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Room temperature epitaxial growth of Zn-doped iron oxide films on c-, a- and r-cut sapphire substrates

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KEYWORDS: Oxide thin film. Room-temperature epitaxy. Van der Waals Epitaxy.
Graphoepitaxy. Pulsed laser deposition.

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4 ABSTRACT. The room temperature growth of zinc-doped iron oxide films (Zn:FeO_x) was studied
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7 on c-cut, a-cut and r-cut sapphire substrates using the pulsed-laser deposition method. Rutherford
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9 backscattering spectrometry, X-ray diffraction analysis, pole figure measurements and
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11 transmission electron microscopy were used to determine the nature of the oxide phases (wüstite
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13 and/or spinel) present in the films, their precise texture and in-plane epitaxial relationships between
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15 films and substrates. On c-cut sapphire, both wüstite and spinel phases were present with a (111)
16
17 texture. The wüstite phase was mainly found at the film-substrate interface, while the spinel was
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19 observed in the upper part of the film. On the a-cut and r-cut substrates, the main phase observed
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21 was the wüstite, with a very small spinel contribution. The (111) and (100) wüstite textures were
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23 obtained on the a-cut and r-cut substrates, respectively. The in-plane epitaxial relationships
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25 between the Zn doped iron oxide phases and the substrates were deduced from transmission
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27 electron spectroscopy observations and pole figure measurements. The possible mechanisms of
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29 the room temperature epitaxial growth of the oxide films on r-cut and a-cut sapphire substrates are
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31 presented and discussed.
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38 **Introduction**

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41 As it has been largely demonstrated in literature, the epitaxy of oxide thin films on single
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43 crystalline substrates usually requires high temperature during the growth ¹⁻⁵. However, for a lot
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45 of industrial applications based on such epitaxial films, it would be necessary to reduce the growth
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47 temperature to avoid atomic interdiffusion between film and substrate, and consequently to
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49 significantly reduce the fabrication cost ⁶. In this framework, research activities have been carried
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51 out to study room temperature (RT) epitaxial growth of oxide films like NiO ^{7,8}, Fe₃O₄ ⁹, V₂O₃ ¹⁰,
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53 CoO and Co₃O₄ ¹¹, and other oxides ¹²⁻¹⁴. In most of these works, the RT epitaxial oxide films
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3 were grown on atomically stepped single crystal sapphire (001) substrates by using the pulsed-laser
4 deposition (PLD) method ⁷⁻¹⁴. Such stepped c-cut sapphire substrates are obtained by a thermal
5 annealing process at high T (1000°C) for a few hours in air ^{15,16}. The surface steps play the role of
6 nucleation centers for the epitaxial growth of the film. On the other hand, PLD is used for the film
7 growth at RT owing to one of the specificities of this method, i.e. the high kinetic energy of the
8 species emitted by the target during laser irradiation. Indeed, such a high kinetic energy (about a
9 few 10th eV) ¹⁷ allows a high surface mobility for the species that leads to the formation of
10 crystalline material at relatively low temperature ^{18,19}.

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23 In addition to the RT epitaxial growth of oxide films on c-cut (001 oriented) sapphire
24 substrates, some other papers report the RT epitaxy of oxide films on single crystal substrates like
25 MgO ²⁰, SrTiO₃ ²¹, bare Si ²²⁻²⁴ or Si covered by a buffer layer ²⁵. However, some other single
26 crystal substrates like a-cut ((110) oriented) and r-cut ((102) oriented) sapphire substrates are
27 currently used for the epitaxial growth of various oxide films ²⁶⁻³¹ with a view of specific
28 applications ³²⁻³⁴. To our knowledge, the RT epitaxy of oxide films on such a-cut and r-cut sapphire
29 substrates has never been reported.

