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Millon

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Iron oxide thin films grown on (001) sapphire substrate by pulsed-laser deposition

C-E Bejjit¹, V. Rogé^{1§}, C. Cachoncinlle¹, C. Hebert^{2,3}, J. Perrière^{2,3}, E. Briand^{2,3}, E. Millon^{1*}

¹ GREMI, UMR 7344 CNRS / Université d'Orléans, 14 Rue Issoudun, 45067 Orléans Cedex 2, France

² Sorbonne Universités, UPMC Paris 06, UMR 7588, INSP, 4 Place Jussieu, 75005 Paris, France

³ CNRS, UMR 7588, INSP, 4 Place Jussieu, 75005 Paris, France

* : Corresponding author : email : eric.millon@univ-orleans.fr

§ : Present address : LIST, 41 rue de Brill, L-4422 Belvaux, Luxembourg

Abstract :

Magnetite (Fe₃O₄) and wustite (FeO) are well-known oxides for their promising magnetic properties. However, growing stable FeO_x thin films with controlled iron oxidation states could be of interest for further applications. In this work, we highlight the formation of different FeO_x-based thin films grown by pulsed-laser deposition (PLD) from Fe or α-Fe₂O₃ targets onto sapphire substrates. Based on X-ray diffraction and Rutherford backscattering spectroscopy analyses, we report on films with various O/Fe ratios obtained by controlling both the substrate temperature and the oxygen pressure in the 10⁻⁵ – 10 Pa range during the PLD growth. Thus, the different crystalline phases of the Fe-O system can be grown: metallic iron, α-Fe₂O₃, Fe₃O₄, and the thermodynamically metastable phase FeO. On one hand, we demonstrate that at low pressures (< 10⁻⁴ Pa) metal-oxide composite thin films with both metallic Fe and Fe₃O₄ phase are epitaxially grown on the sapphire substrates even at room temperature. On the other hand, we highlight that using a α-Fe₂O₃ target, films composed with a mixture of wustite and spinel phases have been obtained at room temperature. The precise growth conditions leading to the formation of FeO-based films or metal-oxide composite films are discussed.

Keywords : pulsed-laser deposition, iron oxide, wustite, magnetite, epitaxy, nanocomposite,

Highlights :

* FeO-Fe₃O₄ composite 111-oriented films are grown at room temperature under 10⁻⁵ Pa

* metal-oxide composite films are epitaxially grown at room temperature from a Fe target

* Fe film grown at room temperature under vacuum shows a rectangle on hexagon epitaxy

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Introduction

Iron oxide thin films have been studied for several decades for their potential applications due to their magnetic [1][2], catalytic [3], and sensing [4] properties. Regarding the Fe-O thermodynamical system, different phases ranging from α -Fe to Fe_{1-x}O (wustite), Fe_3O_4 (magnetite), and α - Fe_2O_3 (hematite) can be obtained upon increasing the oxygen content and depending on the temperature. In particular, wustite and magnetite have been largely investigated due to their ferrimagnetic and unbalanced antiferromagnetic properties, respectively. For example, chemical vapor deposition [5] or rf-sputtering [2][6] methods may be classically used to obtain Fe_3O_4 thin films for ferrimagnetic properties [7]. By laser molecular beam epitaxy, Suturin et al. [8] have grown on (001) GaN substrate different magnetically ordered iron oxide phases, especially (111)-oriented Fe_3O_4 films were found to be epitaxied on the GaN substrate. If the growth of a single-phase Fe_3O_4 film is commonly observed, the main difficulty is the preferred stabilization of FeO instead of Fe_3O_4 . By magnetization measurements, Kim et al. [2] have evidenced particular processing conditions during sputtering deposition that leads to a “ferrimagnetic Fe_{1-x}O ” inside the spinel-based Fe_3O_4 film. Koziol-Rachwa et al. [9] reported on the growth of monolayer-like FeO (001) films (0.17 nm thick) via molecular beam epitaxy on (001) MgO using the reactive deposition of Fe.

Fe_3O_4 films have also been obtained by pulsed-laser deposition (PLD) on (100) MgO substrate and these films exhibit a high structural order following a (100) Fe_3O_4 texturation and a perfect stoichiometry leading to the Verwey transition at 121 K [10]. Pure magnetite PLD films may be produced onto Si (100) [1], glass [11] or c-cut sapphire [12] substrates at relatively moderated growth temperatures (200-500°C) and under an intermediate range of oxygen pressure (10^{-3} to 10^{-2} Pa).

The thin film growth of wustite phase is more challenging due to the tendency of FeO first to decompose into spinel Fe_3O_4 and metal Fe below 575°C and, second to be easily oxidized to the higher valence oxides such as Fe_3O_4 and α - Fe_2O_3 .

In this work, compositions, structures and morphologies of different oxide phases grown by PLD onto c-cut ((001) oriented) sapphire are studied. More specifically, the influence of substrates temperatures ranging from room temperature (RT) to 600°C and partial oxygen pressures ranging from 10^{-5} to 10 Pa are investigated. Our aim is to define the experimental growth conditions allowing the formation a single-phase film (oxide or metallic) Fe- on c-cut sapphire substrates. In this respect, a particular attention is paid to the stability domain (pressure, temperature) of wustite. In addition, we attempt to specify the experimental conditions leading to the formation mixed phases (i.e. metal/oxide composite). By means of two types of targets (Fe and α - Fe_2O_3), we evidence that the FeO phase can be grown at temperature below 575°C and that a nanocomposite film made of Fe and Fe_3O_4 can be produced with monitored experimental conditions.

