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Structural properties of iron oxynitride films obtained by reactive magnetron sputtering

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Abstract

Iron oxynitride films were prepared by magnetron sputtering of an iron target in Ar-N₂-O₂ reactive mixtures using a nitrogen flow rate of 2 sccm and a constant argon pressure of 0.3 Pa. The oxygen flow rate varied from 0 to 2 sccm. The thickness of the films deposited on silicon (100) and glass substrates ranged from 0.5 to 2 μm. In order to determine the chemical composition of the films, Rutherford backscattering spectrometry was used. Whatever the iron, nitrogen and oxygen contents, this study revealed that the film composition was homogeneous along the film depth. The films were characterized by several complementary experimental techniques, such as x-ray diffraction, x-ray photoelectron spectroscopy and ⁵⁷Fe Mössbauer spectrometry, which gave the most accurate information about the short-range order of iron atoms. Due to their different spatial scale efficiency, the analysis by both ⁵⁷Fe transmission and conversion electron Mössbauer spectrometry and x-ray diffraction allowed us to characterize both the structural and microstructural nature of these films. The study of the films by x-ray diffraction indicated an evolution of the structure from iron nitride ε-Fe₂N or ζ-Fe₂N to an fcc intermediate phase and finally to an oxide-like Fe₂(O, N)₃. The hyperfine structure observed on the Mössbauer spectra for the intermediate phase showed the presence of a phase of iron oxynitride Fe_{1.06}O_{0.35}N_{0.65} which is consistent with the x-ray diffraction results.

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1. Introduction

Due to their versatile properties, thin transition metal oxynitride films are frequently used in many decorative, optical and microelectronic coatings. Indeed, in this new class of ceramic materials, it is possible to improve the physical properties of transition metal oxides, such as the optical properties, by adding nitrogen during the film growth. Since metal–nitrogen bonds are less polar than metal–oxygen ones, oxynitride films (MeO_xN_y) appear as potentially attractive materials with an intermediate behaviour between insulating ionic oxides (MeO_x) and conducting metallic nitride (MeN_y) compounds. Recent works on MeO_xN_y thin films have been performed implying the sputtering of different transition metallic targets: Ti, Zr, Ta, Cr, Nb, Fe [1–6]. The authors show that the formation of oxynitride films leads to a systematic variation of physical properties originating from the gradual replacement of oxygen atoms by nitrogen atoms. However, these oxynitride films with various N/O ratios show a complex structure in which a growth competition between metallic nitride and metallic oxide phases occurs, which depends on the reactivity of both oxygen and nitrogen with regards to the transition metal. For intermediate N/O ratios in MeO_xN_y systems, the question arises of when the structure of oxynitride films may be either biphased with the occurrence of $\text{MeO}_x + \text{MeN}_y$ phases or monophased to produce a new crystalline oxynitride phase.

The possibility to prepare iron oxide and iron nitride films by reactive magnetron sputtering has been widely demonstrated [7, 8]. Furthermore, during the sputtering process, metastable and non-stoichiometric phases can also be synthesized. The combination of two reactive gases like nitrogen and oxygen will allow the formation of new materials such as iron oxynitride. Recent studies on iron oxynitride films prepared by molecular beam epitaxy using NO_2 as reactive gas showed that the formation of iron oxynitride remains difficult with high nitrogen content [9, 10].

In this study, we first focused our effort on the synthesis of iron nitride ($\epsilon\text{-Fe}_2\text{N}$ or $\zeta\text{-Fe}_2\text{N}$), iron oxynitrides $\text{Fe}(\text{N}, \text{O})$ and iron oxide-like $\text{Fe}_2(\text{O}, \text{N})_3$ prepared by magnetron sputtering and by varying the oxygen flow. The composition and the structure of the deposited films were studied as a function of the injected oxygen flow rate. The films deposited at room temperature with a thickness which ranges from 500 to 2000 nm were investigated by several complementary experimental techniques, such as x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), x-ray photo-electron spectroscopy (XPS) and finally ^{57}Fe Mössbauer spectrometry, which gives the most accurate information about the short-range order around Fe atoms. The choice of iron as transition metal was motivated by the fact that iron is an active element in Mössbauer spectrometry. Thus, the various types of local environment of Fe atoms can be distinguished and the structural arrangement in iron oxynitrides can be established.

