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Mössbauer study of iron nitride films produced by pulsed laser deposition

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Abstract Iron nitride films were produced by pulsed laser deposition of Fe onto an Al substrate in an N_2 atmosphere and their Mössbauer spectra and powder X-ray diffraction patterns were measured. The nitrogen content of the iron nitride films varied depending on the N_2 pressure. Under high N_2 pressures, γ"-FeN (ZnS structure) and γ"'-FeN (NaCl structure) were obtained. The yields of these two phases could be controlled by varying the Al substrate temperature. γ"-FeN and γ"'-FeN were found to be paramagnetic and antiferromagnetic, respectively, at 5 K.

Keywords Iron nitride film · γ-FeN · Pulsed laser deposition · Mössbauer spectroscopy · XRD

1 Introduction

Pulsed laser deposition (PLD) is a useful technique for preparing multielement films and it has been applied in industry. The composition and morphology of films produced by PLD can be controlled by varying the experimental conditions such as the substrate temperature during deposition, the ambient gas pressure, the laser power, and the laser wavelength. We have produced iron oxide [1] and iron carbide [2, 3] films by PLD.

Iron nitride has many phases and each phase has different magnetic characteristics. Iron nitride films or particles have been prepared by various methods [4–9]. Iron nitrides with low nitrogen contents have been extensively studied, whereas iron nitrides with high nitrogen contents have not been well investigated. FeN has been

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reported to have two phases, γ"-FeN (ZnS structure) and γ"'-FeN (NaCl structure), which generally form simultaneously so that it is difficult to produce a single phase [4–8]. In this study, we report the production of iron nitride films using PLD. These films were investigated by Mössbauer spectroscopy and powder X-ray diffraction (XRD).

2 Experimental

PLD of Fe on Al substrate was performed using a Nd:YAG laser (wavelength: 532 nm, pulse energy: 85 mJ, repetition rate: 10 Hz) while varying the N_2 pressure and Al substrate temperature. A Fe metal sheet was employed as the target material. The focal point of the laser light was continually scanned across the flat surface of the Fe metal target to prevent droplets from forming. The vapor was deposited on an Al substrate and 1.1×10^5 pulses were applied for the irradiation. The pressure of the N_2 atmosphere was maintained at the desired pressure between 1 and 1300 Pa. The Al substrate was maintained at the desired temperature between 100 and 520 K. The film samples were measured by Mössbauer spectroscopy (WISSEL, MDU1200) at 5 and 300 K and XRD (RINT2500, Rigaku; Cu-Kα) patterns were measured to confirm the assignments.

3 Results and discussion

According to Mössbauer spectra and XRD results, various iron nitride films were produced. γ" and γ"'-FeN were dominant in the films produced at N_2 pressures higher than 70 Pa, whereas ε-Fe$_x$N was produced at low N_2 pressures (1.2 Pa). As surface reactions with N_2 gas and thermal reactions of the films are strongly influenced by the substrate temperature, we performed PLD at various substrate temperatures. Films were produced at an N_2 pressure of 70 Pa at various substrate temperatures between 100 and 520 K and Mössbauer spectra were measured at room temperature (Fig. 1). We fitted these spectra by a combination of two components: γ"-FeN (a singlet: S2) [4, 5] and γ"'-FeN (a combination of a singlet S1 and a doublet D1). The absorption of γ"-FeN was dominant at low substrate temperatures (100 K; Fig. 1a), whereas γ"'-FeN was dominant at high substrate temperatures (520 K, Fig. 1c). Table 1 summarizes the Mössbauer parameters.

Mössbauer spectra of the same samples were measured at 5 K (Fig. 2). The spectrum of the film produced at 100 K (Fig. 2a) exhibited a singlet of γ"-FeN as the major absorption, which is similar to the spectrum obtained at room temperature (Fig. 1a). The spectra of the films produced at 300 and 520 K showed two sets of sextets. Since the sextets had broad half widths, the spectra were fitted by assuming distributions of hyperfine magnetic fields. Their Mössbauer parameters agreed with parameters reported in previous studies [4, 5]. The film produced at 520 K (Fig. 2c) was considered to be pure γ"'-FeN. Comparison of the area intensities of the spectra observed at 300 and 5 K (Table 1) reveals that the doublet D1 corresponds to the component with H = 300 kOe and the singlet S1 corresponds to the component with H = 500 kOe. The origin of the two Fe sites is not known. However, it is clear that γ"'-FeN has a crystal structure with two Fe sites. XRD patterns of the

