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Magnetic and structural properties of iron nitride thin films obtained by argon-nitrogen reactive radio-frequency sputtering

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We have prepared iron nitride thin films by reactive rf sputtering of an iron target in an argon-nitrogen plasma. The films present a wide variety of structures and compositions: α expanded bcc iron, amorphous $\text{Fe}_{1-x}\text{N}_x$, γ' - Fe_4N , ϵ - Fe_{2-3}N , and ζ - Fe_2N . Evolutions of the crystallographic structures and of the magnetic properties of the obtained phases are discussed versus the nitrogen concentration in the gaseous flow and the substrate temperature during deposition. © 1995 American Institute of Physics.

I. INTRODUCTION

Fe-N thin films have attracted considerable attention because they are potential candidates for magnetic recording with their large saturation magnetization and their good corrosion resistance.¹ It has even been demonstrated that saturation magnetization can be larger than the bulk iron one for low nitrogen contents.² The origin of the enhanced magnetic moment could occur from the metastable α'' Fe_{16}N_2 phase or from an expanded bcc FeN structure which is also called α FeN.

Several ways for obtaining iron nitride films have been investigated.

(1) Thermal evaporation with a nitrogen partial pressure (either atomic or molecular nitrogen): such a technique is not the most suitable for the preparation of nitrogen-rich Fe-N alloys, but several groups have successfully obtained α , α'' , or γ' FeN phases.^{3,4} Let us also notice that molecular beam epitaxy growth of α'' phase is possible, according to Komuro *et al.*⁵

(2) Reactive sputtering: contrary to thermal evaporation, reactive sputtering allows one to obtain a wide variety of iron nitrides. As underlined by Takahashi *et al.*⁶ or Gao *et al.*,⁷ the use of adapted seed layers like (100) iron buffer grown on (100) MgO substrate accompanied with thermal annealing leads to α or α'' phases. The role of this thermal treatment is to reorder nitrogen atoms in the iron expanded lattice. From another point of view, Xiao and Chien⁸ have sputtered all the iron nitrides (except α'') on unheated substrates and without any other treatment using ammonia reactive gas. These last authors suggest NH_3 is the best solution for growing single phase iron nitrides.

Our present work is devoted to preparation and study of as-deposited sputtered Fe-N films. They have been prepared in a large range of nitrogen partial pressures and with substrate temperatures ranging from ≈ 40 °C (unheated) up to 600 °C. The different structural phases have been identified by x-ray diffraction and Mössbauer spectroscopy. These results are correlated with bulk magnetization measurements.

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II. EXPERIMENTAL PROCEDURES

Iron nitride films are deposited on microelectronic-grade (100) Si wafers in an Alcatel SCM 650 automated sputtering setup. The base pressure is 7×10^{-7} mb and the working pressure 3×10^{-3} mb. The iron target is 500 W rf polarized (≈ 6.3 W/cm²) and the deposition rate is close to 3 Å/s if substrates are located 10 cm above the target. Such sputtering conditions have been chosen because they provide high density and low roughness (110) textured Fe films in pure argon plasma sputtering.⁹ Note that this experimental context leads to a spontaneous (110) α Fe dense plane growth.

Nitrides have been obtained by introducing several controlled amounts of nitrogen in the main argon atmosphere, keeping the total pressure equal to the previous value of 3×10^{-3} mb. The nitrogen percentage x_{N_2} in the gaseous flow ranges from 0% to 40%. The total thickness of each sample was 1250 ± 50 Å. The substrate's temperature is varied between room temperature (unheated substrate) and 600 °C.

These samples were structurally characterized by x-ray diffraction (XRD) with a K_β -filtered $\text{Co } K_\alpha$ radiation (1.788 92 Å) on a $\theta/2\theta$ Philips goniometer operating with a Raytech position sensitive detector. Crystallographic phases were deduced from comparison of experimental diffraction profiles with standard ones (JCPDS data). Some uncertainty is left for the determination of ϵ - Fe_{2-3}N phase because of the relatively large variations of its crystalline parameters among the compositional domain where it exists.

Local magnetic properties have been investigated by conversion electron Mössbauer spectroscopy (CEMS). Mössbauer spectra were recorded at room temperature in the backscattering mode with a He (5% CH_4) gas flow proportional counter. This allows a nondestructive study with a sampling depth of about 2500 Å, encompassing therefore the whole thickness of iron nitride films. The source drive and data storage were of usual design. The ⁵⁷Fe hyperfine pattern was fitted with standard routines where Lorentzian line shapes were assumed.