2. Experimental details

Iron oxynitride coatings were deposited on glass and (100) silicon substrates by magnetron sputtering of an iron target in an $\text{Ar-N}_2\text{-O}_2$ reactive mixture. Reactive sputtering experiments were performed using Alliance Concept AC450 sputter equipment with a vacuum chamber volume of about 70 l. A base pressure of 10^{-5} Pa was obtained with a turbomolecular pump backed with a mechanical one. The working Ar pressure was kept constant at 0.3 Pa using a mass flow rate controller and a constant pumping speed of 10 l s^{-1} . A metallic iron target (purity 99.5%, diameter 50 mm), which was located at 60 mm from the substrate, was dc sputtered with a constant current density of 100 A m^{-2} . The substrates were cleaned with acetone and alcohol before being charged in the deposition chamber and were sputter etched

in a pure argon atmosphere with a negative bias voltage of 200 V for 15 min. In addition, a 10 min pre-sputtering in argon was carried out to clean the iron target, avoiding the presence of impurities in the films (a shield was interposed between the substrates and the target). During the deposition process, the nitrogen flow rate was fixed at 2 sccm (standard cubic centimetres per minute with 1 sccm = 1.66×10^{-3} Pa m³ s⁻¹) and the oxygen flow rate $Q(\text{O}_2)$ was varied between 0 and 2 sccm. The iron-based films were deposited without external heating. The substrate temperature during deposition was lower than 320 K.

The thickness of the films was measured with a Dektak 3030 profilometer while the deposition rates were estimated from the sputtering time. X-ray diffraction (XRD) patterns were obtained using a Phillips X'pert diffractometer with Cu K α radiation. A wavelength of $\lambda = 0.15406$ nm was used to obtain data in a grazing angle of 0.7°. The film compositions were estimated by RBS. The RBS measurements were performed with a van de Graaf accelerator using a 2 MeV He⁺ beam and 2 MeV protons beam. Protons were used because of an increase in sensitivity for light elements. The experimental results were analysed using WiNDF V.7 software based on the IBA DataFurnace code, to extract the depth profiles [11]. In addition, XPS was used to get information on the electronic structure. The XPS measurements were obtained using a Mg (1253.6 eV) anticathode. Since the film's surface was contaminated by carbon and absorbed water vapour, this superficial layer was removed by 5 min ion sputtering (Ar ions of 2 keV) before XPS analysis.

Due to the local probe character of Mössbauer spectrometry and its sensitivity to atomic surroundings, this technique was used to study the different kinds of Fe environments in the FeO_xN_y films. Mössbauer spectra of the films deposited on Si substrates were recorded in a standard transmission geometry using a conventional spectrometer with a constant acceleration signal and a ⁵⁷Co source diffused into a rhodium matrix. The thickness of the Si substrate is 280 μm . This value is appropriate to register good statistics Mössbauer spectra in a reasonable time (up to a few days according to the film thickness). The samples were placed into a cryostat, allowing us thus to perform measurements over the temperature range 4.2–300 K. In addition to the analysis of the whole thickness of the films, their superficial layer was studied by conversion electron Mössbauer spectrometry (CEMS) at 300 K using a Rikon 5 spectrometer (ORTEC) in constant acceleration mode with a standard driving unit. The K emitted electrons were collected with a proportional gas-flow meter (He–5% CH₄). The sensitivity range of CEMS with K conversion electrons is estimated at about 300 nm below the top of the surface layer. Both transmission and conversion electron spectrometers were calibrated using an α -Fe foil, and the isomer shift values are given relative to that of α -Fe at room temperature. The Mössbauer spectra were fitted using the least-square MOSFIT program [12] with a combination of quadrupolar doublets and magnetic sextets composed of Lorentzian lines.

3. Results and discussion

3.1. Chemical composition of the films

The influence of the oxygen flow rate on the chemical composition of the films obtained using the RBS technique is summarized in table 1. For the iron nitride, the chemical composition shows a Fe/N atomic ratio close to 2.2, while the oxygen concentration is close to 0 at.%. Niederdrenk *et al* [13] reported in the literature that the ε -Fe₂N_{1-z} nitride phase is obtained when $0 \leq z \leq 0.33$. Based on these results, our film is composed of either iron nitride ε -Fe₂N or ζ -Fe₂N [13, 14]. When $Q(\text{O}_2)$ is fixed at 0.4 sccm, the average nitrogen concentration is quite constant, whereas the iron and oxygen concentrations vary.

Table 1. Composition of the films determined by RBS measurements.

| $Q(\text{O}_2)$ (sccm) | Fe (at.%) | N (at.%) | O (at.%) | Chemical formula |
|------------------------|-----------|----------|----------|--|
| 0 | 68.9 | 31.1 | 0 | $\text{Fe}_{2.22}\text{N}$ |
| 0.4 | 51.5 | 31.7 | 16.8 | $\text{Fe}_{1.06}\text{O}_{0.35}\text{N}_{0.65}$ |
| 0.7 | 39.4 | 4.7 | 55.9 | $\text{Fe}_{1.95}\text{O}_{2.77}\text{N}_{0.23}$ |
| 1 | 38.4 | 3.3 | 58.3 | $\text{Fe}_{1.87}\text{O}_{2.84}\text{N}_{0.16}$ |
| 1.5 | 40.3 | 0 | 59.7 | $\text{Fe}_{2.02}\text{O}_3$ |