Experimental

FeO_x films were deposited by PLD onto (001) c-cut sapphire single crystal substrates (Crystec GmbH). Two types of targets were used to grow iron oxide films with different O/Fe ratios : a metallic polycrystalline Fe (99.99%) target and a hot pressed ceramic α - Fe_2O_3 (99.9%) one. They were ablated by a frequency quadrupled Nd:YAG laser (266 nm) with a 10 ns pulse duration under a repetition rate of 10 Hz in the experimental set-ups described previously [13][14]. The laser beam irradiates the target under an incidence angle of 45° with a laser energy kept constant at 25 mJ

1 leading to a laser fluence of around 2.5 J/cm². The distance between the target and the substrate
 2 was fixed at 5 cm. the oxygen pressure during films growth is varied from 10⁻⁵ Pa (the vacuum limit)
 3 to 10 Pa, in order to modulate the oxygen content in films [15]. Films obtained by laser ablation of
 4 the α -Fe₂O₃ target were grown under vacuum at different substrate temperatures (RT, 200, 300,
 5 500, and 600°C) while the PLD of FeO_x films was obtained under the different oxygen pressures at
 6 RT and 500°C using the Fe target.

7 The determination of thickness and composition (O/Fe ratio) of films were obtained by
 8 Rutherford backscattering spectrometry (RBS) using the 2 MeV ion accelerator facilities of the
 9 Sorbonne Université (SAFIR). Due to the low RBS yield on light elements, the oxygen content of the
 10 films is determined with a 4% precision. The structural characterization of films was carried out by
 11 X-ray diffraction (XRD) experiments using an X-ray diffractometer (Bruker D8 Discover) with the
 12 CuK α radiation (λ =0.154 nm) in the Bragg Brentano condition for identifications of phases. In
 13 asymmetric geometry, pole figures and ϕ -scan measurements were performed to describe the
 14 texture and the epitaxial relationships between the films and the c-cut sapphire substrate [16].
 15 Scanning electron microscopy (SEM; Field Gun Zeiss Supra 40) was used to obtain information on
 16 the surface morphology of films. The images were obtained by collecting the secondary electrons
 17 with an in-lens detector and a working distance of 3.5 to 4.5 mm under a voltage of 3.0 to 4.0 kV.

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20 Results and Discussion

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22 The experimental growth conditions, the structural properties and the composition of the
 23 two sets of iron oxide films are presented below according to the target used (α -Fe₂O₃ and Fe).
 24 Tables 1 and 2 summarize the results obtained for FeO_x films grown from α -Fe₂O₃ and Fe targets,
 25 respectively.

26

27 Table 1 : composition and structural properties of FeO_x films obtained by laser ablation of a α -Fe₂O₃
 28 target under 10⁻⁵ Pa at different temperatures.

29

Target	Substrate temp. (°C)	RBS O/Fe	XRD Phases	XRD 2 θ (°) Fe ₃ O ₄ (111)	a-axis parameter Fe ₃ O ₄ (nm)	XRD 2 θ (°) FeO (111)	a-axis parameter FeO (nm)
Fe ₂ O ₃	RT	1.33	Fe ₃ O ₄ , FeO	17.94	0.855	36.37	0.427
	200	1.23	Fe ₃ O ₄ , FeO	18.24	0.842	36.35	0.428
	350	1.18	Fe ₃ O ₄ , FeO	18.32	0.839	36.18	0.429
	500	1.15	Fe ₃ O ₄ , FeO	18.32	0.839	36.18	0.429
	600	1.15	Fe ₃ O ₄ , FeO	18.36	0.836	36.18	0.429

30

31 Table 2 : composition and structural properties of FeO_x films obtained by laser ablation of a Fe
 32 target
 33 at RT and 500°C under 3 oxygen pressures (the hematite phase is not taken into account in this
 34 table)

35

Target	O ₂ pressure (Pa)	RBS O/Fe	XRD Phases	XRD 2 θ (°) Fe (110)	a-axis parameter α -Fe (nm)
Fe	10 @RT	1.69	Fe ₃ O ₄	-	-
	10 ⁻¹ @RT	1.38	Fe ₃ O ₄ , Fe	44.69	0.286
	10 ⁻⁴ @RT	0	Fe	44.53	0.287

10 @500°C	1.56	α -Fe ₂ O ₃ , Fe ₃ O ₄	-	-
10 ⁻¹ @500°C	1.47	α -Fe ₂ O ₃ , Fe	44.63	0.286
10 ⁻⁴ @500°C	0.02	Fe	44.69	0.286

a) α -Fe₂O₃ ceramic target

To optimize the formation of the FeO suboxide phase with an O-rich target, one must limit the incorporation of oxygen coming from the surrounding gas and impinging onto the substrate surface during the PLD growth. FeO_x thin films have therefore been grown at RT, 200, 350, 500 and 600°C in vacuum limit conditions (10⁻⁵ Pa). Since the wustite phase in bulk form is stable above 575°C, moderate substrate temperatures have been applied to check the possible formation of this phase even at lower temperatures. Whatever the growth temperatures, films are dense and smooth, as observed on Fig. 1A which shows a typical SEM top view image of the film grown at RT with only few droplets.

The thickness of this film is around 200 nm for a deposition time of 2h leading to an average deposition rate of 2.5x10⁻³ nm/pulse. Such film is very smooth, and according to the SEM cross-section image (Fig. 1b), a columnar growth can be observed.