Bulk magnetization measurements have been performed with either a vibrating sample magnetometer (VSM) or a quantum design superconducting quantum interference device down to 5 K. Room temperature Kerr rotation cycles have also been performed in both longitudinal and polar ge-

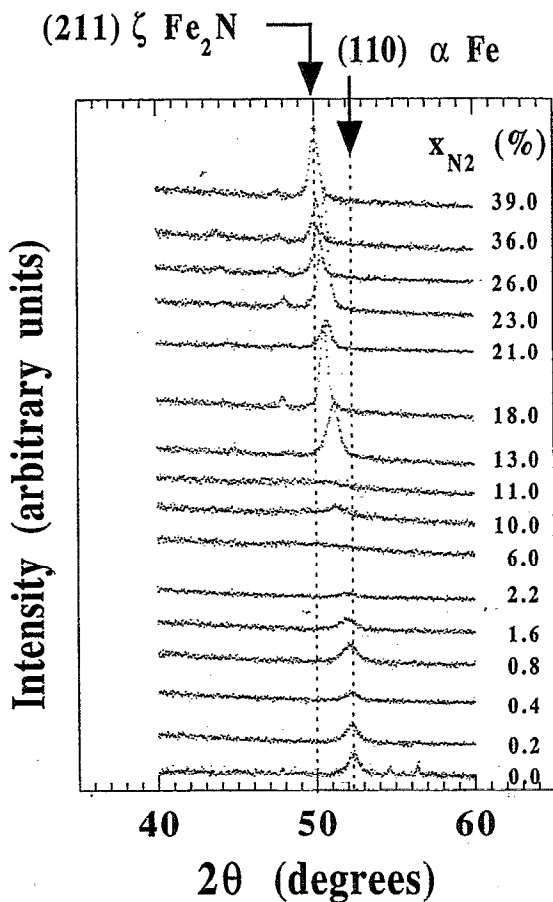


FIG. 1. XRD experiments performed on the series of Fe-N films deposited at room temperature as a function of the nitrogen concentration in the plasma.

ometries, they give similar results to the VSM ones but faster and with a better accuracy for determining coercive fields.

III. RESULTS

A. Crystallographic structure

Structural properties of the films deposited on unheated substrates are illustrated in Fig. 1 which represents the evolution of XRD peaks as a function of the nitrogen partial pressure in the plasma. These results can be summarized as follows.

- (1) At very low nitrogen concentrations, films only show the usual (110) diffraction peak of the bcc iron structure but with a small shift towards low angles. We attribute this to a lattice expansion of bcc Fe which is called α FeN. Lattice expansion reaches up to 0.7%.
- (2) With increasing N_2 concentration, diffraction peaks become broader: it is the signature of an amorphous FeN alloy. This is the first observation, to our knowledge, of an amorphous iron nitride phase.
- (3) For x_{N_2} equal to 0.08, an XRD peak appears at 51.4° , it could be the (111) peak of hexagonal ϵ -Fe₂₋₃N phase, coexisting with amorphous Fe-N.

- (4) For higher values of x_{N_2} ($0.18 \leq x_{N_2} \leq 0.24$), the (101) peak of hexagonal ϵ -Fe₃N phase is observed.
- (5) Finally, for $x_{N_2} \geq 0.26$, the diffraction spectrum only shows the (211) peak of the orthorhombic ζ -Fe₂N phase.

The samples deposited on heated substrates were better crystallized. From a more general point of view, increasing the substrate temperature from 300 to 600 °C leads to a transformation into γ' -Fe₄N of all the iron nitrides which could be obtained at room temperature. This behavior is easy to explain as the γ' phase is the most stable in this range of temperatures. Of course, any combination of these situations could be found for intermediate temperatures.

Finally, XRD indicates the presence of various iron nitride structures in our films. However, because of grain size or texture effects, we cannot accurately estimate their proportions in the samples. A summary of the identified phases versus substrate temperature (T_S) and nitrogen atomic ratio (x_{N_2}) is given in Table I.