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32 In this frame, we have studied the growth by PLD at RT of Zn-doped iron oxide on a-cut
33 and r-cut sapphire substrates. For comparison purpose, ZFO films were also grown on a c-cut
34 substrate, but more complex results obtained with this substrate will be published later in a
35 forthcoming paper. Owing to the experimental PLD conditions used, two iron oxide-based phases
36 are obtained: the Zn-doped wüstite phase Zn:FeO that will be noted "ZFO_w" in the following and
37 the Zn-doped Zn:Fe₃O₄ spinel magnetite phase (noted "ZFO_s"). More precisely, Zn_{1-x}Fe_xO films
38 with (0 < x < 1) can be grown by PLD: following previous work³⁵, the Zn:Fe₃O₄ phase is obtained
39 for 0.65 < x < 1. We have chosen a Zn concentration fixed at around 25% at. (x = 0.75) to avoid the

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3 formation of the wurtzite phase. In addition, the presence of Zn in the iron oxide phases should
4 promote the growth the wüstite phase even at low temperature ($T < 500^{\circ}\text{C}$) as evidenced by Sano
5 et al.³⁶. We present here a detailed structural study of these phases deposited at RT on the various
6 sapphire substrates: growth, textures and epitaxial relationships between these compounds and the
7 different substrates are discussed. Such films could be of interest due to their magnetic properties
8 since wüstite-based films are expected to be antiferromagnetic while magnetite-based films should
9 be ferrimagnetic. These properties would permit the development of magnetite-based storage or
10 spintronics devices^{37,38}, while wüstite could be used as a transparent p-type conductors³⁹ or for
11 magneto-resistance enhancement⁴⁰. However, these interesting physical properties are not the
12 subject of this paper which is devoted to the detailed study of the structural properties of these
13 films.
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30 In our work, in contrary to the common high T annealing of the substrates before the film
31 growth, all the c-, a- and r-cut sapphire substrates were not submitted to a thermal treatment at
32 high T before the growth. Despite this point, we obtained the epitaxial growth at RT of the Zn-
33 doped wüstite (ZFO_w , space group $Fm-3m$) and/or spinel (ZFO_s , $Fd-3m$) phases in the films.
34 Different textures were obtained for these phases on the following type of substrates, i.e. (111) for
35 the c-cut and a-cut sapphire, and (001) for the r-cut one. Well-defined epitaxial relationships were
36 found between films and substrates, and they have been described in the frame of the “domain
37 matching epitaxy” (DME)^{41–44}. The different textures observed depending on the substrates, could
38 be explained either by (i) the graphoepitaxy related to the presence of steps and terraces on the c-
39 cut and a-cut substrates^{44–46}, (ii) a “quasi van der Waals epitaxy” related to the polar nature of the
40 c-cut and a-cut substrate plane and/or film plane^{47–50}, and (iii) an epitaxy related to a low lattice
41 mismatch between the film and substrate in the case of the r-cut sapphire substrate.
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Experimental section

The Zn-doped iron oxide films were grown by PLD onto c-cut, a-cut and r-cut sapphire substrates at RT in vacuum. The substrates furnished by CrysTec GmbH were not annealed at high T before the growth. A frequency quadrupled Nd-doped yttrium aluminum garnet (Nd:YAG) laser (266 nm, $\tau = 7$ ns) was used to ablate a Zn:Fe₃O₄ (Zn_{0.85}Fe_{2.15}O₄) target in the experimental set up already described elsewhere⁵¹. The PLD growth from a Zn:Fe₃O₄ target can lead to the formation of nanocomposite films^{52,53}, i.e. with the presence of the wüstite (Zn:FeO) and spinel (Zn:Fe₃O₄). In contrary to the spinel phase, which has been epitaxially grown at RT⁹, the wüstite phase has never been obtained in these conditions. In our work, we have tried to favor the growth conditions for the epitaxy of the wüstite phase at RT. Indeed, the difference in oxygen composition between the wüstite, [O]/[Fe] = 1.1, and the spinel, [O]/[Fe] = 1.33, means that the film must be grown under a low oxygen pressure. PLD allows oxygen incorporation in the oxide films to be controlled⁵⁴⁻⁵⁸. On one hand, the films on a-cut and r-cut substrates were thus grown under reducing conditions (residual vacuum: $2 \cdot 10^{-7}$ mbar), i.e. a priori the ideal conditions for the formation of the wüstite phase. On the other hand, the ZFO film on c-cut substrate was grown at $7 \cdot 10^{-6}$ mbar leading to the presence of both wüstite and spinel phase.

Atomic force microscopy (AFM) was used to study the surface topography of the bare substrates before the growth, using an AFM NT-MDT Ntegra instrument.