RBS spectra of our films (not shown here) evidence a uniform in-depth distribution of O and Fe elements. The O/Fe ratios deduced from these spectra (Table 1) range from 1.33 at RT to 1.15 at 600°C. These ratios are slightly greater than unity. The O/Fe ratio of pure magnetite is 1.33. For wustite let us remind that from a thermodynamical point of view, this phase is never matched the stoichiometry since the O/Fe ratio is in the range of 1.06 - 1.20 for bulk material [17], depending on the temperature. The obtained values at high temperatures (above 350°C) indicate that the O-content is of same order than the one expected for a FeO film. At low temperatures (below 300°C) the O-contents are not in agreement with a pure wustite film, and the formation of magnetite is required to reach the obtained O/Fe ratios (>1.20). It is also worth noticing that the O/Fe ratio decreases as the substrate temperature increases : at RT, the O/Fe (1.33) would indicate that the film is only constituted by the Fe₃O₄ phase while at 600°C the O/Fe ratio (1.15) would be consistent with the single phase FeO. In addition, the XRD diagrams show that the crystallized part of films is constituted by a mixture of Fe₃O₄ and FeO; a higher content of crystallized Fe₃O₄ phase being qualitatively observed at 600°C. An explanation for the decrease of the O/Fe ratio with the increasing of the temperature could be hypothesized with the presence of amorphous or poorly crystallized oxide phases in the films, such as iron hydroxides. Moreover, as amorphous phases cannot be evidenced by XRD, it should not be excluded that amorphous iron hydroxide matter could be present in films, particularly for those grown at RT. Indeed, at low temperature, water molecules from residual air moisture present in the chamber could be incorporated in the film. Although the PLD chamber is pumped under high vacuum, this phenomenon can occur as it has already been suggested by Beena et al. for In₂O₃ PLD films grown under vacuum [18]. A highest growth temperature (600°C) makes difficult the formation of hydroxides since the residual moisture in the chamber is negligible. This preferred formation of iron hydroxides may explain the higher value of O/Fe observed for FeO_x films obtained at RT. In summary, the obtained compositions indicate that the iron oxide films would be made of a mixture of Fe-O phases.

The $\theta/2\theta$ XRD diagrams recorded on FeO_x films grown under vacuum are presented in Fig. 2a.

For any substrate temperature, the magnetite (ICCD file : 01-071-6336) and the wustite (ICCD file : 00-006-0615) phases are present. Both FeO and Fe₃O₄ crystallites in these composite films are textured along the [111] direction perpendicular to the (001) sapphire basal plane. The a-axis

1 parameters of the magnetite and the wustite deduced from the peak position of the (111)
2 diffraction line, are given in the Table 1. For the Fe₃O₄ film grown at 600°C, the “a” parameter is
3 similar to the value of bulk magnetite (0.837 nm). The same “a” parameter increases with the
4 decrease of the temperature, indicating that tensile stresses occur during growths at low
5 temperatures. On the contrary, the a-axis parameter of the wustite ranges from 0.427 nm at RT to
6 0.429 nm at 600°C. Those values are lower than the bulk one (0.431 nm). The narrowing of the “a”
7 parameter indicates a compression of the FeO unit cell. It is important to note that FeO is formed
8 even at RT and its crystallization is improved by the increase of the temperature, as attested by the
9 decrease of the diffraction peak width.

10 The possible epitaxial relationships of the Fe₃O₄ and FeO crystallites on the c-cut substrate
11 have been studied by pole figure measurements. Fig 2b (left part) shows the pole figures of the
12 (200) wustite diffraction line recorded at 2θ = 42.5° for the FeO_x film obtained at RT. Six well-defined
13 poles are present at the tilting angle ψ = 54.7°, the expected value for the (111) texture of wustite
14 crystallites. Similarly, the pole figure, recorded on the (220) Fe₃O₄ reflection at 2θ = 29.8° also
15 shows 6 poles with hexagonal symmetry at ψ = 35.2°, in agreement with the 111 Fe₃O₄ texture (Fig.
16 2b, right part). Finally, the following epitaxial relationships could be inferred from the two phases :

17
18 Magnetite : (111) Fe₃O₄ // (002) Al₂O₃ and [10-1] Fe₃O₄ // [210] Al₂O₃ (30° rotation) (I)

19
20 Wustite : (111) FeO // (002) Al₂O₃ and [10-1] FeO // [210] Al₂O₃ (30° rotation) (II)

21
22 These relationships imply a 30° rotation of the hexagons of the (111) FeO and (111) Fe₃O₄
23 planes with respect to the hexagonal (001) basal plane of the c-cut sapphire substrate.

24 Regarding the Fe₃O₄ crystallites, such in-plane epitaxial relationships (I) with a “30° rotation”
25 have already been reported for Zn_{1-x}Fe_xO films grown by PLD under vacuum at 500°C on c-cut
26 sapphire [19][20]. These (111)-oriented Fe₃O₄ films are the result of a particular growth induced by
27 the c-cut sapphire substrate used. Indeed, it has been observed that magnetite films grown by PLD
28 under 10⁻³ Pa oxygen pressure at 350°C onto Si (100) substrate are polycrystalline, exhibiting a
29 (311)-preferred orientation [1]. On the contrary, the use of fused quartz substrate leads to the
30 predominant (110) texture for the magnetite thin films obtained by PLD after annealing at 10⁻⁴ Pa at
31 500°C [11]. The growth of 111- textured magnetite film on c-cut sapphire by PLD has already been
32 observed recently by Malikov et al. [21] at moderate substrate temperature (300 - 500°C) under 10⁻³
33 Pa. Regarding the growth of FeO crystallites on c-cut sapphire substrate, the epitaxial relationships
34 (II) evidenced here have not been reported elsewhere. The origin of the epitaxy of (111) FeO onto
35 (002) Al₂O₃ can be found in the electrostatic interactions between these planes since (002) Al₂O₃
36 and (111) FeO are both polar (i.e. constituted either by cations or anions).