B. Mössbauer spectroscopy

Some experimental and calculated CEMS spectra are displayed in Fig. 2. They are representative of the evolution versus nitrogen concentration of the plasma (x_{N_2}) and substrate temperature (T_S). The spectra analysis of crystallized phases was carried out mostly with superimposed discrete six line patterns (magnetic phases) and/or a quadrupole split doublet (nonmagnetic phases). For most of the magnetic nitrides, the intensity behavior within the sextet indicates in-plane magnetization.

Spectra of amorphous magnetic iron nitrides do not exhibit the discrete sextet of crystallized magnetic phases but a broad distribution, they have been analyzed with a hyperfine field distribution according to the histogram method.

So, magnetic components have been attributed, respectively, to pure bcc iron, to iron atoms with a slightly shifted hyperfine field (α expanded bcc iron), to amorphous magnetic Fe-N, to γ' -Fe₄N multisite compound, and to ϵ -Fe₂₋₃N. According to their isomer shifts, paramagnetic components are found to be relevant to ζ -Fe₂N species.

CEMS results have been found to be coherent with XRD along the main lines of our work with evidence for γ' -Fe₄N at high T_S , ζ -Fe₂N for high x_{N_2} , amorphous Fe-N for T_S close to room temperature, and $x_{N_2} \approx 5\%$. However, some discrepancies exist for intermediate T_S and x_{N_2} . In fact, while Mössbauer spectroscopy detects all the iron environments, only the best crystallized phases are revealed by XRD when a mixture of various nitrides sets in.

Let us also notice that a small paramagnetic contribution is found in amorphous phase. This is due to the existence of nonmagnetic iron sites in amorphous Fe-N. Contrary to XRD, it has been possible to estimate the atomic abundances of the various phases from the analysis of the spectra. Some of these results are quoted in Fig. 2.

TABLE I. "Phase diagram" of sputtered iron nitrides. Nitrogen to argon ratio increases along horizontal lines and deposition temperature increases along columns.

600 °C	α -Fe	γ' -Fe ₄ N	γ' -Fe ₄ N	γ' -Fe ₄ N	γ' -Fe ₄ N	γ' -Fe ₄ N
400 °C	α -Fe	α -Fe γ' -Fe ₄ N ϵ -Fe ₂₋₃ N	α -Fe γ' -Fe ₄ N ϵ -Fe ₂₋₃ N	γ' -Fe ₄ N ϵ -Fe ₂₋₃ N	γ' -Fe ₄ N	
200 °C	α -Fe	α -Fe γ' -Fe ₄ N ϵ -Fe ₂₋₃ N	γ' -Fe ₄ N ϵ -Fe ₂₋₃ N Amorphous	γ' -Fe ₄ N ϵ -Fe ₂₋₃ N	ϵ -Fe ₂₋₃ N	ζ -Fe ₂ N
100 °C	α -Fe	γ' -Fe ₄ N ϵ -Fe ₂₋₃ N	γ' -Fe ₄ N ϵ -Fe ₂₋₃ N Amorphous	ϵ -Fe ₂₋₃ N	ϵ -Fe ₂₋₃ N	
Unheated	α -Fe	Amorphous	Amorphous	Amorphous ϵ -Fe ₂₋₃ N	ϵ -Fe ₂₋₃ N	ζ -Fe ₂ N
T_s						
x_{N_2}	0.000	0.046	0.063	0.109	0.205	0.332

