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Iron nitride films produced by arc deposition of iron in a nitrogen atmosphere

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Abstract
Iron nitrides with a high nitrogen content are metastable and can be prepared in the form of fine particles or as a film. An arc discharge of iron metal in a reactive atmosphere provides a convenient method to produce iron-based films. In this study, iron nitride films were formed on an aluminum substrate by arc deposition of iron in a nitrogen atmosphere under a controlled nitrogen flow rate (10–30 sccm). The samples were analyzed by transmission Mössbauer spectroscopy and X-ray diffraction. When the temperature of the aluminum substrate during deposition was maintained at 298 K, ε-$Fe_{3\text{-}2}N$ was obtained for nitrogen flow rates in the range 20 to 30 sccm. When the aluminum substrate was heated to 573 K during deposition with nitrogen flow rates of 15 to 30 sccm, a highly crystalline ε-Fe_2N film was formed.

Keywords Iron nitride · Film · Arc deposition · Mössbauer spectroscopy · X-ray diffraction

1 Introduction

Iron nitrides are useful magnetic materials and have been studied for a long time, especially those with a low nitrogen (N) content. It is known that the basic iron (Fe) crystal structure and the magnetic properties change when small amounts of N atoms enter Fe interstitial positions

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[1]. Generally, however, Fe nitrides with a high N content are metastable; therefore, the material is often prepared in the form of fine particles or as a film [2–5]. We have previously reported the synthesis of single-phase FeN (rock salt type γ'''-FeN or zinc blende type γ''-FeN) based on pulsed laser deposition while controlling the substrate temperature under a N atmosphere [6]. In the present study, we have focused on the synthesis of other metastable Fe nitrides (ε-$Fe_{3\text{-}2}N$ or ζ-Fe_2N) using an arc plasma gun. In studies on Fe_xN particles, it has been reported that ε-Fe_xN has a hexagonal crystal structure for various N compositions in the range $x = 2$ to 3. The magnetic properties of Fe_xN change depending on the temperature: ε-Fe_xN ($2 < x < 2.3$) are paramagnetic at room temperature, but become ferromagnetic at low temperature. The Curie temperature of ε-Fe_xN ($2 < x < 2.3$) decreases as the Fe content x decreases [7–9]. Another Fe_2N compound ζ-Fe_2N has an orthorhombic structure. The ζ-Fe_2N is paramagnetic at room temperature but is antiferromagnetic at low temperature (a Neel temperature of 9 K). The phase boundary between ε-Fe_2N and ζ-Fe_2N has also been the subject of study [10]. An arc plasma gun produces an arc discharge even in an atmosphere with a relatively high pressure [11], thus the possibility of preparing metastable film Fe_2N compounds by generating an Fe plasma in a reactive N atmosphere. In this study, we report production of the metastable Fe nitride films using an arc-plasma deposition of Fe in a N atmosphere.

2 Experimental

An aluminum (Al) plate (0.1 × 20 × 20 mm / purity 99.999%) and ^{57}Fe-enriched metal attached to a natural Fe metal block were employed as the substrate and the evaporation source, respectively. Nitrogen gas (purity 99.99995%) was introduced to the discharge electrode of the arc plasma gun (ULVAC ARL-300) while controlling the flow rate in the range between 10 and 30 sccm using a mass flow controller. The pressure of the N atmosphere surrounding the metal Fe sample was approximately 1×10^{-2} Pa. A total of 10,000 arc discharge pulses of the Fe metal (discharge voltage 100 V; repetition rate 1 Hz; capacitor capacity 360 × 5 μF) were accumulated to obtain a film sample. The anode was arranged coaxially on the outer periphery with respect to the Fe target, and a film was formed on the Al substrate, arranged perpendicularly in an axial direction at a distance of 245 mm from the Fe target. The α-Fe equivalent thickness of a typical film was 800 nm. The substrate during deposition was maintained at the desired temperature of between 298 and 573 K using a ceramic heater. The prepared samples were analyzed by transmission Mössbauer spectroscopy (^{57}Co/Rh, Wissel1200) and X-ray diffraction (XRD; RINT2500, 50 kV, 300 mA).

