Magnetic Properties of Fe₃C Thin Film Prepared by the IBS Method

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The magnetic properties of Fe-C thin film prepared by the ion-beam sputtering method (IBS) using a composite target were investigated. A single-phase Fe₃C thin film was obtained from as-deposited amorphous Fe-C thin films after heated up to 400°C. From magnetization measurement and X-ray diffraction, it was confirmed that the Fe₃C film is single-phase without any impurity phase. Hyperfine parameters were estimated from the results of conversion electron Mössbauer spectroscopy (CEMS) measurement. The central values of the hyperfine field ($B_{\text{hf}} = 205$ kOe), isomer shift ($IS = 0.20$ mm/s), and quadrupole shift ($QS = 0.03$ mm/s) for the film are consistent with those for bulk Fe₃C.

Key words: Fe₃C thin film, ion-beam sputtering (IBS), conversion electron Mössbauer spectroscopy (CEMS), hyperfine structure.

1. Introduction

The crystal structure and magnetic properties of Fe₃C compound have been investigated extensively for a long time, both from the viewpoint of pure physics and from that of the material's application as carbon steel^{1)–5)}.

Recently, Fe-C alloy films^{6),7)} have received considerable attention on account of their soft magnetic properties^{6),8),9)}. On the other hand, there have been only a few reports on Fe₃C thin films^{10),11)}. In view of the low solubility between Fe and Fe₃C at high temperatures, the combination of Fe and Fe₃C has a potential for practical application as a stable magnetic multilayer GMR sensor at high temperatures. In this paper, we report the preparation of a single-phase Fe₃C thin film by the IBS method. Generally, to obtain a thin film with stoichiometric composition by the sputtering method, the composition of the target and the deposition conditions such as gas pressure, substrate temperature, deposition rate and so on, are important. It is difficult to get a reproducible stoichiometric thin film, when an ordinarily sintered or compounded target is used, because of the large difference between the sputtering rates for Fe (2.0 atoms/Ar⁺ ion) and C (0.7 atom/Ar⁺ ion)¹²⁾ in the present case. However, it is possible to prepare an easily reproducible Fe₃C thin film by using a strictly designed composite target. In this paper, we report the crystal structure and magnetic properties of an Fe-C thin film prepared by the ion-beam sputtering method (IBS).

2. Experimental Procedure

Fe-C thin films were prepared by the conventional ion-beam sputtering (IBS) method. The base pressure and sputtering pressure of the IBS apparatus were $< 9 \times 10^{-7}$ Torr and 3.2×10^{-4} Torr, respectively. The beam current and beam voltage of Ar⁺ ions were 40 mA and 1000 V,

respectively. The deposition rate was $\sim 0.4 \text{ Å/s}$ for Fe-C, and the substrate temperature was fixed at $\sim 50^\circ \text{C}$. We used a glass (Corning #7059) substrate. The thickness of the film was fixed at 3000 Å (5000 Å for CEMS measurement). We used a composite target with 5N carbon chips (10 mm $\times$ 10 mm) fixed to an Fe (75 mm ϕ : 3N) target (Fig. 1). Three different composite targets were prepared with the area ratio, Fe:C = ①52.4:47.6, ②49.0:51.0, and ③45.1:54.9, respectively. The sample numbers are the same as the target numbers. It should be mentioned that in the case of using a sintered target with Fe:C = 3:1, the composition of the thin films was not reproducible. It is considered that the composition of the target surface changed gradually in each sample preparation procedure because of the large difference in sputtering rates between Fe and C. Accordingly, for the preparation of reproducible Fe-C thin film, it is necessary to use a composite target with a strictly controlled area ratio of Fe to carbon chip. The magnetization was measured with a conventional vibrating sample magnetometer (VSM). The temperature dependence of magnetization was measured in the magnetic field of 10 kOe in a vacuumed atmosphere ($< 1.0 \times 10^{-5}$ Torr) with heating (cooling) velocity of 4.5°C/min . X-ray diffraction (XRD) with a Cu target was used for the structural analysis. The hyperfine structures were measured by conversion electron Mössbauer spectroscopy (CEMS) at room temperature. The size of the sample for the CEMS was $3 \times 3 \text{ cm}^2$.

3. Results and Discussion

3.1 Magnetization

Figure 2 shows the results of the magnetization as a function of temperature for the Fe-C thin films (samples ①~③) prepared by using composite targets (①~③). From the design of the targets, it is expected that the composition of C increases with increasing number of

Fig. 1 Design of the composite target for IBS.