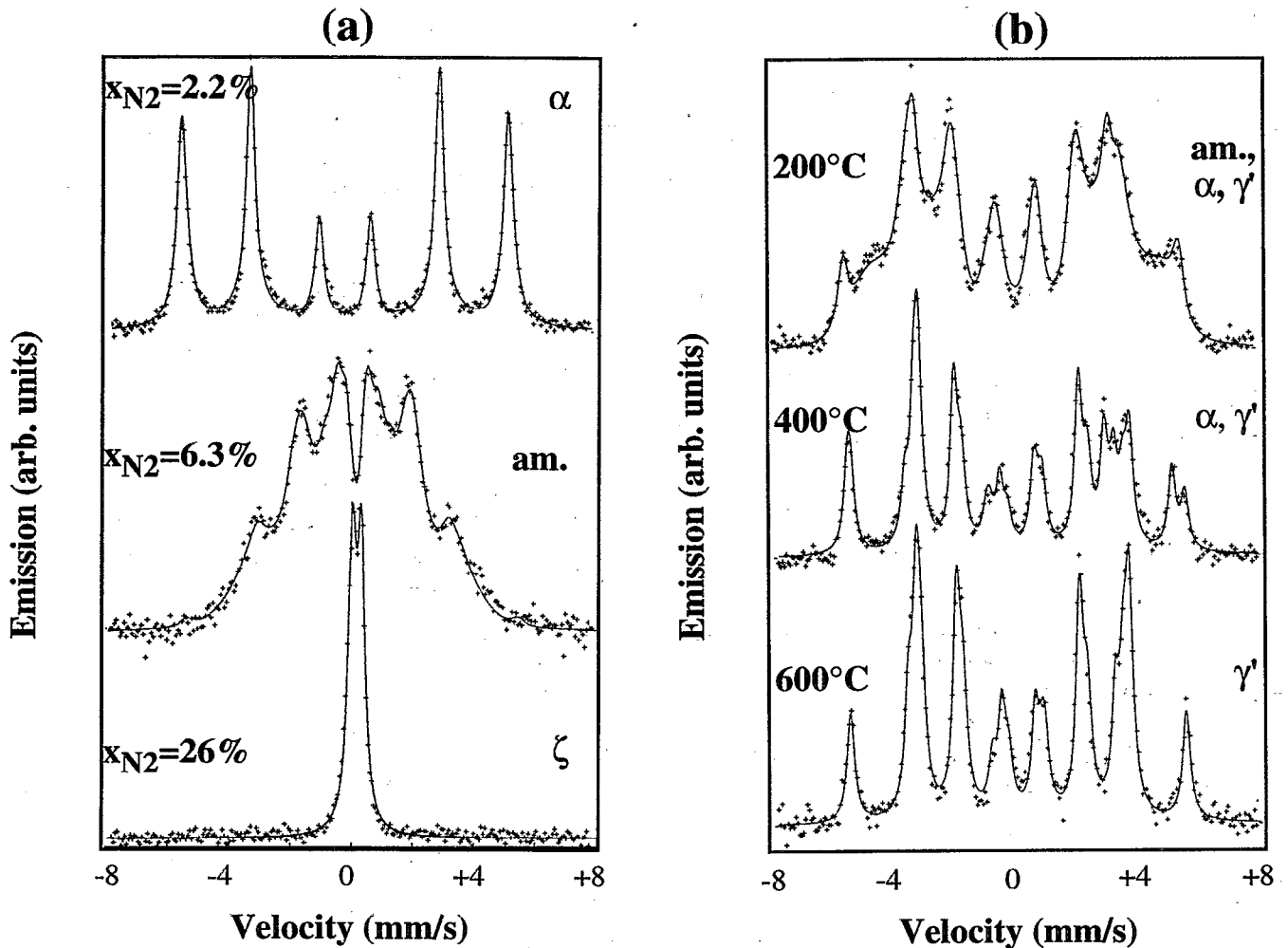


FIG. 2. CEMS spectra recorded for various preparation conditions of FeN films: (a) effect of increasing x_{N_2} for samples deposited on unheated substrates, (b) influence of substrate heating for $x_{N_2} = 6.3\%$. The presence of α -Fe, amorphous $Fe_{1-x}N_x$ (am), γ' -Fe₄N, and ζ -Fe₂N is evidenced. The nature of the different species are also reported in legends.