37 We show here that the growth of FeO-based films is obtained below 575°C by ablating a α-
38 Fe₂O₃ target under high vacuum, but the wustite is always present with the Fe₃O₄ phase. Films
39 constituted by a mixture of 2 phases FeO and Fe₃O₄ are classically grown for a substrate
40 temperature greater than 600°C [22], and the growth of « pure » FeO film may be obtained by
41 doping the target (for example by Si or In [23]) to stabilize the wustite phase. Below 600°C, the FeO_x
42 films are generally mixed with the magnetite phase [1][24], but the presence of wustite in film
43 grown below 600°C has not been yet reported. As determined by asymmetric diffraction, our films
44 are also found to be epitaxied on the c-cut sapphire substrate even at RT.

45
46 **b) Fe metallic target**

1 The use of a non-oxide target, which avoids the incorporation of oxygen coming from the
2 ablated material, allows to expect the formation of low valence state (i.e. Fe²⁺) oxide in films.
3 Indeed, the flux of oxygen species impinging onto the substrate during the growth is easily
4 controlled by the oxygen pressure in the PLD chamber. That is the reason why a Fe metallic target
5 was used. Oxygen incorporation in films results from interactions between the plasma plume and its
6 surrounding gas. In order to modulate the O-content in films, 3 different oxygen pressures have
7 therefore been applied during the growth : 10⁻⁴ , 10⁻¹ and 10 Pa. In addition, the growth of films has
8 been performed at substrate temperatures of 25°C (RT) and 500°C. The main drawback related to
9 the use of a metallic target is the unsuitable formation of droplets due to the thermal effects, which
10 is more important than for a ceramic (oxide) target. By reducing the laser fluence, it is possible to
11 obtain Fe-based films with a very limited content of droplets. Fig 3 shows typical SEM top view of
12 films depending on the growth conditions. Besides some visible droplets, films are relatively
13 smooth, especially at RT under 10⁻⁴ Pa. By increasing both the pressure and the substrate
14 temperature, a granular morphology is revealed, and some cracks appear on the surface.

15 At higher pressures (10¹ Pa), elongated needle-shaped crystallites are formed. The formation
16 of faceted crystallites and the increase of surface roughness of films with the pressure is a well-
17 known feature, already described since a long time for PLD films [25][26].

18 RBS analysis has been performed on the obtained films. The O/Fe ratios deduced from the
19 spectra (not shown here) are presented in the Table 2. At RT and 10⁻⁴ Pa, the oxygen in the film is
20 not detected, meaning that the film is mostly constituted by metallic Fe. At higher temperature
21 (500°C) and at the same pressure, the O/Fe ratio is found to be around 0.01, indicating a weak
22 incorporation of oxygen in the film. At higher pressures (10⁻¹, 10 Pa), the O/Fe ratio is ranging from
23 1.3 to 1.7, in agreement with the formation of an oxide-based film, and it can be noticed that these
24 ratios are higher than expected for a pure FeO film. From the RBS spectra, it is also possible to get a
25 rough estimation of the number of Fe atoms/cm² impinging onto the substrate during the growth at
26 each laser pulse, considering that all Fe atoms coming from the plasma plume are stucked on the
27 substrate without any losses. In the case of films grown at 500°C, the obtained values of the number
28 of iron atoms N_{Fe} are 2.4x10¹³, 1.1x10¹³, and 0.5x10¹³ at cm⁻² pulse⁻¹ for the three oxygen pressures
29 10⁻⁴, 10⁻¹ and 10 Pa, respectively. The oxygen incorporated in the film is only coming from the
30 background gas since a metallic target is used. By considering the kinetic theory of gas and
31 assuming that O₂ would be an ideal gas, a rough estimation of the number density N_{O2} of oxygen
32 molecules arriving on the substrate is :

$$N_{O_2} = N_a (P\Delta t/RT)(3RT/M_{O_2})^{1/2}$$

34
35 with N_a=6.02x10²³ at mol⁻¹, R=8.31 J K⁻¹ mol⁻¹, M_{O2}=32 g mol⁻¹, T=773K, and Δt=1 μs. Δt is the
36 approximate time during which the ablated species are transferred from the target to the substrate
37 for a typical target to substrate distance of 5 cm [27]. This relationship leads to N_{O2} values of
38 7.3x10¹², 7.3x10¹⁵, and 7.3x10¹⁷ molecule cm⁻²pulse⁻¹ at pressures P of 10⁻⁴, 10⁻¹ and 10 Pa,
39 respectively. By comparing N_{Fe} with N_{O2}, one figures that oxygen pressures above 10⁻¹ Pa induce a
40 higher oxygen flux than that of the iron one which leads to formation of oxide phases in the films, as
41 observed experimentally.