To check the composition of the film deposited on Si(100), we recorded the RBS spectrum using an angle of 30° (figure 1), and the atomic concentration was then extracted versus the depth profile, as is shown in figure 1(b). We note in figure 1(a) that the refinement indicates the presence of three elements, i.e. iron, nitrogen and oxygen, which are depth independent (figure 1(b)). Consequently, the oxygen atoms were homogeneously incorporated into the growing film. It is important to emphasize that no trace of minor elements was detected in the film (detection limit about 1 at.%). Thus the depth-independent concentration of the detected elements (Fe, O and N) shown in figure 1(b) indicates that the film is rather homogeneous. Furthermore, the atomic ratio $\text{Fe}/(\text{O} + \text{N})$ is close to 1, and the chemical formula can be written as $\text{Fe}_{1.06}\text{O}_{0.35}\text{N}_{0.65}$. Finally, in the RBS measurements of films prepared with higher oxygen flow rates ($0.7 \leq Q(\text{O}_2) \leq 1$ sccm), the atomic concentration of oxygen increases quickly. The atomic ratio $\text{Fe}/(\text{O} + \text{N})$ is close to 0.66, and the chemical formula can be written as $\text{Fe}_{1.95}\text{O}_{2.77}\text{N}_{0.23}$ or $\text{Fe}_{1.87}\text{O}_{2.84}\text{N}_{0.16}$ (table 1). These films are characterized by a very small content of nitrogen, suggesting $\text{Fe}_2(\text{O}, \text{N})_3$ oxide-like films. Voogt *et al* [9] have reported similar results on magnetite-like and wustite-like oxynitride films produced by NO_2 -assisted molecular beam epitaxy. At this stage it is important to emphasize that these results clearly indicate the transition from iron nitride to iron oxide as shown in figure 2. For $Q(\text{O}_2) = 1.5$ sccm, no nitrogen was detected in the film, and the atomic ratio $\text{Fe}/(\text{O})$ is equal to 0.66 with the following chemical formula: $\text{Fe}_{2.02}\text{O}_3$.

3.2. Films structure

All the films were characterized by x-ray diffraction, and the patterns are shown in figure 3. For the iron nitride film (figure 3(a)), the diffraction peaks could be attributed to three iron nitride films ζ - Fe_2N (orthorhombic), ε - Fe_2N (hexagonal) and ε - Fe_3N (hexagonal) [13, 15]. Since the chemical composition of the films ($\text{Fe}/\text{N} = 2.2$) is not consistent with such a chemical formula, these results confirm that the sputtering process is able to deposit metastable materials [16]. In addition the chemical formula allows us to exclude ε - Fe_3N . The XRD diffractogram of the film deposited with an oxygen flow rate of 0.4 sccm (figure 3(b)) shows changes in the peak positions. This film is rather well crystallized in an fcc structure with a lattice parameter estimated at about 0.452 nm. Such a phase has to be *a priori* attributed to γ''' -FeN (NaCl-type) which shows a very close lattice parameter (0.45 nm). It is important to note that (i) an fcc Ti-O-N phase was also reported in the literature by Chappé *et al* [1] and (ii) the lattice parameters of FeO and γ'' -FeN (ZnS-type) are lower, with values of about 0.43 nm for both structures [17–20]. However, this result does not bring information about the position of oxygen atoms in the films. Since the oxynitride film crystallizes in the same structure as that of γ''' -FeN (NaCl-type), the most probable hypothesis is related to a partial substitution of some nitrogen atoms into the FeN network by oxygen ones. Finally, for the higher oxygen flow rates, the x-ray diffraction patterns presented in figures 3(c) and (d) show broadened peaks which could be attributed to small crystalline grains of iron oxide close to α - Fe_2O_3 [21]. In addition, this