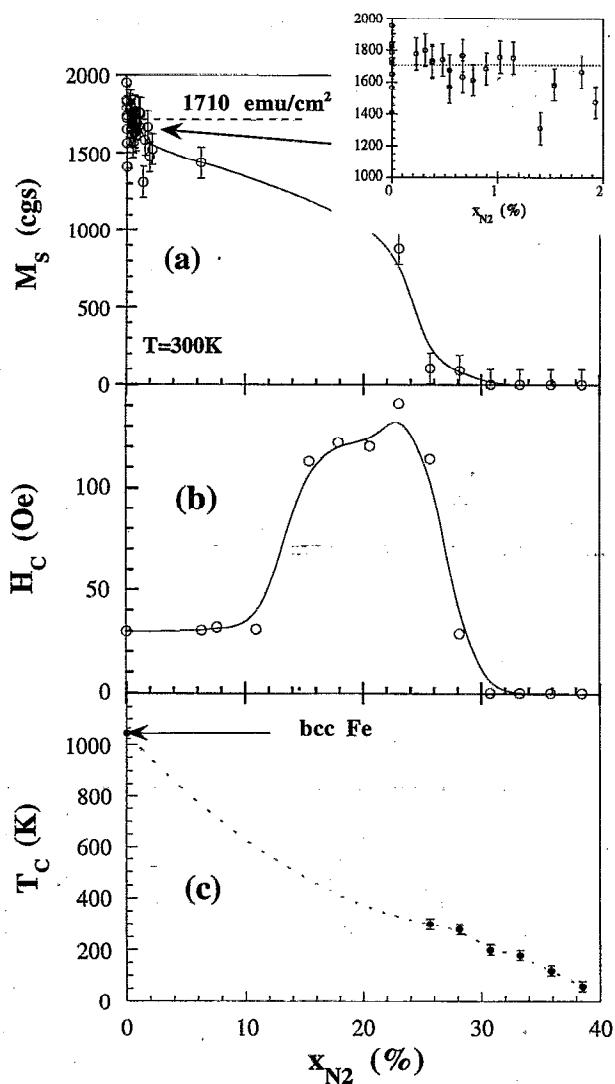


FIG. 3. Summary of the magnetic properties of Fe-N films prepared at room temperature as a function of the nitrogen to argon ratio (x_{N_2}): (a) saturation magnetization at 300 K, (b) coercive field at 300 K, (c) Curie temperature (solid lines are only guides to the eye).

C. Magnetic properties

Concerning the magnetic properties of our samples, several studies have been performed: magnetic anisotropy, saturation magnetization at room temperature and, last, ferromagnetic fluctuations in ζ -Fe₂N phase.

1. Saturation magnetization versus x_{N_2} of samples prepared at room temperature

Figure 3(a) reports saturation magnetization (M_s) dependence with x_{N_2} . One clearly remarks the plateau at ≈ 1700 emu/cm³ for low x_{N_2} . No enhancement of M_s can be observed as confirmed by CEMS spectra which show the usual 330 kOe hyperfine field sextet for these samples.

For increasing x_{N_2} , M_s starts to decrease. Room temperature saturation magnetization sharply decreases to zero values for $x_{N_2} > 0.24$, exactly when ζ -Fe₂N is the only

phase in our samples. Therefore, the ζ phase is found to be paramagnetic at room temperature by magnetization measurements and Mössbauer spectrometry.

2. Magnetic anisotropy and coercivity of iron nitride films

Hysteresis curves have been recorded for both in-plane and out-of-plane field geometries. In all the cases where nitrides are ferromagnetic (i.e., from α -Fe to ϵ -Fe₃N), in-plane magnetization curves saturate at low fields while several kOe are necessary to saturate the out-of-plane ones. This field is found to decrease with the decrease of the saturation magnetization of the nitrides. It means that the origin of the magnetic anisotropy of our iron nitride films is essentially shape anisotropy.

Figure 3(b) shows the dependence with x_{N_2} of the coercive fields (H_c) of iron nitride films deposited on unheated substrates. The increase of H_c up to 140 Oe for $0.18 < x_{N_2} < 0.24$ can be exactly correlated with the presence of ϵ -Fe₃N which is well crystallized. For lower nitrogen concentrations, H_c has low values (≈ 30 Oe), it is coherent with the poor crystallization of the corresponding films. The coercive field of our sputtered iron nitrides is low in all cases and therefore compatible with magnetic recording requirements.

3. Low temperature spin fluctuations in ζ -Fe₂N films

We have investigated low temperature magnetic behavior of iron nitride films prepared at room temperature with a nitrogen flow high enough for obtaining ζ -Fe₂N ($x_{N_2} > 0.24$). Ferromagnetic fluctuations are characterized by Arrott plots: $M^2(H, T)$ is plotted vs H/M at various temperatures. These curves are expected to be linear in a mean field model. Curie temperature is deduced from the H/M curve which passes by the origin. Such Arrott plots are presented in Fig. 4.

The good linear shape of these curves is a sign for the homogeneity of the samples. Our measurements show evidence for a decrease of the Curie temperature T_C from 300 K for $x_{N_2} = 0.25$ down to 60 K for $x_{N_2} = 0.37$. These values are in agreement with those reported by Chen *et al.*¹⁰ for bulk ζ -Fe₂N samples and their dependence versus x_{N_2} is shown in Fig. 3(c).