Rutherford backscattering spectrometry (RBS) using the 2.5 MeV ion accelerator (SAFIR) of the Sorbonne Université, allowed the film thickness and in-depth distribution of the elements to be determined. The spectra, not presented here, show that the Zn-doped iron oxide films are only constituted by Fe, Zn and O atoms, without the presence of any impurities. The precise

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3 concentration profile of the Zn, Fe and O elements has been obtained from the simulation of the
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5 RBS spectra by use of the RUMP simulation program and has allowed to deduce the [O]/[Fe] ratio
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7 in the films.
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11 X-ray diffraction (XRD) has been performed on a Bruker D8 Advance θ - 2θ diffractometer
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13 in modified Bragg-Brentano geometry, working with monochromatized Cu $K\alpha_1$ radiation ($\lambda =$
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15 1.5406 Å) and equipped with a LynxEye detector. The sample was rotated at a speed of 30 rpm
16
17 during measurement. Le Bail profile refinement using the Fullprof software⁵⁹ of the XRD patterns
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19 of ZFO films grown on a-cut and r-cut sapphires enabled to precise unambiguously whether ZFO_w
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21 and ZFO_s phases are both present and to estimate the cell parameters of these phases. For these
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23 refinements, the “zero”-shifts due to the sample positioning were first determined from the 2θ -
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25 shifts of the substrate Bragg peaks, and then fixed to enable the refinement of the cell parameters
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27 of the iron oxide phases. The texture of the films and the in-plane relationships with the substrate
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29 were investigated by pole figure measurements with the help of a Bruker D8 Discover
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31 diffractometer (Cu $K\alpha_{1,2}$ radiation).
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38 For transmission electron microscopy (TEM) observations, thin foils were thinned down
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40 to electron transparency by a focused ion beam (FIB) setup (Dual-beam FEI Helios nanolab 660)
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42 with an electron imaging resolution of 0.6 nm at 15 kV (Field emission gun (FEG)) and a FIB
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44 resolution of 2.54 nm at 30 kV. TEM experiments were performed using a double corrected cold
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46 FEG JEOL ARM 200F microscope, operated at 200 kV and equipped with a post column GATAN
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48 QUANTUM ER electron energy loss spectrometer (EELS). This microscope had also a scanning
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50 setup (STEM mode with dark and bright field detectors) allowing the electron beam to be
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52 monitored with a spatial resolution of about 0.078 nm. Altogether, STEM EELS experiments were
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3 then possible in order to obtain EELS spectra for a nanometer region, EELS profiles or even EELS
4 mapping. All digitized images and spectral data were processed using the commercial
5 Digitalmicrograph (GMS2) software from GATAN.
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14 Results

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17 Before the RT growth of ZFO films on the single crystal substrates, AFM images of the
18 surface of these substrates were registered. Figure 1 shows the surface morphology of the c-cut
19 (Fig. 1(a)), a-cut (Fig. 1(b)) and r-cut (Fig. 1(c)) sapphire substrates as furnished by CrysTec
20 GmbH.
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28 Both c-cut and a-cut sapphire substrates show not very well defined and very narrow steps
29 without terraces, while the surface of the r-cut sapphire does not show any steps or terraces but
30 only a few spikes. This work mainly aimed at checking the possible RT epitaxy of ZFO films on
31 a- and r-cut sapphire substrates. First, we have looked at the possible RT epitaxy of ZFO on a c-
32 cut substrate. Indeed, the RT epitaxy of Zn (25%at.) doped Fe₃O₄ has not been previously reported
33 on c-cut substrate. Therefore, the PLD growth of such a film on a c-cut substrate at RT under a
34 7x10⁻⁶ mbar oxygen pressure has been studied. Figure 2 reports the corresponding XRD pattern of
35 such film and shows first, a broad peak at about 18° related to the (111) spinel phase with refined
36 cell parameter $a_s = 0.8529 \pm 0.0005$ nm, i.e. higher than the expected theoretical value for undoped
37 Fe₃O₄ ($a = 0.83905$ nm, $Fd-3m$). Secondly, a broad asymmetric peak around 36° corresponding to
38 the superimposition of 222 spinel and the 111 wüstite Bragg reflections is observed. Despite the
39 low intensity of the 111 ZFO_w peak, the cell parameter is around $a_w = 0.43217 \pm 0.0005$ nm, a
40 value slightly higher than for the undoped FeO phase ($a = 0.4307$ nm, $Fm-3m$) (Table 1).
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Table 1. Composition determined by RBS and crystallographic features determined by XRD of ZFO films grown at RT on c-cut, a-cut and r-cut sapphires (W: wüstite, S: spinel). The values of [O]/[Fe] does not consider oxygen bound to zinc and are only related to oxygen associated to iron.