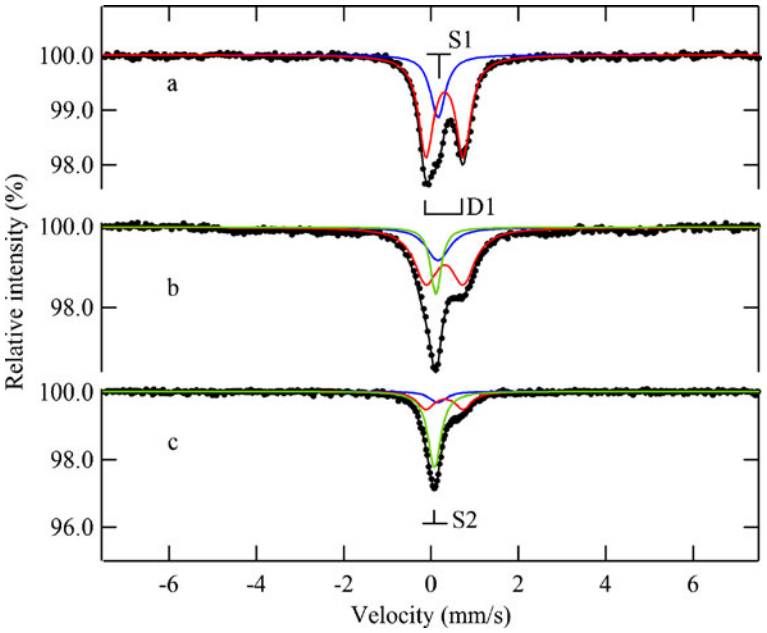

Fig. 1 Room-temperature Mössbauer spectra of films produced by PLD of Fe onto an Al substrate in 70 Pa N_2 for substrate temperatures during PLD of **a** 520, **b** 300, and **c** 100 K

Table 1 Mössbauer parameters of the films in Figs. 1 and 2

Sample	Substrate temp. while deposition (K)		Measured at 300 K			Measured at 5 K		
			δ (mm/s)	ΔEq (mm/s)	Yields (%)	δ (mm/s)	H* (kOe)	Yields (%)
a	520	D1	0.31	0.85	75.5	0.45	299	71.2
		S1	0.16	–	24.5	0.31	504	28.8
b	300	D1	0.31	0.85	61.3	0.45	306	54.6
		S1	0.16	–	20.1	0.32	509	22.5
		S2	0.11	–	18.6	0.22	–	22.9
c	100	D1	0.31	0.85	32.4	0.45	300	31.3
		S1	0.16	–	10.4	0.26	490	9.2
		S2	0.08	–	57.2	0.21	–	59.5

*Hyperfine magnetic field having the maximum population in the distribution

films were measured, and the intensity ratio of the peaks of γ"-FeN [6] and γ"'-FeN changed varying the Al substrate temperature, which were in good agreement with the Mössbauer results.

In previous studies, γ"-FeN and γ"'-FeN always formed simultaneously and no method for preparing a single phase of γ"-FeN or γ"'-FeN has been reported. However, in this study, the yields of the two phases could be varied and pure γ"-FeN and γ"'-FeN could be obtained by varying the substrate temperature during PLD. We are currently performing density functional calculations to help clarify the structure of γ"'-FeN.

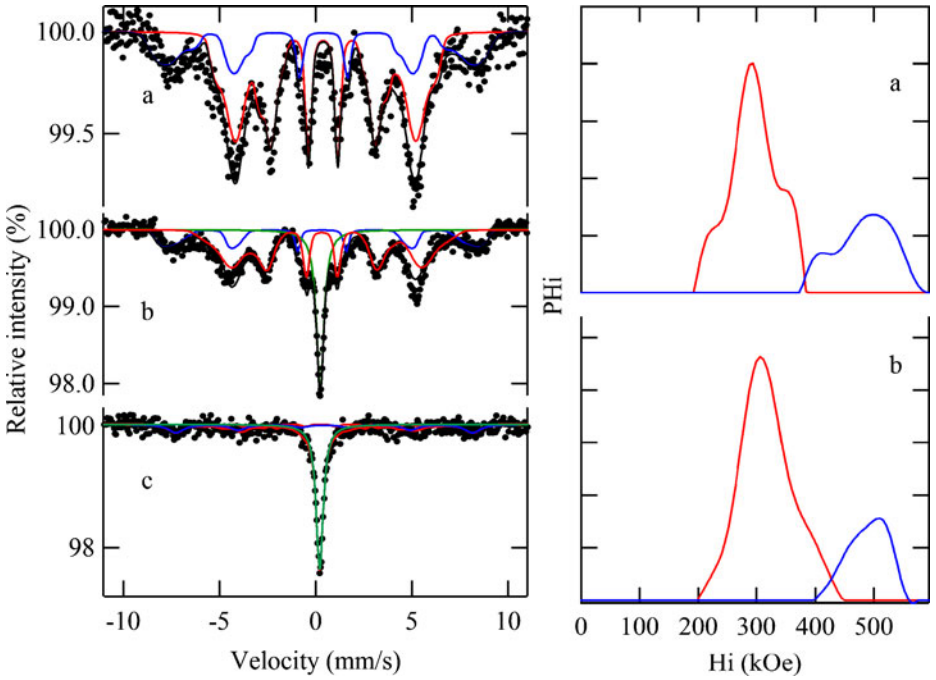

Fig. 2 Mössbauer spectra measured at 5 K of the films produced by PLD of Fe onto an Al substrate in 70 Pa N_2. Substrate temperatures during PLD were **a** 520, **b** 300, and **c** 100 K. The hyperfine magnetic field distributions are indicated on the right-hand side

4 Conclusion

PLD in N_2 ambient gas produced iron nitride films whose compositions could be controlled by varying the ambient N_2 gas pressure and the Al substrate temperature. Films produced at a high N_2 pressure (> 70 Pa) consisted of γ”-FeN and γ”’-FeN. The γ”-FeN and γ”’-FeN yields could be controlled by controlling the substrate temperature during deposition. Pure γ”-FeN and γ”’-FeN were obtained and their Mössbauer spectra and XRD patterns were observed.

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