3 Results and discussion

3.1 Films deposited for a substrate temperature of 298 K

The film samples were produced by maintaining the Al substrate temperature at 298 K during deposition for variation in the N flow rate (10–30 sccm). The XRD patterns for the samples are shown in Fig. 1. The film produced with a N flow rate of 10 sccm (Fig. 1a) showed patterns for Al and α-Fe without other species being present, while the peak positions of Al and α-Fe were almost identical. The film produced with the N flow rate of 15 sccm (Fig. 1b) had a broad peak

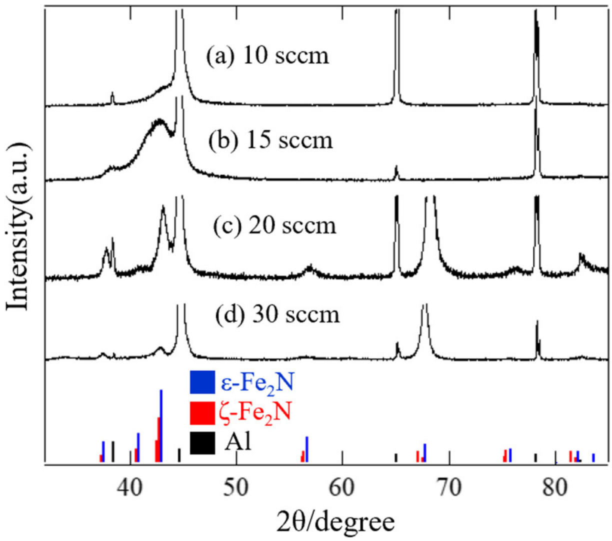

Fig. 1 X-ray diffraction patterns for films produced by arc deposition of Fe onto an Al substrate at 298 K. Nitrogen flow rates: **a** 10 sccm, **b** 15 sccm, **c** 20 sccm, **d** 30 sccm

at low angle that was assigned to an Fe nitride. The main component of the film consisted of Fe nitride or α-Fe with a large number of defects. When the film was produced under a N flow rate of 20 sccm, new diffraction peaks appeared. These new patterns corresponded to the peaks for ε-Fe_2N (PDF # 04–007-1467) or ζ-Fe_2N (PDF # 00–050-0958). The peak intensity at 67° was considerably greater than that reported in the literature [12], which might be caused by an enhancement from orientation of the film sample in a specific crystal plane (300). A similar XRD pattern was observed at a N flow rate of 30 sccm, and the peak position shifted to lower angle because of the increase in the lattice constant caused by the insertion of N atoms in the Fe lattice [13]. The Mössbauer spectra measured at room temperature are shown in Fig. 2. The Mössbauer parameters are summarized in Table 1. The samples produced at N flow rates of 10 sccm (Fig. 2a) and 15 sccm (Fig. 2b) showed broad absorption signals with well distributed hyperfine magnetic fields, signifying the presence of α-Fe containing many lattice defects. In the sample produced at a N flow rate of 20 sccm (Fig. 2c), in addition to a sextet of α-Fe, a component of the distributed hyperfine magnetic fields was observed; the hyperfine magnetic field had two local maxima at 7.8 and 18.6 T. It has been reported that ε-$Fe_{2.4}N$ fine particles at 4.2 K had two sextets of $H = 8$ and 18 T [14]. Although slight discrepancies due to different sample shapes existed, the film was assigned as ε-$Fe_{2.4}N$. The main component of the sample produced under a N flow rate of 30 sccm was a paramagnetic doublet (Fig. 2d) of ε-Fe_xN ($2.0 < x < 2.3$), because it was reported that ε-Fe_xN ($2.0 < x < 2.3$) with a high N content was paramagnetic at room temperature [15]. Another weak doublet component (X) was found in the spectrum (Fig. 1d). To the best of our knowledge, the Mössbauer parameters of the doublet X fitted none of the parameters reported previously. Species X might be an Fe nitride with a high N content and having a similar structure to that of ε-Fe_2N.