Substrate	Composition	[O]/[Fe]	a_w	a_s	Preferential orientation	FWHM RC
c-cut	$Zn_{0.24}Fe_{0.76}O_{1.15}$ ($Zn_{0.24}O_{0.24}$)($Fe_{0.76}O_{0.91}$)	1.19	0.43217 ± 0.005 nm	0.85289 ± 0.005 nm	(111) W (111) S	$\sim 1.8^\circ$
a-cut	$Zn_{0.23}Fe_{0.77}O_{1.12}$ ($Zn_{0.23}O_{0.23}$)($Fe_{0.77}O_{0.89}$)	1.15	0.43435 ± 0.005 nm	-	(111) W	$\sim 1.9^\circ$
r-cut	$Zn_{0.23}Fe_{0.77}O_{1.1}$ ($Zn_{0.23}O_{0.23}$)($Fe_{0.77}O_{0.87}$)	1.13	0.4317 ± 0.005 nm	0.8415 ± 0.005 nm	(100) W (100) S	4.7°

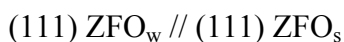
TEM analysis was led to precisely investigate the epitaxial growth of the ZFO film on c-cut sapphire substrate. Figure 3(a) shows a typical high resolution electron microscopy (HREM) image of a cross section of the film. The orientation of the sample is such that the electron beam is parallel to the [210] direction of Al_2O_3 sapphire (visible at the bottom of the image) and thus parallel to the film/substrate interface. In the upper region of the film, one can notice distinctly that we are dealing with a columnar growth with column widths of a few tens of nanometers whereas the bottom of the film appears more “uniform” without visible boundaries over a thickness of about 15 nm by contrast with the upper region.

By extracting and enlarging smaller regions from these parts of the film (shown in Fig. 3(b) for the rough images and 3(c) for the corresponding filtered images), an analysis of the lattice