42 The θ/2θ XRD diagrams confirm the incorporation of oxygen at elevated pressures and allow
43 to determine the nature of phases. On XRD patterns depicted in Fig 4, different phases can be
44 identified : metal iron α-Fe cubic phase (ICCD file : 00-006-0615), magnetite (ICCD file : 01-071-
45 6336) and hematite α-Fe₂O₃ (ICCD file : 00-033-0664), depending on the temperature and the
46 oxygen pressure. At RT, under vacuum, a pure Fe film is obtained. However, with an increasing of
47 the pressure, i.e. at 10 Pa, the film is oxidized in magnetite. For the higher temperature (500°C) and

1 above 10^{-1} Pa, films are composed of the α -Fe, Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ phases leading to a metal-oxide
 2 composite. At 10 Pa, metal Fe does not exist anymore, and the film is only constituted by a mixture
 3 of the magnetite and hematite $\alpha\text{-Fe}_2\text{O}_3$ phases. At low pressure (10^{-4} Pa), only metal iron is
 4 observed, in agreement with RBS analyses. The growth by PLD of pure $\alpha\text{-Fe}$ films with a 110-
 5 texturation on c-cut sapphire has already been documented in the literature: by laser ablation of a
 6 Fe target, De La Cruz et al. [28] observed such texturation by growing films at RT under vacuum.
 7 Nevertheless, according to their experiments, for substrate temperatures above 450°C , the 200-
 8 texturation takes place. This is not in agreement with our results for which the 200-orientation of α -
 9 Fe crystallites is not evidenced. Finally, it is important to note that the wustite phase is not present
 10 whatever the experimental conditions used, while a metal-oxide composite may be obtained under
 11 around 10^{-1} Pa.

12 Regarding the intensity of the peaks and their full width at half maximum (FWHM), the $\alpha\text{-Fe}$
 13 phase is more crystalline than the oxide ones. A strong 110-texturation of the Fe crystallites is
 14 observed for films grown under 10^{-4} and 10^{-1} Pa regardless of the temperature. Specifically, a "pure"
 15 Fe film is obtained under vacuum and present a 110 texturation of iron crystallites. To check the
 16 angular distribution of the Fe crystallites along the [110] direction, ω -scans have been recorded on
 17 the 110 Fe reflection for films grown under vacuum at RT and 500°C , for a fixed 2θ position at
 18 44.53° and 44.69° , respectively. The corresponding rocking curves are given on Fig. 5 : the FWHM of
 19 the peaks are 0.94° and 0.37° , respectively. These low values indicate a good mosaicity of films, the
 20 structural disorder being more important at low growth temperature (RT) as it is classically
 21 observed in PLD films.

22 On the contrary, different orientations can be noticed for the magnetite, and at RT under 10^{-1}
 23 Pa it is possible to grow a composite film constituted by both 110-textured $\alpha\text{-Fe}$ and 111-oriented
 24 Fe_3O_4 . Pole figure measurements were realized on these two phases : the same angular positions
 25 ($2\theta = 29.8^\circ$, $\psi = 35.2^\circ$) lead to a pole figure for the 220 Fe_3O_4 diffraction line exhibiting the 6-fold
 26 symmetry already observed for films obtained by laser ablation of $\alpha\text{-Fe}_2\text{O}_3$ target (see paragraph
 27 "a"). To check the possible in-plane relationships of the 110-textured Fe film, a pole figure was
 28 performed on the "pure" Fe film grown at 500°C under vacuum (Fig. 6a).
 29

30 The pole figure depicted on Fig 6a) shows 6 well-defined poles at declination angle $\psi = 45^\circ$.
 31 The 6 observed poles could agree with a hexagonal symmetry, but in fact, due to the rectangular
 32 geometry of the (110) Fe plane involving a 2-fold symmetry, they correspond to 3 sets of 2 poles
 33 induced by the 3-fold symmetry of the rhombohedral Al_2O_3 basal plane. It may be found that the
 34 relationships reads:
 35

36 Out-of-plane : $(110) \text{Fe} // (002) \text{Al}_2\text{O}_3$
 37 In-plane : $[-110] \text{Fe} // [210] \text{Al}_2\text{O}_3$ and $[001] \text{Fe} // [010] \text{Al}_2\text{O}_3$
 38

39 This relationships between the Fe film and the (001) Al_2O_3 does not correspond to a
 40 "hexagon on hexagon" epitaxy as it has been observed for FeO and Fe_3O_4 grown on c-cut sapphire.
 41 This is also not the classical "cube on cube" epitaxy observed for Fe film grown on (100) MgO
 42 substrate which are defined as : $(100) \text{Fe} // (100) \text{MgO}$ and $[011] \text{FeO} // [110] \text{MgO}$ [29]. Despite
 43 that 110-oriented Fe films grown on c-cut substrate have already been identified [28], the in-plane
 44 epitaxial relationship of such films has never been reported previously.

45 With this result, we may suggest a schematic view of the interface Film/Substrate based on
 46 the crystallographic directions involved in the epitaxy of (110) Fe film on (001) Al_2O_3 substrate (Fig.
 47 6b). The observed "rectangle on hexagon" epitaxy is based on a good film/substrate mismatch

1 which can be described by the domain matching epitaxy (DME) approach [30]. The DME is based on
2 the coincidence between “m” and “p” lattice units of the substrate and the film, respectively. The
3 “m” and “p” values satisfy the following relation : $m \times d_s = p \times d_f$ with d_s and d_f being the respective
4 distance between atoms (ions) in the substrate and the film on parallel directions. Thus :

5 - For $[-110] \text{ Fe} // [210] \text{ Al}_2\text{O}_3$, it is found $m=1$ and $p=2$ leading to a lattice mismatch of 1.70%
6 and to an epitaxial domain size of 0.8 nm

7 - For $[001] \text{ Fe} // [010] \text{ Al}_2\text{O}_3$, it is found $m=3$ and $p=5$ leading to a lattice mismatch of 0.14%
8 and to an epitaxial domain size of 1.4 nm