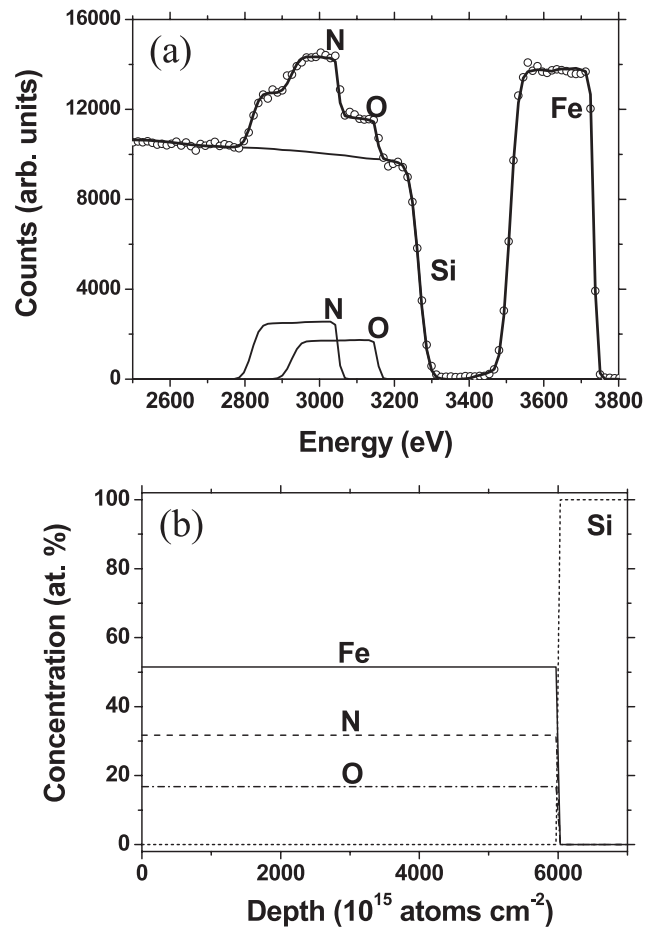


Figure 1. The RBS spectrum of 2 MeV protons obtained with an angle of 30° (a) and the RBS depth profiles (b) for the film deposited with an oxygen flow rate of 0.4 sccm.

result is consistent with the chemical composition ratio determined from RBS measurements, as shown in figure 2.

To obtain further information about the nature of bonds involving iron atoms, XPS analyses were performed after an argon-ion bombardment to remove impurities from the film surface after air exposure (figure 4). Thus, for a film prepared without oxygen, the spectrum has been fitted with one component with the binding energy values of Fe $2p^{3/2}$ (and $2p^{1/2}$) equal to 707.6 eV (720.75 eV) for Fe_2N . These values are in agreement with those reported by Jiang *et al* [21]. As can be observed in figure 4(b) for the film prepared with 0.4 sccm of oxygen, the Fe $2p^{3/2}$ broad peak can be deconvoluted by a curve-fitting procedure into two components at 707.2 and 710.0 eV, which can be attributable to Fe–N and Fe–O bonds, respectively. Let us emphasize that the main binding energy values characteristic of FeO [22] are 709.5 and ~ 716 eV for Fe^{2+} , while the energy in iron nitrides is 707.6 eV. Consequently, this iron oxynitride film does contain both Fe–O and Fe–N bonds in spite of the absence of the binding energy value ~ 716 eV. Finally, for the film prepared with 0.7 sccm of oxygen, the peaks are shifted to lower energy. The two main peaks appear at about 710.8 and 723.6 eV, which is consistent with values reported for ferric oxide in the literature [23–32]. It is well established

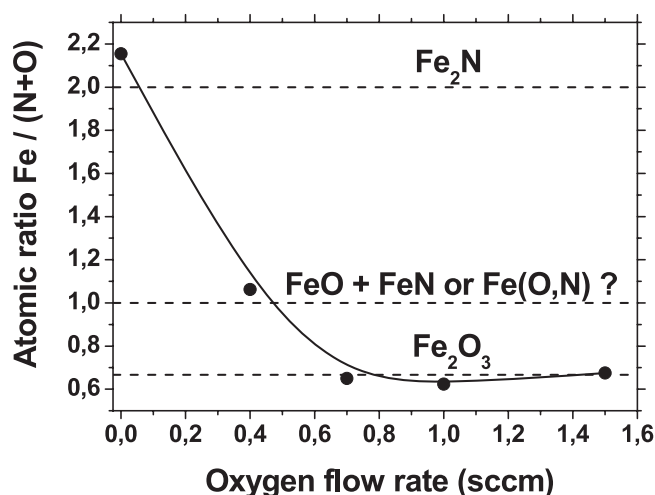


Figure 2. Evolution of the atomic ratio of Fe/(N + O) versus the oxygen flow rate.

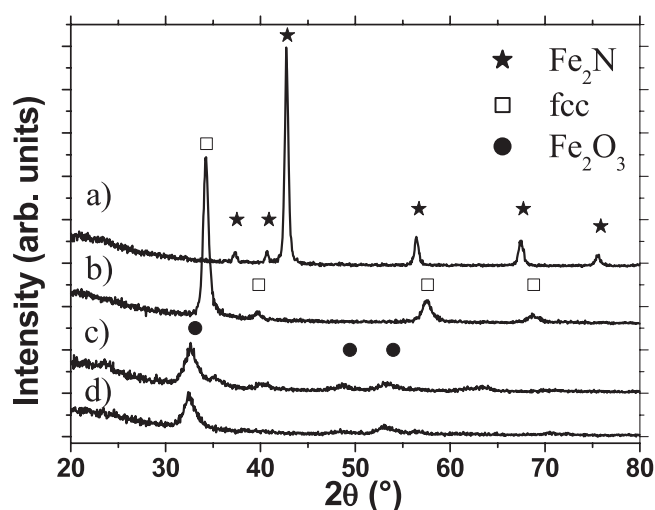


Figure 3. Influence of the oxygen flow rate on the x-ray diffractograms of films deposited on glass. (a) $Q(O_2) = 0$ sccm, (b) $Q(O_2) = 0.4$ sccm, (c) $Q(O_2) = 0.7$ sccm and (d) $Q(O_2) = 1$ sccm.