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3 fringes through Fast Fourier Transforms (FFTs) allows establishing the structural characteristics
4 and then the corresponding phases. The FFTs presented in Fig. 3(d) reveal that the bottom part of
5 the film is consistent with a face centered cubic structure along a [-101] direction with a lattice
6 parameter of 0.43 nm. This agrees with the wüstite phase (FeO) doped with Zn (confirmed by
7 chemical analyses, not shown). The corresponding orientation relationships between sapphire and
8 ZFO_w are the following:
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25 As far as the upper region is concerned, the FFT of the enlarged image shows also a face
26 centered cubic structure but with a lattice parameter close to that of the spinel phase Fe₃O₄. Zn is
27 also present in the chemical composition of the compound and the orientation relationships
28 between wüstite and magnetite are:
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41 To confirm the presence of both phases, a spectroscopic analysis using EELS method has
42 been used. In Fig. 3(a), two spots are indicating the two pointed regions from which one obtained
43 the EELS spectra presented in Fig. 4.
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49 These spectra correspond to the L₂ and L₃ thresholds of Fe whose positions are indicative
50 of the valence state of Fe. A 1 eV displacement of the L₃ peak towards lower energies for the bottom
51 of the film is clearly meaning a decrease in the valence state of Fe and then consistent with the
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3 presence of the wüstite phase at the bottom of the film. Similar shift for these compounds has been
4 reported in previous works ⁶⁰. The presence of the wüstite phase is also in agreement with the
5 [O]/[Fe] ratio deduced from RBS measurements, the obtained values being between 1.13 and 1.19
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7 (Table 1).
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13 The XRD θ - 2θ patterns recorded on the ZFO films grown on the a- and r-cut substrates are
14 presented in Fig. 5. The data regarding the lattice parameters and the full width at half maximum
15 (FWHM) of the rocking curves are summarized in Table 1. The XRD pattern (Fig. 5(a)) recorded
16 for the film grown on the a-cut sapphire shows the presence of the 111 wüstite reflection at about
17 $2\theta = 35.75^\circ$. The 111 and 222 spinel peaks which would appear at 18° and 36.6° respectively, are
18 not observed in this pattern. Profile refinement using a single FeO phase leads to satisfying
19 modelisation of the observed peak and suggests that the film is constituted of a pure wüstite phase.
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30 In Fig. 5(b), the XRD pattern corresponding to the film grown on the r-cut substrate shows
31 a wide peak at about 41.75° . Best profile refinement is obtained by considering simultaneous
32 presence of 200 and 400 Bragg reflections of ZFO_w and ZFO_s phases, respectively, showing a
33 significant texture of these films. Due to the limited number of observed diffraction peaks, it is not
34 possible to retrieve the proportional distribution of each phase from the refinement.
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43 For the ZFO films grown on the a-cut substrate, the rocking curve (not shown here) of the
44 respective 111 reflection peaks is rather narrow, i.e. 1.9° , taking into account the RT growth. On
45 the contrary, for the ZFO film grown on the r-cut substrate, the value of the rocking curve of the
46 002 ZFO_w reflection was much more important, i.e. 4.7° . In this latter case, the crystalline quality
47 of the film is poorer. It must be noticed that in the case of the epitaxial growth of various oxide
48 films on r-cut sapphire substrate, the surface plane of the oxide film was tilted with respect to the
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(102) plane of sapphire. This phenomenon was observed for instance in the epitaxial growth of ZnO⁶¹, CeO₂⁶², MgO^{63,64} or Fe₃O₄⁶⁵. The tilt can be important, for example the (100) MgO may epitaxially grow on (102) Al₂O₃ with a tilt up to 5 or 6°, depending upon the growth temperature. From such results, it was concluded that the surface state of r-plane sapphire is an important factor leading to the tilted growth of the epilayer⁶³⁻⁶⁵. In our present case, it is not surprising that the epitaxial growth of ZFO on r-plane Al₂O₃ occurs at RT with a tilt of about 4.7°.

Figure 6(a) shows the results of the epitaxial relationships study between the wüstite phase and the a-cut substrate. The phi-scan performed on the {200} planes of the ZFO_w phase ($2\theta = 42.391^\circ$; $\psi = 56.22^\circ$) shows 6 peaks separated by 60°. In addition, phi-scan of the {104} planes of sapphire ($2\theta = 35.14^\circ$; $\psi = 57.55^\circ$) was also performed to deduce the crystalline orientations of the film with respect to the substrate. It shows 2 peaks separated by 180° and located at about 6.2° of the closest peak of the film. Figure 6(b) shows the pole figure recorded with the 200 ZFO_w reflection ($2\theta = 42.39^\circ$) for the same film grown on the a-cut substrate. This figure presents 6 well defined poles at ψ equal to 56.22°, in agreement with the phi-scan in Fig. 6(a). Some other poles from the substrate are also observed at: i) $\psi = 29^\circ$ corresponding to the 113 Al₂O₃ reflection (owing to the angle between (110) and (113) planes (28.78°) and the Bragg reflection of (113) plane: $2\theta = 43.36^\circ$) and ii) $\psi = 64^\circ$ corresponding to the -123 Al₂O₃ reflection (angle between (110) and (113) planes = 64.01° and $2\theta (-123) = 43.36^\circ$).

From the azimuthal positions of the respective peak/poles of ZFO_w and Al₂O₃, it is demonstrated that the epitaxial relationships on the a-cut sapphire substrate correspond to the superposition of the hexagons of the (111) ZFO_w plane on the rectangular lattice of the a-cut

sapphire, with a slight disorientation between the two lattices, as shown in Fig. 7(a). Given this pattern, no match can be observed between the two lattices.