Mössbauer spectra of the films produced at N flow rates of 20 sccm and 30 sccm were measured at 3 K (Fig. 3) where the dominant doublet in the spectra observed at 298 K was absent. The Mössbauer parameters are summarized in Table 2. The Mössbauer spectrum of the film produced under a N flow of 20 sccm (Fig. 3a) was fitted as the combination of α-Fe and a

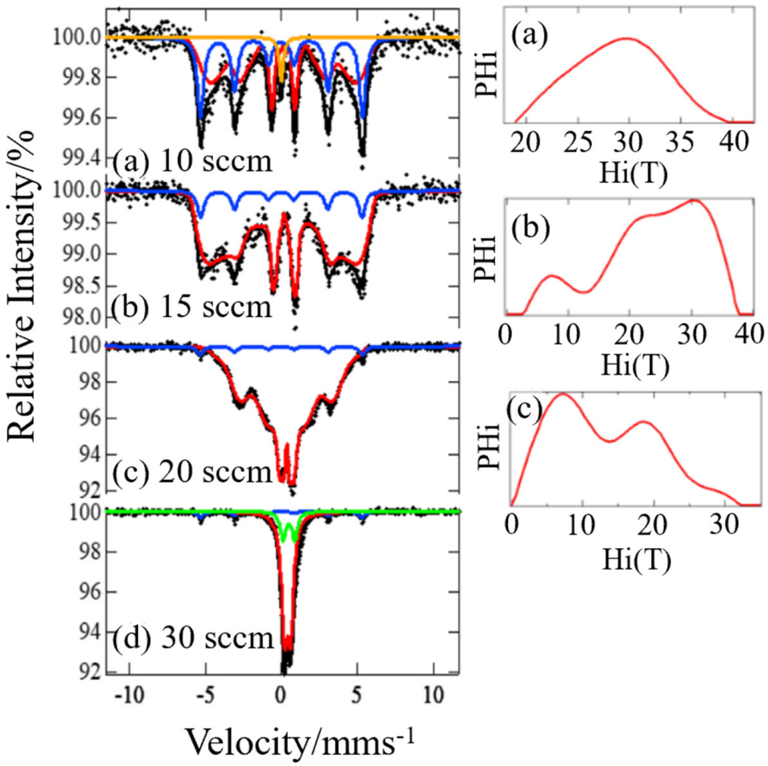

Fig. 2 Room-temperature Mössbauer spectra for films produced by arc deposition of Fe onto an Al substrate at 298 K. Nitrogen flow rates: **a** 10 sccm, **b** 15 sccm, **c** 20 sccm, **d** 30 sccm. The distributions of hyperfine magnetic fields are indicated on the right side

component with a distribution of hyperfine magnetic fields. It has been reported that ε-Fe_2N and ζ-Fe_2N exhibit a doublet ($\delta = 0.57$, $\Delta E\text{q} = 0.29$) and are maintained even at 4.2 K [15, 16]. As the distribution of the hyperfine magnetic fields had a local maxima at $H = 13.4$ and 25.2 T,

