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Growth and characterization studies of Fe₄N thin films prepared by ion beam assisted evaporation

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Thin films of iron nitrides have been prepared using an ion beam assisted evaporation method. X-ray diffraction and Mössbauer spectrometry show that the films generally consist in a mixture of Fe and Fe₄N phases. For high source powers and temperatures higher than 300 °C it was possible to obtain the pure Fe₄N phase. © 1995 American Institute of Physics.

Recently, thin films of iron nitrides have attracted much attention due to their excellent magnetic properties, their corrosion and wear resistance and their potential applications as magnetic recording heads and media. Almost all the reported work has used reactive sputtering.^{1,2} In most cases, the thin films were a mixture of different phases. Nevertheless, stable iron nitrides of single phase γ' -Fe₄N, ϵ -Fe₂₋₃N, and ζ -Fe₂N have recently been obtained using an ammonia reactive gas.¹ Molecular beam epitaxy has also been used in order to obtain the metastable Fe₁₆N₂ phase.^{3,4} Other attempts of reactive evaporation with a Kaufman type ion source have been made,^{5,6} but the nitrogenated phases were not well characterized.

In this letter, we report the first study of the growth of Fe–N films using the electron cyclotron resonance microwave plasma assisted evaporation method. The reactive gas was pure nitrogen. The low pressures ($>8 \times 10^{-6}$ Torr) required for stable operation of the electron cyclotron resonance (ECR) source are compatible with the use of an electron beam gun. Moreover, the ECR microwave plasmas are well known to provide high ion densities at low energies (10 to 25 eV). Owing to these low energies, the lattice damage is expected to be reduced. The ECR plasma source is becoming popular for providing the activated nitrogen in the growth of the III–V nitrides as well as in the *p*-type doping of the II–VI family of semiconductors, but it was never used for the preparation of metallic films. We show the influence of the deposition parameters (nitrogen pressure, ion source power, substrate temperature, and bias) on the appearance of different Fe–N phases and, in particular, the growth of the pure Fe₄N phase. The films have been characterized by x-ray diffraction and Mössbauer spectrometry.

The plasma generation chamber and the growth chamber were evacuated by a cryogenerator with a pumping rate of 1000 ℓ /s. The background pressure was 10^{-8} Torr. Iron was evaporated from an electron beam gun. The deposition rate (1 Å/s or 8×10^{14} atoms $\text{cm}^{-2} \text{s}^{-1}$) was monitored and controlled by a quartz microbalance system. The samples were deposited on (111) Si substrates. Their thickness was 2400 Å. The nitrogen flow in the ion source was regulated by maintaining the total pressure P_{N_2} in the evaporation chamber at a constant value. The 2.45 GHz microwave energy of the ECR

source could vary from 10 to 250 W. A 875 G axial magnetic field was used to create electron cyclotron resonance and to promote efficient coupling of the microwaves to the plasma. The distance between the source and the substrate was 15 cm. The convergence on the substrate of the plasma beam was not optimized by external magnetic coils. A SiO₂ quartz liner was used inside the ECR cavity.

The samples were also analyzed by conversion electron Mössbauer spectrometry (CEMS). This backscatter technique is ideally suited to thin layer characterization of Fe-containing materials. It is sensitive to a thickness of about 1500 Å of the surface layer of the sample. The CEMS measurements were performed at room temperature by using a proportional gas flow electron counter with He–4%CH₄ gas. The Mössbauer source was ⁵⁷Co in a rhodium matrix. A conventional constant acceleration Mössbauer spectrometer was used. The Mössbauer spectral parameters were obtained in the conventional way by fitting Lorentzian line shapes to the experimental data by the least-squares method. All isomer shift data are given with respect to the α -Fe standard at room temperature. X-ray diffraction measurements were performed with the $K\alpha$ radiation of cobalt ($\lambda=1.789$ Å).