Actually, the explanation of the epitaxial growth of ZFO_w on Al₂O₃ is in the frame of the domain matching epitaxy (DME), with m lattice units of the film matching with p lattice units of the substrate⁶⁴, as shown in figure 7(b). This figure presents the in-plane lattices of ZFO_w and sapphire which are superimposed considering the 6.2° of rotation between the (2-20) plane of ZFO_w and the (1-1-4) plane of the sapphire. The interception of these planes with the in-plane lattices (traces) corresponds to the traces of the (200) plane of ZFO_w and the (10-4) plane of the sapphire chosen to carry out the phi-scans measurement. It can be seen in figure 7(b) that there is a coincidence of sites between the two lattices leading to a matching domain forming a parallelogram. Since the Bravais lattice of the sapphire is hexagonal, it is not possible to easily determine the directions which correspond to the sides of this parallelogram. We have therefore described the epitaxial relationships between the two lattices by instead considering rather the planes which form the parallelogram, as follows:

Out-of-plane: (111) ZFO_w // (110) Al₂O₃

In-plane (I) (11-2) ZFO_w // (1-12) Al₂O₃

In-plane (II) (-871) ZFO_w // (1-1-4) Al₂O₃

In-plane (III) (3-1-2) ZFO_w // (1-1-1) Al₂O₃

Only the shortest side of the parallelogram corresponds to a perfect fit of m lattice units ($m = 5$ for ZFO_w and $p = 1$ for Al₂O₃). Therefore, lattice mismatches are determined by considering

the interatomic distances shown in figure 7(c). It appears that these distances are very close between the two lattices, corresponding to low mismatch values (cf. Table 2).

Table 2. Epitaxial relationships of Zn:FeO wüstite films grown at RT on a-cut and r-cut sapphires.

Substrate	Epitaxial relationships	Domain matching relationships		Lattice mismatch δ (%)	Domain size D (nm)
		m	p		
a-cut	(11-2) ZFO _w // (1-12) Al ₂ O ₃	5	1	1.2	1.52
	(-871) ZFO _w // (1-1-4) Al ₂ O ₃	-	-	-1.38	2.12
	(3-1-2) ZFO _w // (1-1-1) Al ₂ O ₃	-	-	-2.21	2.78
r-cut	[100] ZFO _w // [010] Al ₂ O ₃	11	10	-0.06	4.7
	[010] ZFO _w // [2-1-1] Al ₂ O ₃	6	5	-1.28	2.6

Figure 8(a) displays the phi-scans of the ZFO film grown on r-cut sapphire recorded by selecting the {111} planes. It shows 4 peaks separated by 90° and located for the closest one at about 45.5° of the (006) substrate plane. The corresponding pole figure is shown in Fig. 8(b). Similarly, the pole figure (Fig. 8(b)) for the ZFO film grown on the r-plane Al₂O₃ was also recorded. From the azimuthal positions of the peaks/poles, the following epitaxial relationships were deduced:



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3 Such orientation relationships correspond to the superposition of the square lattice plane
4 (001) of ZFO_w on the rectangular lattice of the (102) plane of Al_2O_3 substrate as shown in Fig.
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11 These two relationships lead in both case to rather large lattice mismatch, 9% for (I) and
12 15.6% for (II), respectively. Regarding the DME, as indicated in Table 2, a coincidence for relation
13 (I) is obtained with 10 substrate units and 11 film units giving a -0.06% lattice mismatch. For the
14 relation (II) the coincidence is realized with 5 substrate units and 6 film units with a -1.28%
15 mismatch (Fig. 9(b)).
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23 Discussion

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27 In the previous works reported on the RT epitaxy of oxide films, results were usually
28 obtained on c-cut sapphire substrates, and two main points play a role on this epitaxy. The first is
29 the presence of steps and terraces on the c-cut surface. These steps and terraces are due to a miscut
30 and / or a high T annealing of the c-cut sapphire substrate^{15,16}, which will play the role of
31 nucleation centers for the epitaxial growth. This kind of growth corresponds to the graphoepitaxy
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112 In the case of the cubic oxides (NiO , Co_3O_4 , Fe_3O_4 , ...), epitaxially grown at
113 RT or at high T on c-cut substrate, the observed texture is (111), i.e. a plane which is also a polar
114 plane⁴⁵. The epitaxial growth concerns thus two polar planes, and this situation is very similar to
115 the quasi van der Waals epitaxy^{48,49} where there is only very little or no chemical bonding between
116 the atoms of the film and substrate. Indeed, the stability and the epitaxy of the film-substrate
117 interface are related to the weak electrostatic interaction between the two polar planes⁵⁰.