Table 1 Mössbauer parameters for the spectra in Fig. 2

Flow rate /sccm	Component	δ /mms^{-1}	ΔEq /mms^{-1}	H /T	Γ /mms^{-1}	Yields /%
10	α-Fe	0.01(1)	0.01(0)	33.0(2)	0.50(3)	38.0
	γ-Fe	0	–	–	0.32(2)	3.4
	α-Fe/N_2	0.14(2)	0.01(5)	30.0*	–	58.6
15	α-Fe	0.01(2)	0.01(1)	32.9(1)	0.50(2)	10.8
				7.6*		
	α-Fe/N_2	0.16(5)	0.09(3)	20.4*	-	89.2
				31.0*		
20	α-Fe	0.01(1)	0.01(5)	33.0(1)	0.50(4)	8.7
	ε-$Fe_{2.4}N$(FeII)	0.34(7)	0.02(4)	18.6*	–	91.3
	ε-$Fe_{2.4}N$(FeIII)	0.34(7)	0.02(4)	7.8*	–	
30	α-Fe	0.01(2)	0.01(6)	33.0(3)	0.50(1)	9.0
	ε-$Fe_{2.3}N$	0.42(4)	0.38(0)	–	0.46(7)	73.9
	X	0.52(7)	1.02(5)	–	0.36(2)	17.1

*Hyperfine magnetic field at the mode of the distribution

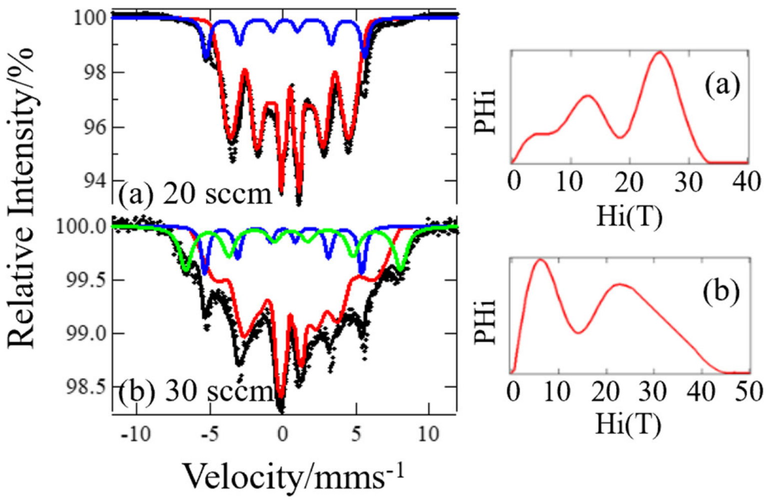

Fig. 3 Mössbauer spectra measured at 3 K for films produced by arc deposition of Fe onto an Al substrate at 298 K. Nitrogen flow rates: **a** 20 sccm, **b** 30 sccm. The distributions of hyperfine magnetic fields are indicated on the right side

the assignment of the film was confirmed to be ε-$Fe_{2.4}N$ though the material may contain a large number of defects.

The spectra of the film produced at a N flow rate of 30 sccm showed a combination of three components: two sets of sextets (α-Fe and an unassigned species X) and a component with a hyperfine magnetic field distribution. The unassigned component X had a large hyperfine magnetic field $H = 46.0$ T, which might correspond to the species found as a paramagnetic doublet in the spectrum measured at 298 K (Fig. 2d). The species X did not correspond to any of the Fe nitride species reported in the literature. The large H value for species X might be an impurity Fe oxide, which was not found in the XRD profile (Fig. 1d). Further study is required on this aspect. The main component having the distributed hyperfine magnetic fields had two local maxima at 9.6 T and 23.6 T. These values were in good agreement with the values for fine particles of ε-$Fe_{2.3}N$ ($H = 11$ T, 24 T) previously reported [17]. In addition, Mössbauer spectra of the sample produced under a N flow of 30 sccm were measured for variation in temperature (Fig. 4). The main component was a paramagnetic doublet above 9 K, which was completely split magnetically at 6 K. From these measurements, the component was found to possess a Curie temperature Tc between 6 and 9 K.