that the XPS Fe 2p core-level spectra of α -Fe₂O₃ and γ -Fe₂O₃ are almost identical to each other [27]. Thus, the film prepared with 0.7 sccm O₂ can be associated to Fe₂O₃. Therefore these results give further evidence for the phase changes from iron nitride to oxide with an intermediate oxynitride film which can be attributed either to a mixture of γ''' -FeN and Fe_{1-x}O or to the occurrence of an iron oxynitride Fe_{1.06}O_{0.35}N_{0.65}. To obtain a detailed description of the oxynitride film structure, Mössbauer analyses were performed.

3.3. ⁵⁷Fe Mössbauer spectrometry

The Mössbauer spectra of the samples recorded at 300 and 77 K are displayed in figures 5 and 6. The hyperfine structure at ⁵⁷Fe in Fe_{2.2}N film deposited without oxygen shows an

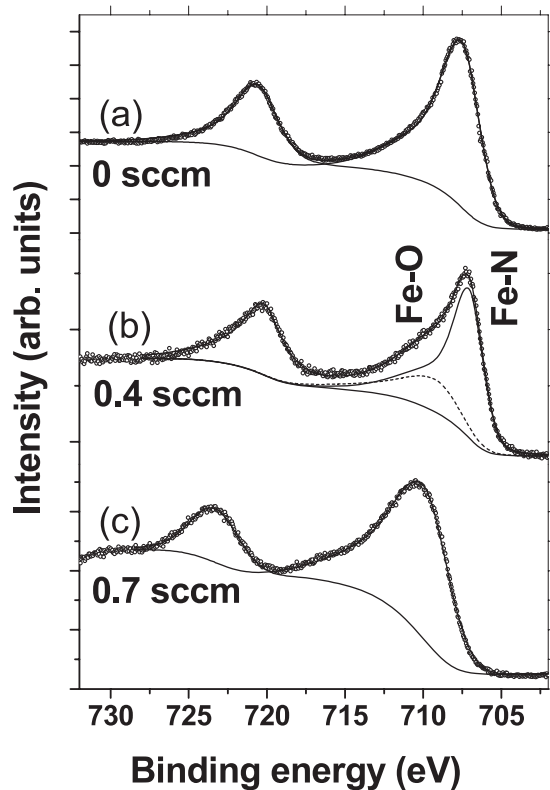


Figure 4. Effect of the oxygen flow rate on the XPS spectra for the Fe 2p level.

asymmetrical paramagnetic doublet (figure 5(a)), which might be attributed *a priori* to either ϵ -Fe₂N or ζ -Fe₂N. The Mössbauer spectrum was well fitted with two quadrupolar doublets with isomer shift (and quadrupolar splitting) values of 0.42(2) mm s⁻¹ (0.27(2) mm s⁻¹) and 0.35(2) mm s⁻¹ (0.41(2) mm s⁻¹), respectively. The two components were unambiguously attributed to iron sites with two nitrogen atoms as nearest neighbours and three nitrogen neighbours, respectively. Indeed, previous results [27, 28] showed that ζ -Fe₂N was characterized by a single quadrupolar doublet, and a slight deviation from the ideal Fe₂N up to ϵ -Fe₂N phase favours the occurrence of a second quadrupolar Fe site. Based on the model given by Jack [29], the stoichiometry calculated in terms of site occupation from the Mössbauer analysis can be written as ϵ -Fe_{2.137}N. This result is rather consistent with the composition determined by RBS, as listed in table 1. In addition, we present for the same film the Mössbauer spectrum obtained at 77 K (figure 6(a)). The comparison between the 300 and 77 K spectra suggests that no magnetic transition takes place down to 77 K.

When $Q(O_2) = 0.4$ sccm, the Mössbauer spectrum in figure 5(b) gives evidence for the formation of a paramagnetic phase at room temperature, which is *a priori* new. This film contains a new oxynitride compound with NaCl-type structure as described in our previous paper on the chemical environment of iron atoms in iron oxynitride films [30]. The main Mössbauer results are compared to those of the iron nitride and iron oxide-like compounds. The spectrum of this sample were deconvoluted into two single lines and three quadrupolar doublets; their isomer shift and quadrupole splitting values are summarized in table 2. The