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3 In the case of the ZFO epitaxial growth on c-cut substrate, the epitaxial relationships are
4 the same as those observed in the case of the growth of ZFO on this substrate at elevated
5 temperature⁵², i.e. the growth occurs with a "30° rotation" of the hexagons of the (111) ZFO plane
6 on the hexagon of the (002) sapphire plane. It should be reminded that, in this work, the substrate
7 was not thermally treated, so the AFM image shows presence of steps, but however much less
8 defined than the ones obtained with a high thermal treatment at 1000°C. Moreover, after the film
9 growth, the AFM images (not shown) does not show any steps or terraces which is rather different
10 from the results commonly reported in which steps and terraces are present at the surface of the
11 oxide films grown at RT on c-cut substrates annealed at high temperature before the growth. In
12 our case, polar nature of the c-cut sapphire substrate and of the (111) plane of the Zn-doped iron
13 oxide may lead to an electrostatic interaction at this interface. Therefore, it seems reasonable to
14 conclude that both the graphoepitaxy and the quasi van der Waals epitaxy are at the origin of the
15 RT epitaxy of ZFO on c-cut sapphire substrate. Concerning the film grown on the a-cut substrate,
16 it must be noticed that this substrate is also either a pure cationic or a pure oxygen one. Our results
17 show that the RT epitaxy of the wüstite phase is based on the (111) ZFO_w plane, despite the fact
18 that the a-cut substrate and the (111) ZFO_w present very different atomic configuration, i.e. a
19 symmetry mismatch between the substrate (2-fold) and the (111) ZFO_w film (3-fold).
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43 An interesting point which can be noticed is that such epitaxial relationship (111) ZFO_w //
44 (110) Al₂O₃ corresponds to an epitaxy of a hexagon on a rectangle with different symmetries for
45 these two planes. One can ask thus why an epitaxy with a square (ZFO_w) on a rectangle (r-cut
46 Al₂O₃) is not observed while the square and rectangular configurations would be more relevant.
47 Concerning the DME, it is possible to obtain the lattice mismatch δ and domain matching epitaxy
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D in terms of the epitaxial relationships with (001) ZFO_w // (110) Al₂O₃. The calculated values of δ and D are the following:

$$[100] \text{ ZFO}_w // [001] \text{ Al}_2\text{O}_3 \quad m = 3 \quad p = 1 \quad \delta = 0.02 \% \quad D = 1.3 \text{ nm}$$

$$[001] \text{ ZFO}_w // [1-10] \text{ Al}_2\text{O}_3 \quad m = 19 \quad p = 10 \quad \delta = 0.13 \% \quad D = 8.3 \text{ nm}$$

The comparison of these values with those given in Table 2 for the (111) ZFO_w // (110) Al₂O₃ indicates that the epitaxy of the square (001) ZFO_w on the rectangular (110) Al₂O₃ is better in terms of DME. The reason why this epitaxy is not observed is certainly related to the fact that the (100) ZFO_w plane is not a polar plane, i.e. O and Fe are present in this plane. It can be concluded that the van der Waals epitaxy based on the electrostatic interaction between the (111) ZFO_w and the (110) Al₂O₃ is preferred to the simple “square on rectangular” epitaxy.

It follows thus that the (111) ZFO_w texture could be explained in the frame of an electrostatic interaction due to the “quasi Van der Waals epitaxy”. Indeed, the (111) plane in the wüstite (FCC structure) is a polar plane, and the a-cut sapphire plane is also a polar plane. An electrostatic interaction between these two polar planes is thus envisaged in a similar way to the quasi van der Waals epitaxy.

For the ZFO film grown on the r-cut substrate, the (100) wüstite texture is observed. This is rather surprising since this situation is *a priori* similar to the a-cut substrate case. Indeed, the r-cut plane is either a pure oxygen plane or a pure cationic plane, and it presents a rectangular atomic configuration. As for the a-cut surface plane, the (111) wüstite texture could be expected, but the (100) wüstite texture is observed. This means that both the graphoepitaxy and/or van der Waals epitaxy cannot be envisaged to explain the epitaxial growth of ZFO on the r-cut sapphire substrate.