As mentioned in the introduction, different experimental parameters can be changed. It was possible to modify the power and the nitrogen flow of the ion source and to modify the temperature and the bias of the substrate. In order to find the best evaporation conditions, the ion current arriving on the substrate biased at a negative value of 235 V was measured as a function of the source power and of the nitrogen pressure P_{N_2} . As expected, the ion current increases with an increasing power. But, surprisingly, a maximum of the ion current versus the pressure was observed for $P_{\text{N}_2}=2 \times 10^{-5}$ Torr, which corresponds to a nitrogen flow of 2 sccm. This current was estimated at 8×10^{14} ions $\text{cm}^{-2} \text{s}^{-1}$ for a source power of 150 W. For higher pressures, the ion current decreases, as if the recombinations between electrons and ions in the plasma were more efficient. Therefore, the evaporation pressure in the present study was chosen to be equal to 2×10^{-5} Torr. It was also verified that the films prepared at this pressure contained more nitrogen than the films prepared at higher pressures, $P_{\text{N}_2}=10^{-4}$ Torr, for example.

Samples were prepared at $P_{\text{N}_2}=2 \times 10^{-5}$ Torr with different ion source powers. The temperature was fixed at 300 °C. The corresponding Mössbauer spectra are repre-

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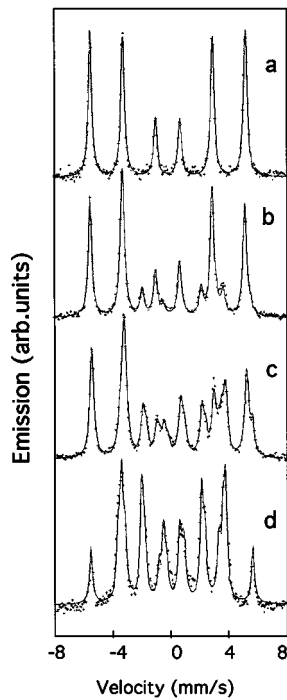


FIG. 1. CEMS spectra of films prepared with different source powers [(a) 0 W; (b) 75 W; (c) 150 W; (d) 225 W]. The substrate temperature was fixed at 300 °C.

sented in Fig. 1. The sample prepared under a molecular nitrogen flow [Fig. 1(a)] shows the classical sextuplet of pure iron with the hyperfine field $H_f=330$ kOe. For a low source power $P=75$ W [Fig. 1(b)], the film consists of a predominant iron phase (77%) mixed with Fe_4N phase (23%). At $P=150$ W [Fig. 1(c)], the spectrum shows the Fe_4N phase mixed with iron in equal proportions and, at the highest power $P=225$ W [Fig. 1(d)], the iron has disappeared and the Fe_4N phase is now mixed with 9% of a paramagnetic phase. This first series of experiments shows that the ion source power must be higher than 150 W to obtain another crystallographic phase than pure iron. The Mössbauer spectrometry results represented here were confirmed by x-ray diffraction experiments.

The influence of the substrate temperature T_s was studied with samples prepared at $P=2 \times 10^{-5}$ Torr with a source power of 150 W. At $T_s=20$ °C, x-ray diffraction shows a very large peak between 48° and 52° which corresponds to an ill-crystallized phase and the Mössbauer spectrum has been fitted with a mixture of pure iron (46%) with a disordered phase comprising iron with interstitial nitrogen atoms (21%), amorphous Fe_4N (16%) and amorphous Fe_2N (17%) [Fig. 2(a)]. For $T_s=150$ °C, the x-ray diffraction spectrum always shows an ill-crystallized phase with two large peaks at 48° and 52° corresponding to the $Fe_4N(111)$ and $Fe_\alpha(110)$ peaks, respectively, and the Mössbauer spectrum can be fitted with a Fe_4N phase mixed with pure iron in equal proportions [Fig. 2(b)]. For $T_s=300$ °C, the film, already represented in Fig. 1(c), is well crystallized, with a mixture of α -Fe and Fe_4N . The spectrum represented in Fig. 2(c) corresponds to a sample prepared with the same conditions, except the substrate bias which was fixed at -235 V. In these

