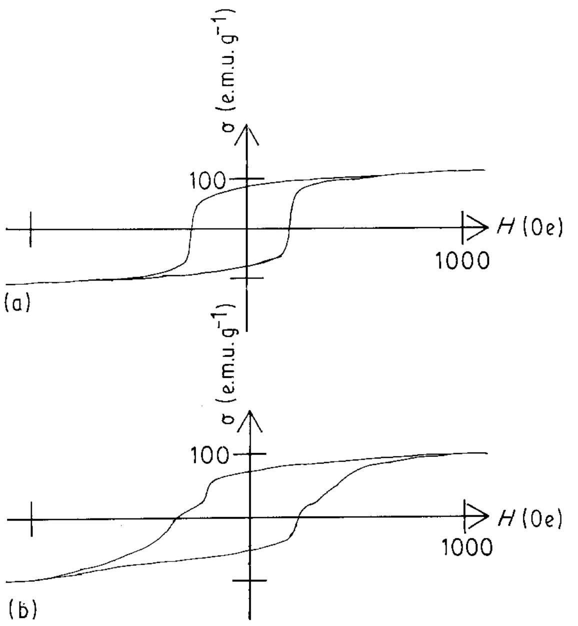

Figure 11 Hysteresis loops of Fe–C films deposited on SiO_2 glass at 350 °C under (a) 5 and (b) 10 Pa (target composition C/Fe = 30/70, r.f. power 200 W).

demagnetization field. Because the deposited Fe_3C film has the in-plane magnetization, K_1 of the Fe_3C film is as follows

$$K_1 < 2\pi\sigma_s^2 \quad (2)$$

where σ_s is about 100 e.m.u. g^{-1} (= 800 e.m.u. cm^{-3} or 1 T), then

$$K_1 < 1 \times 10^5 \text{ J m}^{-3} \quad (3)$$

Because the Fe_3C film did not show any perpendicular hysteresis loop, K_1 of the Fe_3C film might be of the order of 1×10^4 J m^{-3}. Blum and Pauthenet reported that the K_1 of Fe_3C was 10^6 J m^{-3} from H_c of the Fe_3C particles [12]. However, they did not report the particle size and shape. This difference might be caused by the effect of shape anisotropy on H_c.

4. Conclusion

The synthesis and magnetic properties of Fe_3C film were investigated in detail. α-Fe was the major phase in the deposited film at a substrate temperature of 300 °C or below under an argon pressure of 10–20 Pa. Fe_3C films were obtained at 350 °C or above at pressures below 10 Pa. The Fe_3C content in the films increased with increasing the substrate temperature and decreasing argon pressure. The target composition had little effect on which phase was favoured. The AES spectrum and the thermomagnetic measurement revealed that the films deposited at 350 °C and 5 Pa were composed only of Fe_3C single-phase without free carbon.

The saturation magnetization and coercivity of the Fe_3C film were 120 e.m.u. g^{-1} and 250 Oe, respectively. The film was magnetized along the longitudinal direction. The magnetocrystalline anisotropy of Fe_3C was presumed to be around 10^4 J m^{-3}.

Acknowledgement

This work was supported in part by a Grant-in-Aid for Scientific Research (B), the Ministry of Education, Science and Culture.

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Received 12 November 1991
and accepted 14 August 1992