9 It is important to note that the use of a Fe target does not allow to obtain the wustite phase
10 whatever the oxygen pressure, at RT or 500°C. The formation of FeO-based film under vacuum is
11 effective by using a $\alpha\text{-Fe}_2\text{O}_3$ target. On the contrary, the laser ablation of a Fe target only leads to
12 the growth of an iron film or a metal-oxide Fe/Fe₃O₄ film depending on the oxygen pressure. This
13 difference would indicate that the formation and the stabilization of FeO find its origin in the path
14 related to the oxygen species arriving onto the substrate surface. The following hypotheses could be
15 suggested:

16 - Using Fe target : oxygen species allowing the oxidation are O₂ molecules coming from the
17 gas. The formation of FeO_x film is mainly due to the thermal oxidation of Fe on the substrate which
18 is not in favor of FeO formation.

19 - Using $\alpha\text{-Fe}_2\text{O}_3$ target : a great part of the oxygen incorporated in the film is due to various
20 species (oxygen atoms, ions, excited) coming from the target and present in the plasma during the
21 plume expansion. The high reactivity of these O species would enhance the formation of the
22 metastable wustite phase.

23

24

25 **Conclusions**

26

27 The different phases $\alpha\text{-Fe}$, Fe_{1-x}O, Fe₃O₄ , and $\alpha\text{-Fe}_2\text{O}_3$ of the Fe-O system have been
28 obtained by PLD on c-cut sapphire. The presence of these phases depends on the substrate
29 temperature and the oxygen pressure, as it has largely been reported in the literature.
30 Nevertheless, the nature of the target used for the ablation also plays a crucial role on the relative
31 stability of the Fe-O phases, in addition to the substrate temperature and the oxygen partial
32 pressure. Two major results are reported :

33 - A wustite-based film is only observed by using a $\alpha\text{-Fe}_2\text{O}_3$ target at moderated substrate
34 temperature (below 600°C) under high vacuum (below 10⁻⁴ Pa). Irrespectively from the substrate
35 temperature (RT to 600°C), thin films constituted by a mixture of the wustite and Fe₃O₄ are formed.
36 Below the temperature of thermodynamical stability of wustite (575°C), the wustite phase is always
37 observed, even at RT. However, it cannot be grown without magnetite. These oxide composite films
38 show noticeable crystallographic features : both FeO and Fe₃O₄ phases are 111-textured and show
39 very well-defined epitaxial relationships with the (002) Al₂O₃ basal plane.

40 - A metal/oxide composite film constituted by a mixture of $\alpha\text{-Fe}$ and Fe₃O₄ can be formed at
41 RT or 500°C, under intermediate pressure range (roughly around 10⁻¹ Pa), when using a Fe target.
42 The magnetite and the iron crystallites are (111) and (110) oriented, respectively. Both phases show
43 in-plane epitaxial relationships with c-cut sapphire. Under 10⁻⁴ Pa, a pure $\alpha\text{-Fe}$ 110-oriented film is
44 obtained at RT or 500°C. The in-plane epitaxial relationships between the $\alpha\text{-Fe}$ (110) crystallites and
45 the c-cut sapphire substrate have been studied in detail and are found to be : $[-110] \text{ Fe} //$
46 $[210] \text{ Al}_2\text{O}_3$ and $[001] \text{ Fe} // [010] \text{ Al}_2\text{O}_3$

1 Such epitaxy which has not been reported previously, can be correctly described by the
2 domain matching epitaxy approach. Works are now in progress to investigate by HRTEM and STEM
3 techniques the microstructural properties of composite films (the iron metal-wustite and the
4 magnetite-wustite films) to highlight the orientations of crystallites inside the nanocomposite film.

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11
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1 **Figure captions**

2

3 Fig 1 : SEM top view (a) and cross section (b) of the FeO_x film grown at RT under 10⁻⁵ Pa from laser
4 ablation of a α-Fe₂O₃ target

5

6 Fig. 2 : FeO_x films grown under vacuum by laser ablation of a αFe₂O₃ target.

7 a) θ/2θ XRD patterns of films grown at different temperatures (the (006) Al₂O₃ peak located
8 at 2θ= 41.68° corresponding to the c-cut sapphire substrate was removed).

9 b) Pole figures of the film grown at RT, recorded on the (200) FeO and (220) Fe₃O₄ diffraction
10 lines at 2θ = 42.5° and 29.8°, respectively.

11

12 Fig 3 : SEM top view of the FeO_x films grown at RT (left) and 500°C (right) under 10, 10⁻¹ and 10⁻⁴ Pa
13 oxygen pressures by laser ablation of a Fe target

14

15 Fig. 4 : θ/2θ XRD patterns of FeO_x films grown at RT (left) and 500°C (right) under different oxygen
16 pressures by laser ablation of a Fe target

17

18 Fig. 5 : ω-scan recorded on the (110) Fe reflection of films grown at RT (left) and 500°C (right) under
19 vacuum (10⁻⁴ Pa) by laser ablation of a Fe target. The 2θ angular position was fixed at 44.52°
20 and 44.65°, respectively.