IV. DISCUSSION

Our results shed light on the problem of preparing iron nitride films by reactive sputtering: the use of nitrogen in reactive gas mixture is a good solution to obtain all the various Fe-N phases. We indicate the preparation conditions of single phase iron nitrides. Such phases can be obtained on unheated substrates except single phase γ -Fe₄N which requires substrate heating during sputtering.

Concerning the synthesis of α' -Fe₁₆N₂, we did not find in this batch of samples the conditions to obtain it. We did not either measure any enhancement of the saturation magnetization. However, we cannot conclude that α' -Fe₁₆N₂ has a larger M_s than bulk iron.

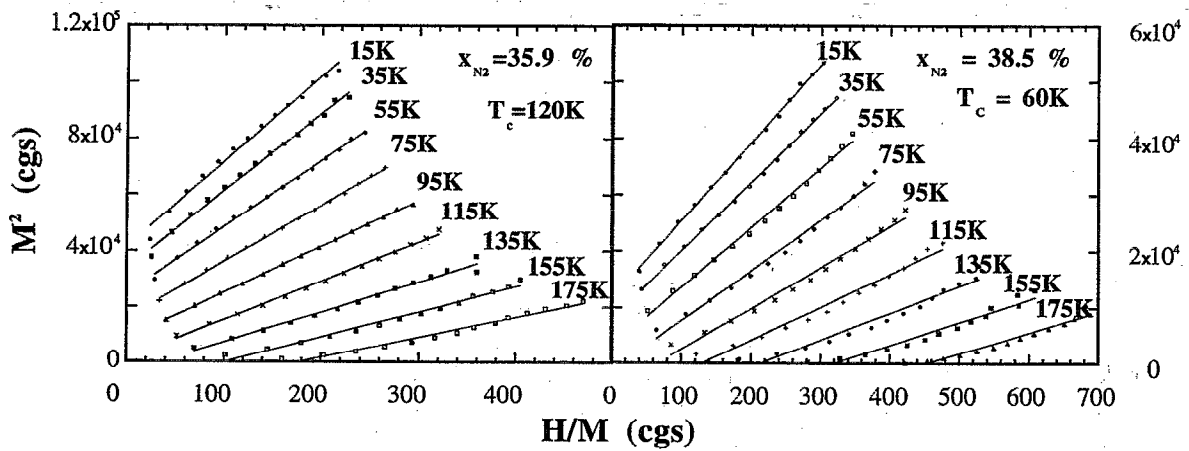


FIG. 4. Characterization of the ferromagnetic transition of samples with a stoichiometry close to ζ -Fe₂N phase: Arrott plots.

One of the most original results of our study is that we have obtained amorphous Fe-N alloy on unheated substrates. It presents a large saturation magnetization ($\sim \alpha$ Fe), soft magnetic properties (coercive field ~ 25 Oe), and a rather large domain of existence versus the plasma composition (from $x_{N_2} \approx 5\%$ up to 20%). This disordered phase transforms into Fe or Fe₄N when T_S is increased. Let us also notice that success in preparation of this amorphous phase is related to the total thickness t_f of the films: for $t_f > 5000$ Å, amorphous iron nitride tends to transform into Fe or Fe₄N as well as for heated substrates. This behavior is attributed to a plasma heating of the substrates during the deposition duration ($\approx 1-5$ h).

Concerning low nitrogen concentrations, the α Fe-N phase presents a non-negligible lattice expansion. From naive band structure considerations, we would expect an enhanced magnetization in such a nitride compared to pure iron. We do not find any increase of M_S , so it proves that a structural expansion of iron nitride structure is not enough for an increase of magnetization.

V. CONCLUSION

Using a conventional argon-nitrogen gaseous mixture, we have been able to produce iron nitride films in a large range of atomic concentrations and equilibrium phases: Fe,

Fe₄N, Fe₂₋₃N, Fe₂N. By varying the stoichiometry of Fe₂N, we could control the Curie temperature of the films between room temperature and 60 K. These preparation conditions have even allowed us to obtain expanded α Fe-N and a new amorphous iron nitride with soft magnetic properties. Further, these results show that an increase of the lattice parameter is not sufficient for the stabilization of a higher spin material. Other effects related for instance to local order could play a crucial role.

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