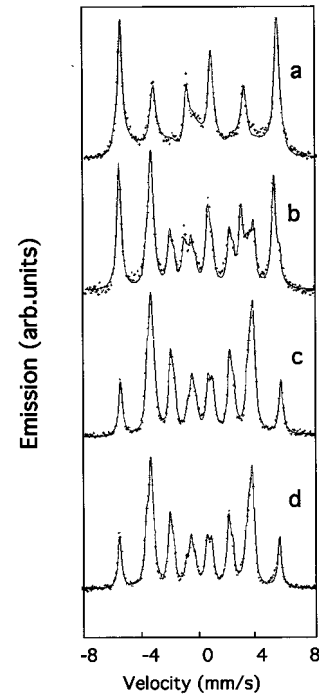


FIG. 2. CEMS spectra of films prepared at different substrate temperatures [(a) 20 °C; (b) 150 °C; (c) 300 °C; (d) 450 °C]. The source power was 150 W. The sample c was prepared with a substrate bias of -235 V.

conditions, the ion current was about four times higher and the film consists of a pure Fe_4N phase. The x-ray diffraction (Fig. 3) shows that the film presents a preferred orientation with very intense (200) peaks. Finally, for $T_s=450$ °C, the spectrum also corresponds to a pure Fe_4N phase [Fig. 2(d)].

The simple cubic structure of the γ' - Fe_4N nitride can be viewed as a fcc iron lattice with an additional nitrogen atom at the center of the cell. This structure has two inequivalent iron sites, one occupying the corner (FeI) and the other the face centers (FeII), in the ratio of $FeI/FeII=1/3$. As already proposed,⁷ the Mössbauer spectrum of the Fe_4N phase has been deconvoluted in three subspectra which are due to two different iron crystallographic sites. The one with the higher

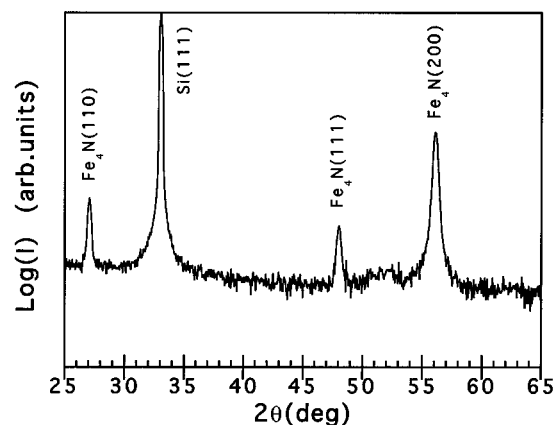


FIG. 3. X-ray diffraction patterns of Fe_4N films. The substrate temperature was 300 °C, the substrate bias was -235 V and the ion source power was 150 W.

TABLE I. Mössbauer parameters of Hf, IS, and QS of the Fe₄N films.

	Hf(kOe)	IS(mm/s)	QS(mm/s)	Relative intensity
FeI	341	0.23	0	0.25
FeIIA	217	0.31	0.16	0.50
FeIIB	218	0.31	-0.33	0.25

internal field (Hf=340 kOe) is attributed to the FeI site and the other two with Hf=217 kOe to the crystallographic FeII site. For each sextet, the relative intensity behavior is in the 3:2:1:1:2:3 ratio indicating a random orientation of the magnetic domains. The orientation of the electric field gradient (EFG) relative to the local magnetization direction \mathbf{M} divides the FeII sites into two categories, FeIIA and FeIIB positions having the EFG perpendicular and parallel, respectively, to \mathbf{M} . The resulting Mössbauer spectrum consists of three magnetic sextets with the intensity ratio FeI/FeIIA/FeIIB=1/2/1. The isomer shifts IS of FeIIA and FeIIB must be equal, but it is expected that the quadrupole splitting QS in spectrum FeIIA must be half of that of FeIIB and of opposite sign when \mathbf{M} is parallel to the $\langle 100 \rangle$ direction. Moreover, the FeI

atoms are in a cubic coordination with six iron near neighbors and they must present a null quadrupole splitting. The determined Mössbauer parameters are tabulated in Table I. They are in excellent agreement with those of M. J. Clouser.⁷

In summary, thin film iron nitrides have been prepared by ECR microwave plasma assisted evaporation. The reactive gas was pure nitrogen. X-ray diffraction and Mössbauer spectrometry experiments showed that these films generally consist in a mixture of Fe and Fe₄N phases, with variable proportions depending on the deposition parameters. For high source powers and temperatures higher than 300 °C, it was possible to obtain the pure Fe₄N phase.

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