21

22 Fig. 6 : a) Pole figure recorded on the (200) Fe reflection at 2θ = 65° for a Fe film grown at 500°C
23 under 10⁻⁴ Pa by laser ablation of a Fe target

24 b) Schematic view of the interface showing the matching between (110) Fe and (002) Al₂O₃
25 planes

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Fig. 1

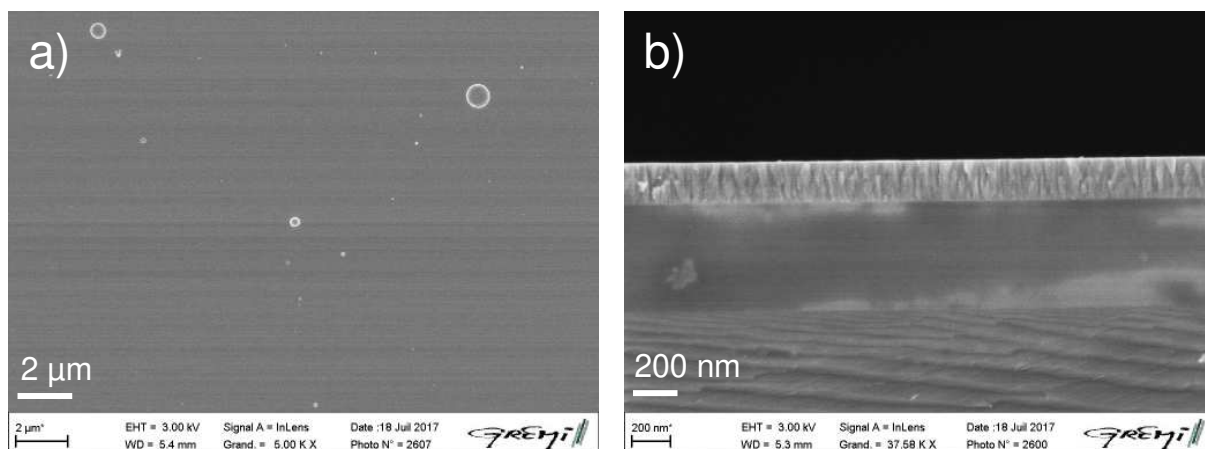
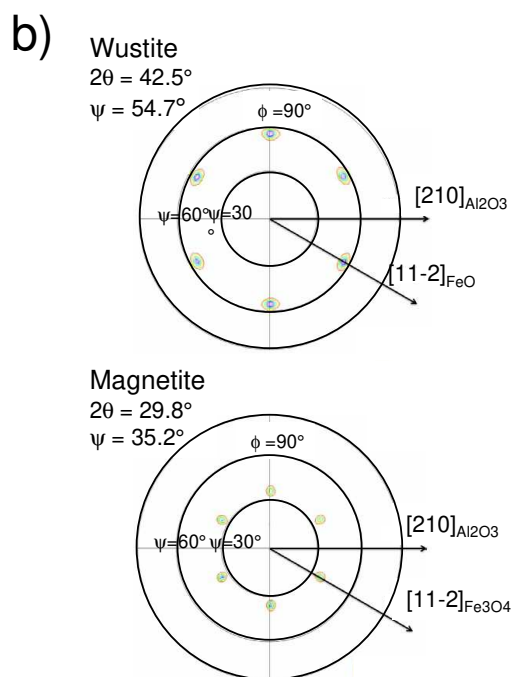
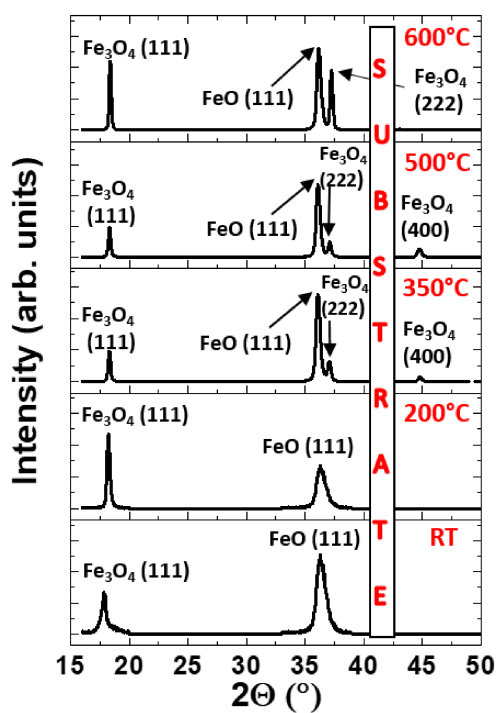
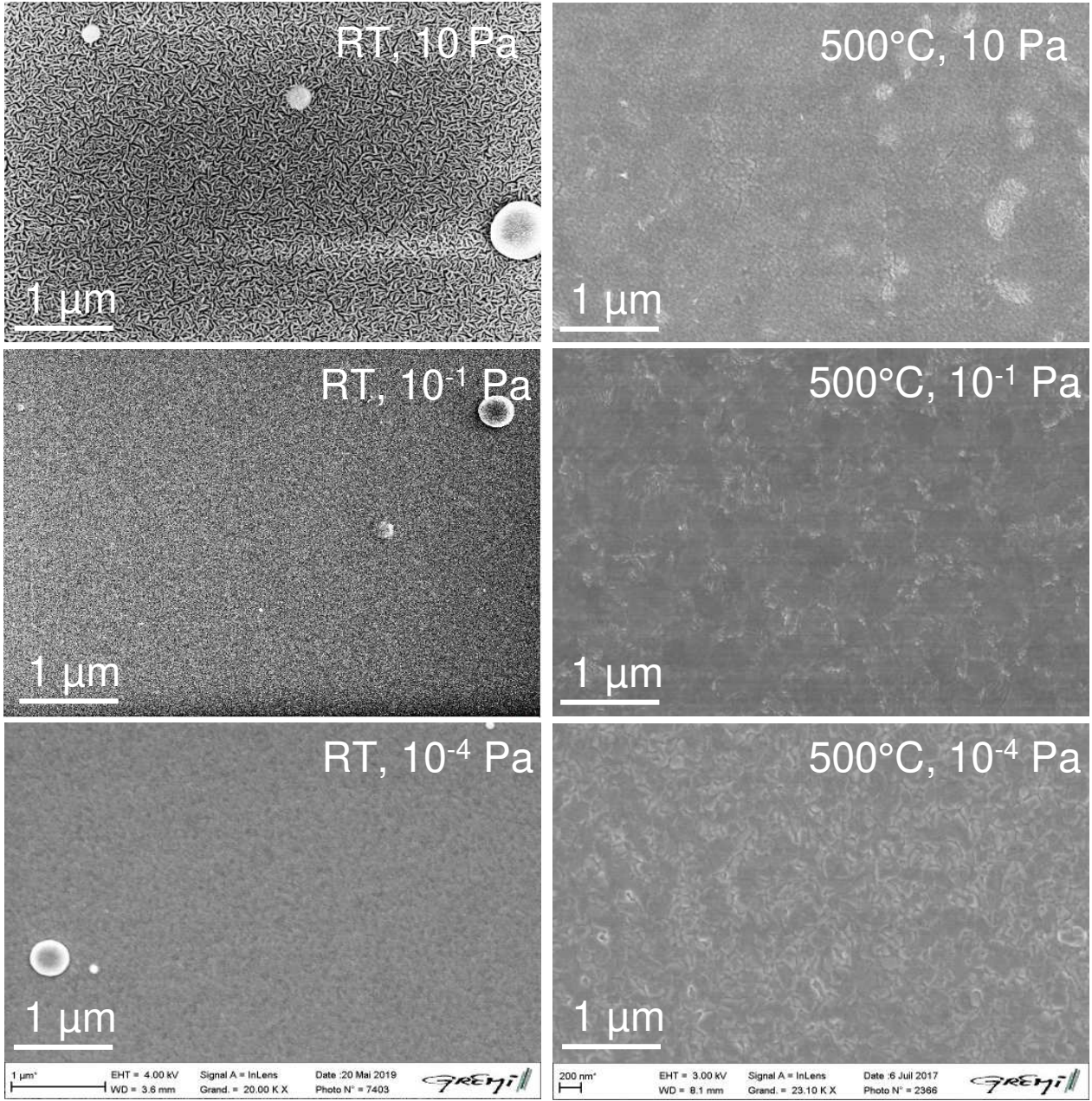


