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Phase composition of nanocrystalline iron films deposited in a nitrogen atmosphere

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The phase composition of iron films prepared by pulsed-plasma deposition in a controlled nitrogen atmosphere is investigated by Mössbauer spectroscopy. The observed changes in the phase composition are dictated by the nanocrystalline structure of the samples and the dynamics of the substrate temperature during film deposition. © *1999 American Institute of Physics.* [S1063-7834(99)02110-3]

The last few years have witnessed a concerted effort to find new magnetically soft magnetic thin-film materials having a large magnetic saturation induction for modern electronic devices. Compounds of the Fe–N type are of special interest in this regard, because small additives of nitrogen to iron-base thin films increase the magnetic moment, improve the corrosion properties of the films, and decrease the coercive force.[1,2]

The development of methods for the preparation of nanocrystalline materials[3] has extended the potential capabilities for the synthesis of various alloys. This trend is mainly attributable to the fact that the chemical activity of the materials exhibits a strong dependence on the dimensions of the nanocrystallites.[4] Research at the present time is aimed primarily at powders, which after deposition on a substrate are placed in some particular gas atmosphere.[5] The end result comprises complex composite formations with interesting physical properties. At the practical level, however, continuously condensed media are of greater interest. The properties of such materials can differ from the properties of the nanoparticles from which they are formed, owing to interaction effects between them.

In this paper we report a Mössbauer spectroscopy study of the phase composition of iron films as a function of the nitrogen pressure in a vacuum chamber. The films were prepared by pulsed-plasma deposition (PPD). The deposition atmosphere was established by preliminary evacuation of the vacuum system to 10^{-6} torr with freezing-out of the oil vapor, followed by the injection of spectrally pure nitrogen, whose pressure was varied from 10^{-5} torr to 10^{-2} torr. The temperature of the substrate was equal to room temperature at the start of deposition. The samples had a thickness $\sim 10^3$ Å, which was measured by x-ray fluorescence analysis. The rate of condensation of the iron film in a 100 μs pulse was 10^4-10^5 Å/s.

The pulsed nature of the plasma was created by laser pulses from an LTI-207 solid-state laser and by the discharge of a capacitor bank in the vapor of the atomized target. A distinguishing feature of the film deposition process, apart from a high evaporation rate, is high-energy saturation of a plasma with iron and nitrogen as its main components.