Table 2 Mössbauer parameters for the spectra in Fig. 3

Flow rate /sccm	Component	δ /mms^{-1}	ΔEq /mms^{-1}	H /T	Γ /mms^{-1}	Yields /%
20	α-Fe	0.01(3)	0.01(1)	33.0(4)	0.50(2)	9.9
	ε-$Fe_{2.4}$N(FeII)	0.45(6)	0.14(2)	25.2*	–	90.1
	ε-$Fe_{2.4}$N(FeIII)	0.45(6)	0.14(2)	13.4*	–	
30	α-Fe	0.01(2)	0.01(4)	33.5(2)	0.50(2)	10.5
	ε-$Fe_{2.3}$N(FeII)	0.52(4)	0.38(3)	23.6*	–	72.5
	ε-$Fe_{2.3}$N(FeIII)	0.52(4)	0.38(3)	9.6*	–	
	X	0.57(8)	0.01(5)	46.0(6)	1.00(5)	17.0

*Hyperfine magnetic field at the mode of the distribution

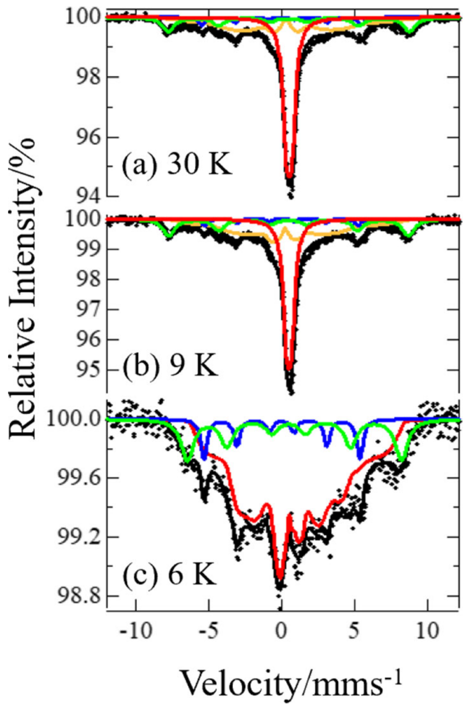

Fig. 4 Mössbauer spectra measured at various temperatures for the film produced by arc deposition of Fe onto an Al substrate at 298 K. Nitrogen flow rate: 30 sccm; measurement temperatures: **a** 30 K, **b** 9 K, **c** 6 K

3.2 Films deposited for a substrate temperature of 573 K

The samples produced at a substrate temperature of 298 K exhibited distributed hyperfine magnetic fields, and thus it was found that the samples did not have uniform lattice structures

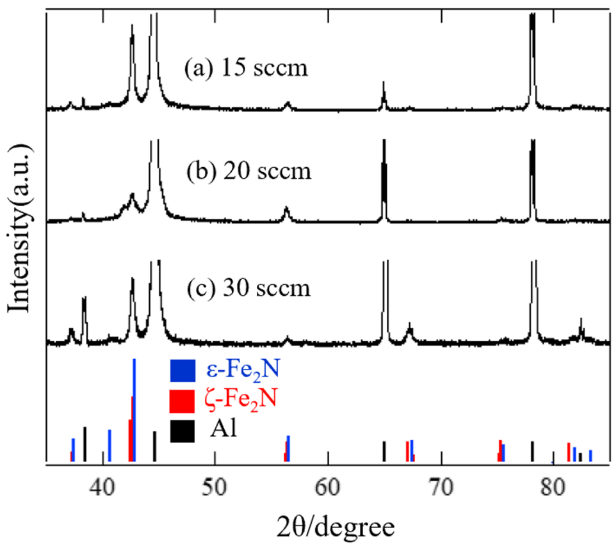

Fig. 5 X-ray diffraction patterns for films produced by arc deposition of Fe onto an Al substrate at 573 K. Nitrogen flow rates: **a** 15 sccm, **b** 20 sccm, **c** 30 sccm