Fig. 2

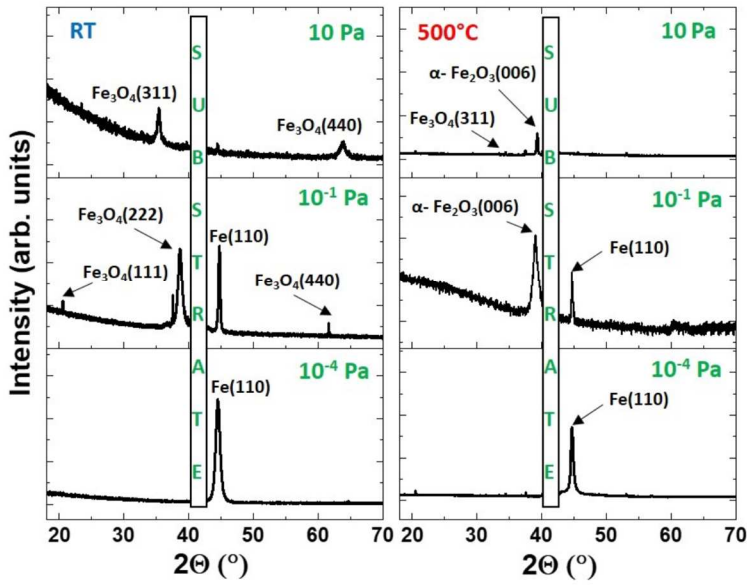


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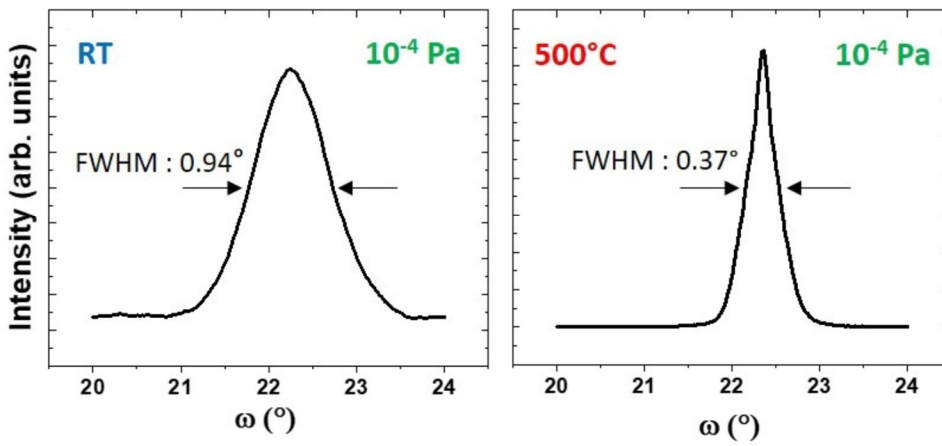
Fig. 3



1 Fig.4



17 Fig.5



33 Fig.6