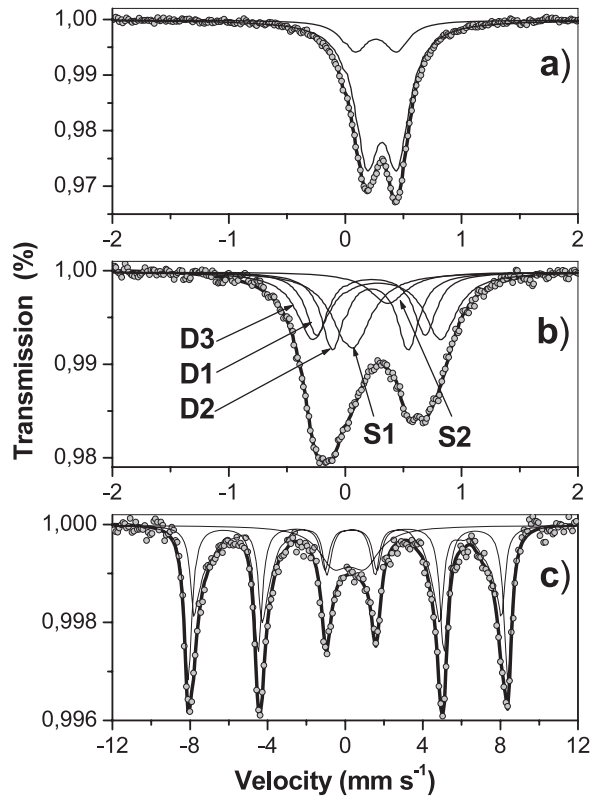


Figure 5. 300 K Mössbauer spectra of the films prepared with (a) $Q(\text{O}_2) = 0$ sccm, (b) $Q(\text{O}_2) = 0.4$ sccm and (c) $Q(\text{O}_2) = 0.7$ sccm.

Table 2. Hyperfine parameters of the $\text{Fe}_{1.06}\text{O}_{0.35}\text{N}_{0.65}$ film at 300 K, measured ratio of the various components, and calculated ratio based upon a binomial distribution of oxygen.

| | IS (mm s^{-1}) ± 0.01 | QS (mm s^{-1}) ± 0.02 | Measured ratio (%) ± 2 | Calculated ratio (%) ± 2 |
|----|---|---|-------------------------------|---------------------------------|
| S1 | 0.15 | 0.00 | 20 | 18 |
| S2 | 0.48 | 0.00 | 8 | 6 |
| D1 | 0.34 | 0.90 | 20 | 20 |
| D2 | 0.33 | 0.64 | 23 | 27 |
| D3 | 0.39 | 1.08 | 29 | 29 |

mean isomer shift values of the first two components deduced from the analysis are close to those of the cubic γ'' -FeN (S1) and γ''' -FeN (S2) phases, and are in agreement with those reported in the literature [19, 31]. The origin of the remaining components can be associated to iron sites located in a non-stoichiometric NaCl-type structure with vacancies. Let us emphasize that the paramagnetic ε -Fe₂N phase can be excluded due to too high quadrupolar splitting parameters [13]. Similar Mössbauer results were reported by Rissanen *et al* [19] on iron nitride films prepared by a sputtering method. In their fitting model, the quadrupolar splitting is assigned to be due to the occurrence of impurities and structural defects. The environments of an Fe site in this oxynitride film were modelled by means of a binomial distribution, assuming

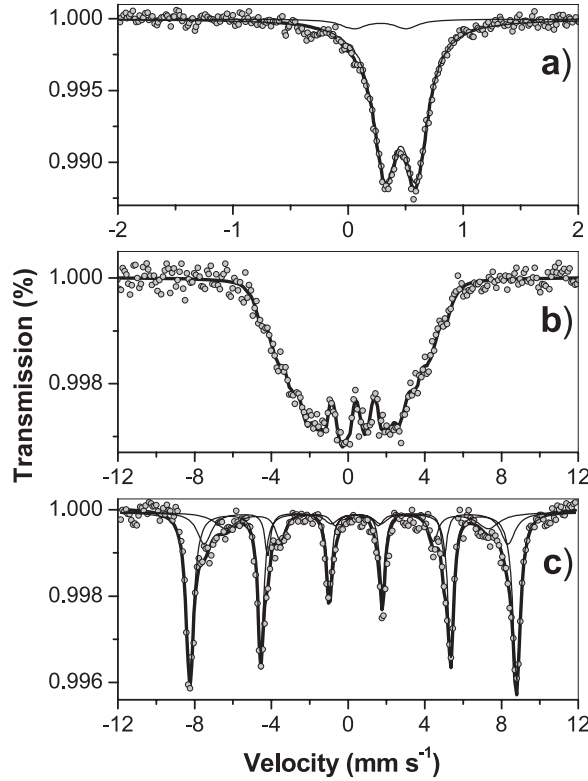


Figure 6. 77 K Mössbauer spectra of the films prepared with (a) $Q(O_2) = 0$ sccm, (b) $Q(O_2) = 0.4$ sccm and (c) $Q(O_2) = 0.7$ sccm.

a random distribution of the iron environments. The probability $P(m, x)$ that one iron atom possesses m oxygen atom as first neighbours is given by the equation

$$P(m, x) = x^m (1 - x)^{n_1 - m} C_{n_1}^m$$

where m ranges from 0 to 6 for octahedrally surrounded irons while x and $(1 - x)$ correspond to the relative content of oxygen and nitrogen, respectively. n_1 is fixed to 4 (6) for a tetrahedral (octahedral) coordination. The oxygen content, $\frac{\%O}{\%O + \%N}$, is $x = 0.346$ according to RBS data.