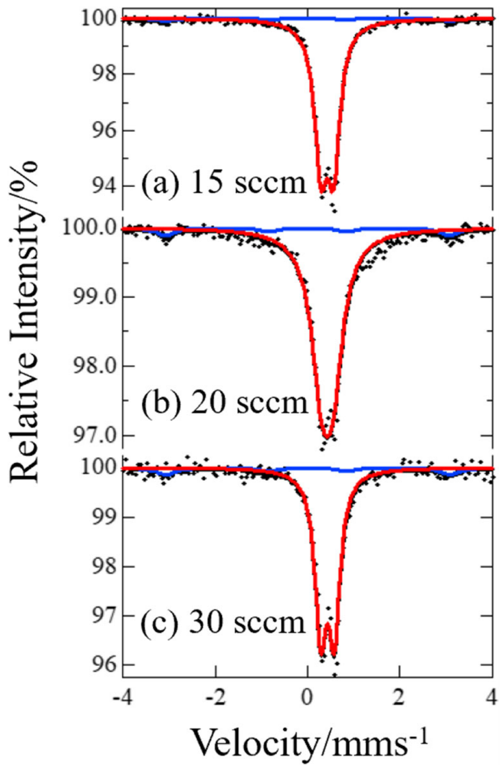

Fig. 6 Room-temperature Mössbauer spectra for films produced by arc deposition of Fe onto an Al substrate at 573 K. Nitrogen flow rates: **a** 15 sccm, **b** 20 sccm, **c** 30 sccm

and contained lattice defects. Therefore, an Al substrate was heated to 573 K with a ceramic heater and arc deposition of Fe was similarly performed in a N atmosphere to promote a thermal reaction during the formation of the film and in so doing produce a film sample of high crystallinity. The XRD patterns of the samples produced under 15, 20 and 30 sccm of N flow (Fig. 5) were similar to those for ε-Fe_2N (PDF # 04–007-1467) and ζ-Fe_2N (PDF # 00–050-0958). The widths of the peaks were less than those for the samples produced at room temperature (Fig. 1), indicating that heating of the substrate decreased the number of lattice defects. All the Mössbauer spectra measured at room temperature (Fig. 6 and Table 3) showed paramagnetic doublets. The Mössbauer spectra of the identical samples were also measured at low temperature (Fig. 7 and Table 4). The spectrum for the sample produced at a N flow of 15

Table 3 Mössbauer parameters for the spectra in Fig. 6

Flow rate /sccm	Component	δ /mms^{-1}	ΔEq /mms^{-1}	H /T	Γ /mms^{-1}	Yields /%
15	α-Fe	0.01(3)	0.01(1)	32.9(5)	0.50(5)	9.1
	ε-Fe_xN^*	0.43(2)	0.28(3)	–	0.33(9)	90.9
20	α-Fe	0.01(1)	0.01(5)	33.0(1)	0.50(1)	16.1
	ε-Fe_2N	0.43(7)	0.25(4)	–	0.53(7)	83.9
30	α-Fe	0.01(2)	0.01(4)	33.0(1)	0.50(1)	15.5
	ε-Fe_2N	0.44(5)	0.28(2)	–	0.34(6)	84.5

* $2.0 < x < 2.5$

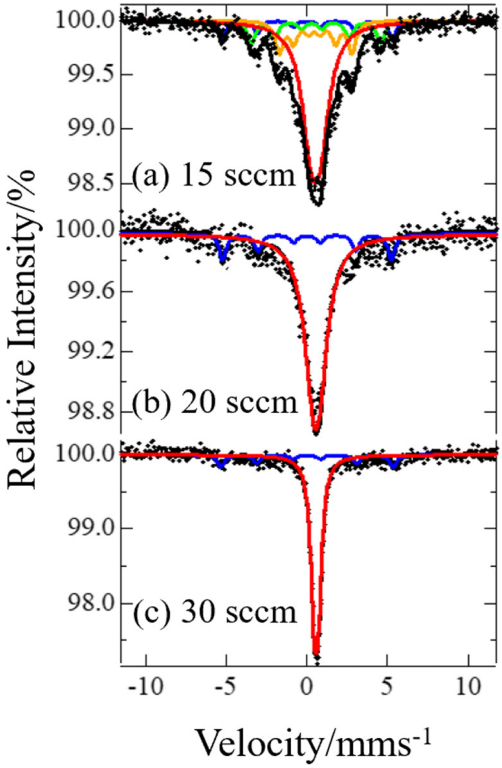

Fig. 7 Mössbauer spectra measured at 3 K for films produced by arc deposition of Fe onto an Al substrate at 573 K. Nitrogen flow rates: **a** 15 sccm, **b** 20 sccm, **c** 30 sccm