In the proposed technology, the interaction effects of the

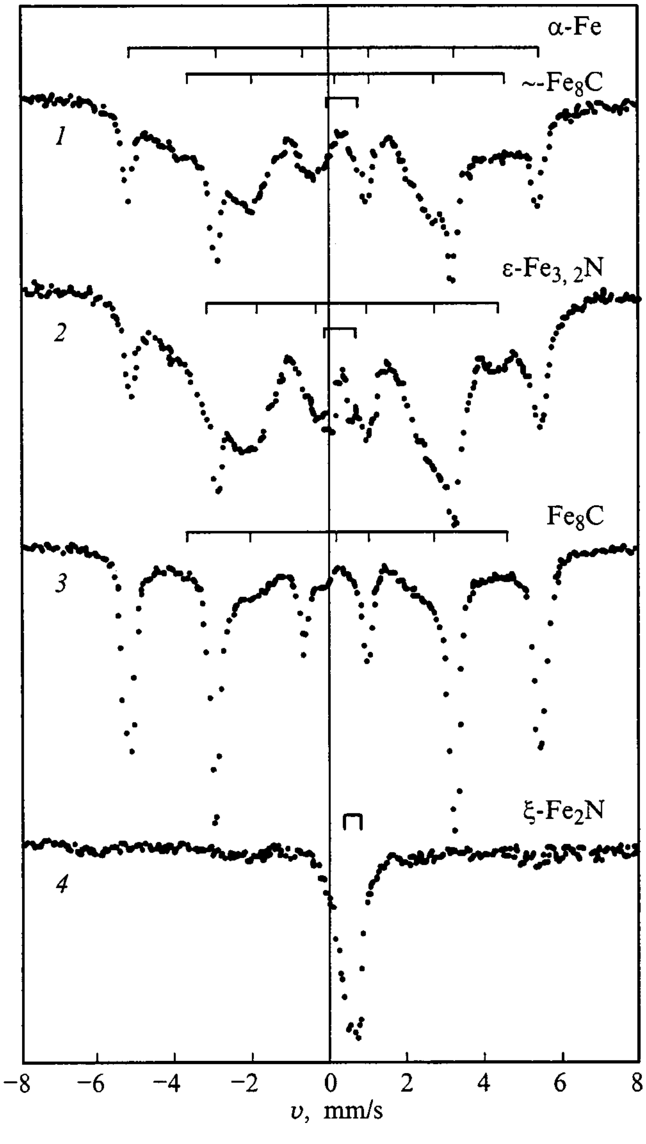

FIG. 1. Variation of the Mössbauer spectra of Fe–N films as a function of the nitrogen atmosphere pressure: (*1*) $P = 10^{-6}$ torr; (*2*) 10^{-5} torr; (*3*) 10^{-4} torr; (*4*) 10^{-2} torr.

TABLE I. Parameters of the Mössbauer spectra of Fe–N films.

No.	P, torr	H, kOe	δ, mm·s^{-1}	ε, mm·s^{-1}	S, %	Postulated composition	Literature data H, kOe	Literature data δ, mm·s^{-1}	Literature data ε, mm·s^{-1}	Refs.
1	10^{-6}	330	0	0	26	α-Fe,				
		~250	~0.15	0	72	~Fe_8C	245	~0.17		6, 7
		0	0.19	0.6	2					
2	10^{-5}	331	0.01	0	20	α-Fe,				
		~234	0.27	0.06	75	ε-carbonitride	230	0.24	0.10	8
		0	0.16	0.8	5	or ε-$Fe_{3.2}N$	238	0.33		9
3	10^{-4}	332	−0.01	0	76	ε-Fe,				
		251	0.16	0	24	~Fe_8C	245	~0.17		6, 7
4	10^{-2}	0	0.58	0.29	100	ε- or γ-Fe_2N	0	0.42	0.27	10

laser beam with the vapor adsorbed on the surface of the target and bombardment of the target with high-energy plasma particles in the presence of an applied electric field increase the atomic nitrogen content of the Fe–N vapor system, promoting an increase in the reactivity of the system. The results of mass spectroscopic analysis shows that the quantity of ionized atomic nitrogen increases to 15–20%.

The Mössbauer spectra of the investigated films are shown in Fig. 1, and the parameters of these spectra are summarized in Table I. The spectra were recorded with a Co^{57}(Cr) source at room temperature. The spectral lines for films prepared at $P=10^{-6}$ torr and 10^{-5} torr are very broad and evolve on a U-shaped base, as it typical of the ultradisperse or amorphous state. Electron microscope examinations of iron films prepared by PPD show that the samples consist of nanocrystallites with dimensions $\leqslant 50$ Å (Refs. 11 and 12).

The spectrum of film No. 1 contains two sextets, which can be identified with the phases αFe and iron carbide Fe_8C (Ref. 6). The formation of the second phase is caused by the high carbon content of the films (~20 at.%). Auger spectroscopy data show that this effect is quite typical of $3d$-metal films prepared by PPD.[13] The fraction of bound carbon is <10 at.% in this case.

Two sextets are also observed for film No. 2. In addition to αFe, a phase also emerges with a magnetization similar to that of Fe_8C, but with a larger isomeric shift. According to published data, these parameters are typical of the compound ε carbonitride or ε $Fe_{3.2}N$ (Ref. 9).

Unusual results are exhibited by the spectra of film No. 3: They do not contain nitride compounds. The phase composition of this sample repeats the composition of film No. 1 with the one exception that αFe is now predominant.

To explain these data, we have investigated the substrate temperature during film deposition. Our previous work with Ni–N films provided guidelines for setting up these experiments. We observed that, when nickel is spray-deposited in a nitrogen atmosphere at a pressure of 10^{-4} torr, the substrates are strongly influenced by temperature to the point of deformation.[14] To analyze the substrate temperature dynamics, we predeposited a Pd–Cu thin-film thermocouple on the substrate during the PPD process.

The results are shown in Fig. 2. In the first few minutes as the film is being deposited, the substrate temperature increases to 500–600 K. This behavior is attributable to a large quantity of heat being released on the substrate by the high current density of evaporated material. After the plasma is turned off, the substrate temperature remains constant for a certain period of time and then begins to drop exponentially. The substrate temperature is lower in low vacuum (curves *1* and *3*). A different picture is observed for film No. 3 (curve *2*): After the temperature rises to $T\sim 520$ K it suddenly jumps up to $T\sim 750$ K. This rise can be identified with heat release from the decomposition of iron nitride.