Due to the presence of single lines $S1$ and $S2$, the probability that a tetrahedral Fe ($n_1 = 4$) is surrounded by nitrogen is 0.18 ($P(0, 0.346)$) whereas for an octahedral Fe ($n_1 = 6$) surrounded by nitrogen, the probability is 0.06 ($P(0, 0.346)$). All the other octahedral Fe atoms must be surrounded by at least one oxygen atom. Considering that the remaining components (quadrupolar doublets D1, D2 and D3) are associated to a NaCl-type structure, one observes a good agreement between the calculated and the measured area, as listed in table 2. Thus in this study, quadrupolar doublets D1 and D2 with iron in the Fe^{3+} sites are due to the Fe nuclei surrounded by vacancies or one and two oxygen atoms. Borsa [31] has shown the presence of a paramagnetic oxynitride phase for uncapped γ' - Fe_4N films after exposure to air at room temperature. This paramagnetic phase is characterized by an isomer shift of $0.34(2) \text{ mm s}^{-1}$ and a quadrupolar splitting of $0.88(2) \text{ mm s}^{-1}$. For the last quadrupolar doublet D3, we note a slight increase of the isomer shift ($IS = 0.39(2) \text{ mm s}^{-1}$), which can be attributed to more oxygen in the next neighbourings of an Fe site.

Table 3. Hyperfine parameters of the $\text{Fe}_{1.95}\text{O}_{2.77}\text{N}_{0.23}$ film at 77 K, measured ratio of the various components, and calculated ratio based upon a binomial distribution of nitrogen.

| Component | IS (mm s^{-1}) ± 0.01 | 2ε (mm s^{-1}) ± 0.02 | H_{hf} (T) ± 0.2 | Measured ratio (%) ± 2 | Calculated ratio (%) ± 2 |
|--------------------------------|---|---|----------------------------------|-------------------------------|---------------------------------|
| $\alpha\text{-Fe}_2\text{O}_3$ | 0.49 | -0.14 | 52.6 | 66 | 62 |
| Fe-O-N ^I | 0.57 | 0.00 | 48.0 | 24 | 30 |
| Fe-O-N ^{II} | 0.64 | -0.03 | 42.2 | 10 | 8 |

Nevertheless, the presence of FeO wustite has to be excluded in this film because this phase is characterized by the following hyperfine parameter values: IS = 0.52(2) mm s^{-1} (QS = 0.45(2) mm s^{-1}) and 0.93(2) mm s^{-1} (1.11(2) mm s^{-1}) [32–34]. Indeed, these values do not agree with those of components D1, D2 and D3. In addition, the investigations of Voogt *et al* [9] performed on wustite-like oxynitride $\text{Fe}_{1-x}\text{O}_{1-y}\text{N}_y$ films show that the isomer shift values are ranged between 0.67 and 0.73 mm s^{-1} . Furthermore, our x-ray diffraction results indicate a lattice parameter of 0.452 nm, close to the value of pure γ''' -FeN (NaCl-type). Hence the presence of a mixture of iron nitride with wustite (FeN/FeO) can be excluded. On cooling down to 77 K, as is shown in figure 6(b), the Mössbauer spectrum clearly shows a broad line asymmetrical magnetic sextet which can be well described by means of a hyperfine field distribution correlated to that of the isomer shift. The average magnetic hyperfine field (mean isomer shift) deduced from the analysis is 18.5 T (0.40 mm s^{-1}). Comparing the magnetic hyperfine field value with that of FeO (~ 44 T, IS = 1.00 mm s^{-1}) at 77 K, this result gives further evidence that the film does not significantly contain FeO as wustite-type.