Fig. 2 Magnetization as a function of temperature at 10 kOe for sample①–③. Vertical arrows indicate T_c for each sample in the cooling process.

samples. None of the magnetization versus temperature (M-T) curves were repeatable during the heating and the cooling processes. As-deposited films are amorphous and crystallized during heating up to 400 °C. For sample①, the rapid decrease in magnetization at around 280°C corresponds to crystallization of Fe_3C from an amorphous state. To confirm the crystallization, we performed XRD measurements before and after the rapid decrease in magnetization. The XRD pattern under 280°C showed that the state was still amorphous, but the pattern above 280°C showed a crystalline state. As a result, it is considered that the crystallization temperature ($T_{crys.}$) of sample ① is about 280 °C. The extrapolated Curie temperature for the amorphous state of sample ① is estimated at around 330 °C. For sample ②, T_c and $T_{crys.}$ overlap each other, as can be seen in Fig. 2. For sample ③, the Curie temperature for the amorphous state was estimated at 265 °C. Though it is not clear in the figure, a step in the magnetic susceptibility is observed at around 320 °C, which corresponds to $T_{crys.}$ for sample③. Accordingly, $T_{crys.}$ increases with increasing C composition. In contrast, T_c of amorphous Fe-C decreases with increasing C composition. Even at 400 °C, sample ① still shows a small amount of magnetization caused by the precipitated pure Fe phase, whereas the magnetization disappears from samples ② and ③ at this temperature.

After cooling to room temperature, the magnetization was 120.5 emu/g for sample ②. This value agrees with the bulk magnetization (122–130 emu/g) at 10 kOe^{4),5)}. The Curie temperature (T_c) was estimated from the M^2 -T

Fig. 3 Magnetization curves for samples ①–③ (a) as-deposited and (b) after heating to 400°C

plot for each sample. The estimated T_c 's are shown by the vertical arrows in Fig. 2. The estimated T_c for sample ② was $227 \pm 5^\circ\text{C}$ which almost matches that of bulk Fe_3C ^{4),5),13)}. It is considered that the slight difference in T_c for Fe_3C between samples ① and ② is due to the solubility of C in Fe_3C . For sample ③, the T_c is estimated to be $247 \pm 5^\circ\text{C}$, which agree well with the T_c of the Fe_5C_2 phase described in a later section.

Figure 3 shows magnetization curves for samples ①–③, (a) as-deposited and (b) after heating to 400°C. The as-deposited samples show a smaller coercive force than the heated samples. The magnetization at 10 kOe decreases with increasing carbon composition. The results of magnetization measurement for the heated

Table 1 Magnetic properties for samples ①–③ after heating.

	M (emu/g) (10 kOe)	T_c (°C)
Reference for bulk Fe_3C	122–130 ^{4),5)}	208–215 ^{4),5),13)}
Sample ① (Fe+ Fe_3C)	140	213 ± 5
Sample ② (Fe_3C)	120.5	227 ± 5
Sample ③ (Fe_3C + Fe_5C_2)	110	247 ± 5

Fig. 4 X-ray diffraction patterns for samples ①~③ (a) as-deposited and (b) after heating to 400°C.

samples are listed in Table 1. From the table, we conclude that sample ② is Fe_3C thin film without any impurity phase.

In order to confirm the structure of these thin films, an X-ray diffraction analysis was carried out.

3.2 X-Ray Diffraction

Figure 4 shows the X-ray diffraction patterns of (a) as-deposited and (b) heated samples. The as-deposited samples show a broad peak around $2\theta = 42^\circ$. This result indicates that the structures of as-deposited films are amorphous, and that samples become crystalline after heating to 400°C. As shown in Fig. 4 (b), the heated samples of ①, ②, and ③ consist of $\text{Fe}_3\text{C} + \alpha\text{-Fe}$, Fe_3C , and $\text{Fe}_3\text{C} + \text{Fe}_5\text{C}_2$ ^{14),15),16)}, respectively. It should be noted that sample ② is Fe_3C single phase. In contrast, sample ① is Fe-rich and sample ③ is carbon-rich compared with the stoichiometric Fe_3C . These results agree well with the magnetization measurement mentioned in the previous section. The remaining magnetization in sample ① at 400°C is from segregated $\alpha\text{-Fe}$. It is considered that the rather high T_c for sample ③ is related to Fe_5C_2 phase. The Curie temperature for Fe_5C_2 is $247 \pm 3^\circ\text{C}$ ^{5),17)}, which agrees with the $247 \pm 5^\circ\text{C}$ measurement for the thin film. To confirm the hyperfine structures of the Fe_3C thin film, Mössbauer spectroscopy measurement was carried out.