It has been shown[8] that the ε-carbonitride phase decomposes at $T=520$ K, and the $Fe_{3.2}N$ phase decomposes at $T=720$ K. We can assume that, during deposition at $P=10^{-4}$ torr, either ε carbonitride or a mixture of ε carbonitride and $Fe_{3.2}N$ forms. An ε carbonitride–$Fe_{3.2}N$ phase transition takes place when the substrate temperature rises to $T=520$ K. The heat released in this transition causes the temperature to rise sharply, and the iron nitride decomposes at $T=720-750$ K with precipitation of the αFe phase.

At $P=10^{-2}$ torr only one quadrupole doublet is observed in the Mössbauer spectrum; it is interpreted as the ε-Fe_2N or ξFe_2N phase.[10] Obviously, the nitrogen concentration in the chamber is sufficient to produce a nitrogen-enriched Fe_2N phase throughout the entire volume of the film and, at the same time, the resulting substrate temperature is lower than the temperature at which this compound decomposes.

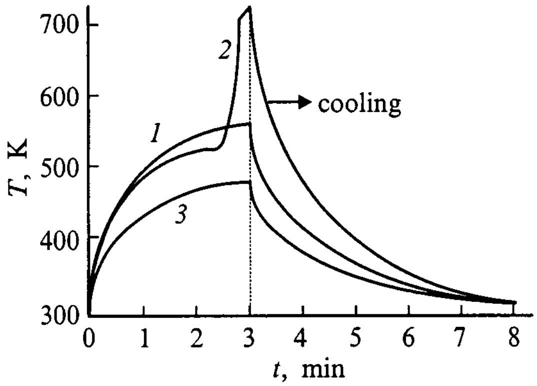

FIG. 2. Time dependence of the substrate temperature at various nitrogen atmosphere pressures: (*1*) 10^{-5} torr; (*2*) 10^{-4} torr; (*3*) 10^{-2} torr.

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[1] T. K. Kum and M. Takahashi, Appl. Phys. Lett. **12**, 492 (1972).

[2] K. K. Shih, M. E. Re, and D. B. Pove, Appl. Phys. Lett. **57**, 412 (1990).

[3] W. Siegel, Nanostruct. Mater. **3**, 1 (1993).

[4] M. L. Cohen and W. D. Knight, Phys. Today **43**, 42 (1990).

[5] C.-M. Hsu, H.-M. Lin, and K.-R. Tsai, J. Appl. Phys. **76**, 8, 4793 (1994).

[6] J. M. Dubois and G. Le Gaër, Acta Metall. **25**, 609 (1974).

[7] E. Bauer-Grosse and G. Le Caër, Philos. Mag. B **56**, 485 (1987).

[8] C. A. Santos, B. A. S. Barros, J. P. Souza, and J. R. Baumvoll, Appl. Phys. Lett. **41**, 237 (1982).

[9] G. M. Chen, N. K. Jaggi, J. B. Butt, Yeh, and L. H. Schwartz, J. Phys. Chem. **87**, 5326 (1983).

[10] M. Chabanel, C. Janot, and J. P. Motte. C. R. Acad. Sci. (Paris) **222**, 13419 (1968).

[11] G. I. Frolov, V. S. Zhigalov, S. M. Zharkov, and I. R. Yarullin, Fiz. Tverd. Tela (St. Petersburg) **36**, 970 (1994) [Phys. Solid State **36**, 526 (1994)].

[12] G. I. Frolov, O. A. Bayukov, V. S. Zhigalov, L. I. Kveglis, and V. G. Myagkov, JETP Lett. **61**, 63 (1995).

[13] V. S. Zhigalov, G. I. Frolov, and L. I. Kveglis, Fiz. Tverd. Tela (St. Petersburg) **40**, 2074 (1998) [Phys. Solid State **40**, 1878 (1998)].

[14] V. S. Zhigalov, G. I. Frolov, V. G. Myagkov, S. M. Zharkov, and G. V. Bondarenko, Zh. Tekh. Fiz. **68**, 136 (1998) [Tech. Phys. **43**, 122 (1998)]

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