sccm was fitted as a combination of three sets of sextets and a doublet. The components were assigned as ε-$Fe_{2.5}N$ (2 sets of sextets), ε-$Fe_{2.04}N$ (a doublet) [15, 17] and α-Fe (a sextet). When the doublet was fitted assuming a quadrupole splitting, the value $\Delta E\text{q} = 0.92(5)$ mm/s was larger than that of ε-Fe_2N reported in the literature ($\Delta E\text{q} = 0.28$ mm/s) [14]. Assuming that the doublet arose from a contribution of very low hyperfine magnetic fields, the hyperfine magnetic field was estimated to be 1.7 T that corresponded to $Fe_{2.04}N$ reported in literature [15]. In the samples produced at N flow rates of 20 sccm and 30 sccm, the main components maintained their doublet nature even at 3 K, thus, the spectrum was assigned to ε-Fe_2N [15]. In particular, the Mössbauer spectrum of the sample produced at 30 sccm featured a doublet with a narrow linewidth because of the high crystallinity. However, ε-Fe_2N and ζ-Fe_2N both

Table 4 Mössbauer parameters for the spectra in Fig. 7

Flow rate /sccm	Component	δ /mms^{-1}	ΔEq /mms^{-1}	H /T	Γ /mms^{-1}	Yields /%
15	α-Fe	0.01(1)	0.02(1)	33.5(3)	0.50(3)	9.0
	ε-$Fe_{2.5}$N(FeII)	0.45(4)	0.27(3)	26.0(3)	0.60(6)	13.1
	ε-$Fe_{2.5}$N(FeIII)	0.52(2)	0.06(6)	14.3(7)	0.60(10)	18.6
	ε-$Fe_{2.04}$N	0.56(4)	0.49(1)	1.7(2)	0.95(4)	59.3
20	α-Fe	0.01(1)	0.02(5)	33.2(1)	0.50(2)	18.1
	ε-Fe_2N	0.57(6)	0.33(3)	–	0.98(3)	81.9
30	α-Fe	0.01(1)	0.01(4)	33.2(5)	0.50(4)	15.6
	ε-Fe_2N	0.58(3)	0.27(2)	–	0.52(8)	84.4

maintained the doublet nature at low temperature, and the Mössbauer parameters had close values [15, 16], thus the possibility that ζ-Fe_2N was produced could not be discounted. However, the difference in lattice arrangement for Fe between the ε-phase and the ζ-phase was large, and thus it was considered more reasonable for the films with the same Fe lattice arrangement (ε-Fe_xN) to have been produced under all the N flow rate conditions used in the present study, rather than for a rapid phase change (ε-phase to ζ-phase) of the lattice structure of Fe_2N to have occurred.

4 Conclusion

Iron nitride films were successfully synthesized on an Al substrate by an arc-plasma-gun in a N atmosphere. Specifically, the arc discharge of metallic Fe decomposed the N molecules with almost simultaneous formation of Fe nitride. When the temperature of the Al substrate during deposition was maintained at 298 K, films consisting of ε-$Fe_{3\text{-}2}N$ were obtained for N flow rates greater than 20 sccm. However, such films were found to contain a larger number of lattice defects. When the substrate was heated to 573 K, highly crystalline films were produced for N flow rates greater than 20 sccm and the films consisted of ε-Fe_2N. It was demonstrated that the composition of ε-$Fe_{3\text{-}2}N$ was able to be controlled by varying the flow rate of N and the temperature of the Al substrate.

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