3.3 Conversion Electron Mössbauer Spectroscopy

The hyperfine structure of the sample with target ②, which is considered to be stoichiometric Fe_3C from magnetization measurement and XRD, was measured by conversion electron Mössbauer spectroscopy (CEMS). Figure 5 shows the Mössbauer spectra and the results of analysis for a film with a thickness of 5000 Å, (a) as-deposited and (b) after annealing at 400°C for 1 hour. The dots in the figure show the experimental results and

Fig. 5 Mössbauer spectra and the results after analysis for the film (5000 Å) made from target ②, (a) as-deposited and (b) after annealing at 400°C for 1 hour.

Table 2 Central values of the hyperfine parameters obtained after analysis of the CEMS spectrum compared with those of bulk Fe₃C.

	As-deposited	Annealed	Reference for bulk Fe ₃ C ^(18,19,20)
B _{hf} (kOe)	212 ± 3	205 ± 3	208 – 210
IS (mm/s)	0.17 ± 0.01	0.20 ± 0.01	0.18 – 0.30
QS (mm/s)	0.00 ± 0.01	0.03 ± 0.01	0.01 ± 0.05

the solid line shows the analyzed result of the fitting by a least mean square method using sextet Lorenz functions. The spectrum for as-deposited film (Fig. 5(a)) show fairly broad peaks, which are typical for an amorphous state. We assumed a Gaussian distribution for the analysis. The distribution curve obtained by the fitting is shown in the right inset of Fig. 5(a). The mean value of the hyperfine field is estimated to be 212 kOe and the half width of the distribution is 125 kOe. The isomer shift (IS) and the quadrupole shift (QS) are estimated to be 0.17 mm/sec and 0.00 mm/sec., respectively. The intensity ratio of the sextet for this spectrum is 3:2:1:1:2:3, which means that the direction of the magnetic moment is randomly oriented. The Mössbauer spectrum and the results of analysis for an annealed sample are shown in Fig. 5(b). This spectrum shows a sharp line width compared with the as-deposited state, and no other impurity phase is observed. However, the sextet shows a slightly asymmetric intensity ratio. This asymmetric spectrum is typical for the distribution of IS and QS. Accordingly, this spectrum is fitted with a distribution of the hyperfine field, isomer shift, and quadrupole shift.²¹⁾ In this fitting, we assume linear distribution of the isomer shift and quadrupole shift with respect to the hyperfine field distribution. The mean values of B_{hf}, IS and QS are 205 ± 3 kOe, 0.20 ± 0.01 mm/s, and 0.03 ± 0.01 mm/s, respectively. The values agree well with those of bulk Fe₃C (B_{hf} = 208–210 kOe, IS = 0.18–0.30 mm/s, and QS = 0.01 ± 0.05 mm/s)^(18,19,20). The intensity ratio of the sextet is 3:2.4:1:1:2.4:3, which indicates that the average direction of the magnetic moment is canted 30 deg. from in-plane to out-of-plane. The clearest difference between as-deposited and after annealed sample is in the distribution of the hyperfine field. The narrow line width for the spectrum of the annealed sample is consistent with crystallization of Fe₃C. This result suggests that the present Fe₃C thin film includes no impurity phase with some distortion. Table 2 shows the results of the analysis of the hyperfine parameters compared with those for bulk Fe₃C. From this table, it is shown that the Fe₃C thin film has almost the same values as bulk Fe₃C.

4. Summary

1. The Fe-C thin films were prepared by ion-beam sputtering (IBS), using a composite target. A single-phase Fe₃C thin film was obtained from as-deposited amorphous Fe-C thin films after heating to 400°C.
2. Hyperfine parameters were estimated from the conversion electron Mössbauer spectroscopy (CEMS). The mean values of the hyperfine field (B_{hf} = 205 kOe),

isomer shift (IS = 0.20 mm/s), and quadrupole shift (QS = 0.03 mm/s) for this film show similar values to those of bulk Fe₃C.

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