Finally, the spectrum of the sample prepared with $Q(\text{O}_2) = 0.7$ sccm is included in figure 5(c). It is interesting to see that in this case the nature of the deposited film changed considerably, since there is a clear indication of the presence of the magnetic iron oxide phase. In addition to the paramagnetic doublet having an isomer shift (quadrupolar splitting) value of 0.27(2) mm s^{-1} (1.50(2) mm s^{-1}), the spectrum was described with a sextet with a magnetic field (isomer shift) of 50.9(5) T (0.38(2) mm s^{-1}) and a distribution of hyperfine fields linearly correlated to a distribution of isomer shifts. In addition, the depth-dependent hyperfine structure is obtained by comparing conversion electron Mössbauer spectrum (sensitive to up to about 300 nm) to the spectrum recorded in transmission geometry at 300 K which allows us to probe all the sample thickness, as represented in figure 7. The main difference in the hyperfine structure comes from the disappearance of the central quadrupolar doublet. The profile as obtained by RBS shows some composition changes from about 400 nm, at which a significant increase in nitrogen content is noted. Thus this paramagnetic doublet can be attributed to the increase in nitrogen content (from 10 to 2 at.%) near the film substrate. In order to remove any ambiguity about the nature of this film, we carried out measurements at 77 K, as shown in figure 6(c). One clearly observes the vanishing of the quadrupolar doublet observed at room temperature. The spectra were decomposed into three magnetic components. The hyperfine data are listed in table 3. The interpretation is done by examining the hyperfine parameter values. Thus, from the Mössbauer spectrum, one concludes that the first sextet is unambiguously attributed to the hematite $\alpha\text{-Fe}_2\text{O}_3$ [35]. However, the films are not pure oxides and are not well crystallized. Since the RBS measurements indicate the presence of nitrogen in the films, the two magnetic sextets can be attributed to Fe ions having at least one (Fe-O-N^I) or two nitrogen and more (Fe-O-N^{II}) nearest neighbours. The Mössbauer data (table 3) obtained by considering Fe ions in octahedral sites are in good agreement with those calculated for $x = 0,077$ ($x = \frac{\%N}{\%O+\%N}$), using the binomial distribution. This result gives further evidence of the substitution of nitrogen in the oxygen sublattice.

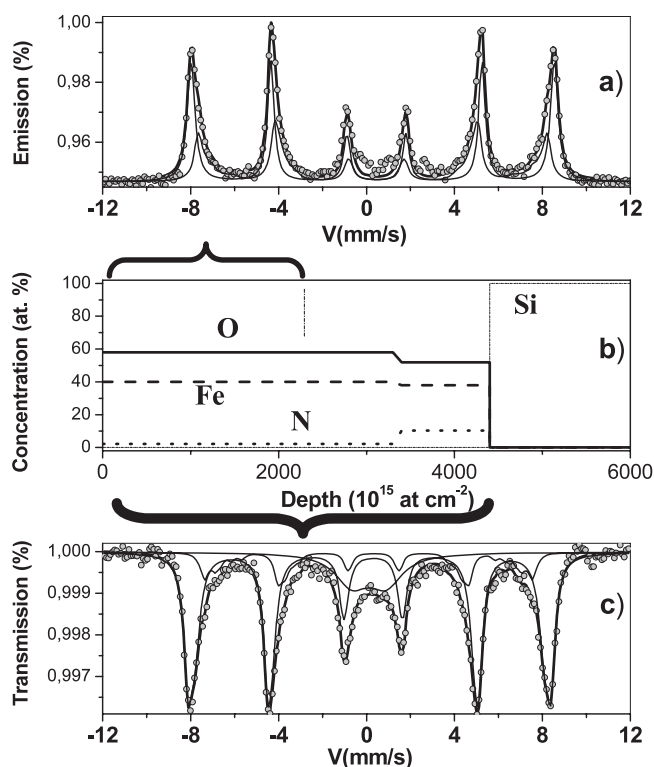


Figure 7. RBS depth profiles (b), conversion Electron Mössbauer spectrum (a) and transmission Mössbauer spectrum (c) for the film deposited with an oxygen flow rate of 0.7 sccm.

4. Conclusions

FeO_xN_y films were deposited on silicon and glass substrates by magnetron sputtering of an iron target in various $\text{Ar-N}_2\text{-O}_2$ reactive mixtures using constant argon and nitrogen flow rates and different oxygen flow rates. In this work, the effect of the oxygen flow rate on the structural properties was investigated.

When the oxygen flow rate is lower than 0.7 sccm, the films are rather well crystallized, while their composition remains homogeneous with respect to their depth. The increase in the oxygen rate leads to drastic changes in the film structure that evolves from a nitride to an oxynitride and finally to an oxide-like phase. Films deposited without oxygen show an atomic Fe/N ratio close to 2.2, in agreement with a $\epsilon\text{-Fe}_2\text{N}$ -type structure. This structure is confirmed by Mössbauer analyses at both 300 and 77 K. When the oxygen flow rate is fixed at 0.4 sccm, a new iron oxynitride is synthesized with non-negligible nitrogen and oxygen concentrations. This film crystallizes in an fcc structure with a lattice constant of about 0.452 nm, i.e. close to that measured for $\gamma''\text{-FeN}$ (NaCl-type). In this new compound, the atomic ratio $\text{Fe}/(\text{N} + \text{O})$ is very close to 1. XPS analyses show the occurrence of both nitride and oxide bonds, confirming the oxynitride nature of the film. Mössbauer spectrometry evidences the formation of a new paramagnetic phase at room temperature with various chemical environments of iron atoms. For higher oxygen flow rates, FeO_xN_y oxide-like films were deposited, as confirmed by XRD, XPS and Mössbauer analyses.

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