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3 We mentioned above the specific problem of the tilt in the epitaxy on r-cut substrate, but
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5 another parameter is the growth temperature, which plays an important role in the epitaxial growth
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7 of oxide films on the r-cut substrate. For example in the case of CeO₂ films grown on a r-cut
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9 substrate thermally treated at high T (1000°C), steps and terraces are formed at the surface and a
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11 pure (100) CeO₂ texture is observed for example ^{28,67,68}. Moreover, the steps are formed along the
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13 [010] direction of the r-cut substrate, which is one of the in-plane directions of the epitaxy. On the
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15 contrary, when the r-cut substrate is not thermally treated at high temperature, steps and terraces
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17 are not formed, and both (111) and (100) CeO₂ textures are observed ^{28,67,68}. Further studies on
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19 CeO₂ films on r-cut substrates have shown that the growth temperature plays an important role on
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21 the film texture ⁶⁹. Indeed, the texture of CeO₂ films changed from (001) at 150°C to a mixed (001)
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23 and (111) textures at 300°C, and finally to pure (111) for increasing temperatures ⁴. In our work,
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25 the presence of steps and terraces on the r-cut substrate (Fig. 1(c)) is not clearly evidenced from
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27 the AFM images, and furthermore only the (100) ZFO_w texture is observed. Moreover, our films
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29 are grown at RT, and we can thus assume that the (100) ZFO_w texture is due to the low growth
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31 temperature of the film in a similar way to the case of the CeO₂ film grown on r-cut sapphire
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33 substrates ⁶⁹.
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41 **Conclusion**

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44 Using a Zn:FeO_x target, the wüstite (Zn:FeO) and/or spinel (Zn:Fe₃O₄) phases were
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46 obtained on c-cut, a-cut and r-cut sapphire single crystal substrates by pulsed laser deposition at
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48 room temperature. Depending upon substrates, the two textures, (111) or (100), may be obtained,
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50 and poles figures showed the RT epitaxy of the films on all substrates. The possible origin of these
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52 distinct textures and epitaxial relationships has been discussed according to both the
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54 « graphoepitaxy » and the « quasi van der Waals epitaxy » for the films grown on the c-cut and a-
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3 cut substrates. For the film grown on the r-cut, the (100) texture is obtained as it has been observed
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5 in other cases. An important point in the RT epitaxy of the ZFO films is the high kinetic energy of
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7 the species emitted by the target during the laser ablation. Such a high kinetic energy of these
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9 species will give them the possibility to move on the substrate on sufficient long distances to find
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11 their site in the growth of the crystal structure. Finally, this work shows that the RT epitaxy of the
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13 oxide films is quite possible on various sapphire substrates (c-cut, a-cut and r-cut), and this opens
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15 the way to the PLD growth of oxide films on substrates like MgO, MgAl₂O₄ or others at RT.
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42 Author Contributions

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44
45 The manuscript was written through contributions of all authors. All authors have given approval
46
47 to the final version of the manuscript. VD performed the XRD characterizations and LeBail
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49 refinement, analyzed and interpreted the corresponding data and drafted the article. XP performed
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51 the TEM and EELS measurements, analyzed and interpreted the corresponding data and drafted
52
53 the article. SO performed the AFM measurements. MP and TR performed LeBail refinement,
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3 analyzed and interpreted the corresponding data. CH and MN synthesized PLD films, performed
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5 RBS measurements, analyzed and interpreted the corresponding data. MGV revised the
6
7 manuscript. CC and EM analyzed and interpreted the data and drafted the article. JP conceived
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9 and designed the project, analyzed and interpreted the data and drafted the article.
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47 **ABBREVIATIONS**

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50 RT, room temperature; PLD, pulsed-laser deposition; ZFO_w , wüstite phase Zn:FeO; ZFO_s , Zn-
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52 doped Zn:Fe₃O₄ spinel magnetite phase; Nd:YAG, Nd-doped yttrium aluminum garnet; AFM,
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54 atomic force microscopy; RBS, Rutherford backscattering spectrometry; XRD, X-ray diffraction;
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3 TEM, transmission electron microscopy; FIB, focused ion beam; FEG, Field emission gun; EELS,
4 electron energy loss spectrometer; STEM, scanning transmission electron microscopy; HREM,
5 high resolution electron microscopy; FFT, Fast Fourier Transform; FWHM, full width at half
6 maximum; DME, domain matching epitaxy.
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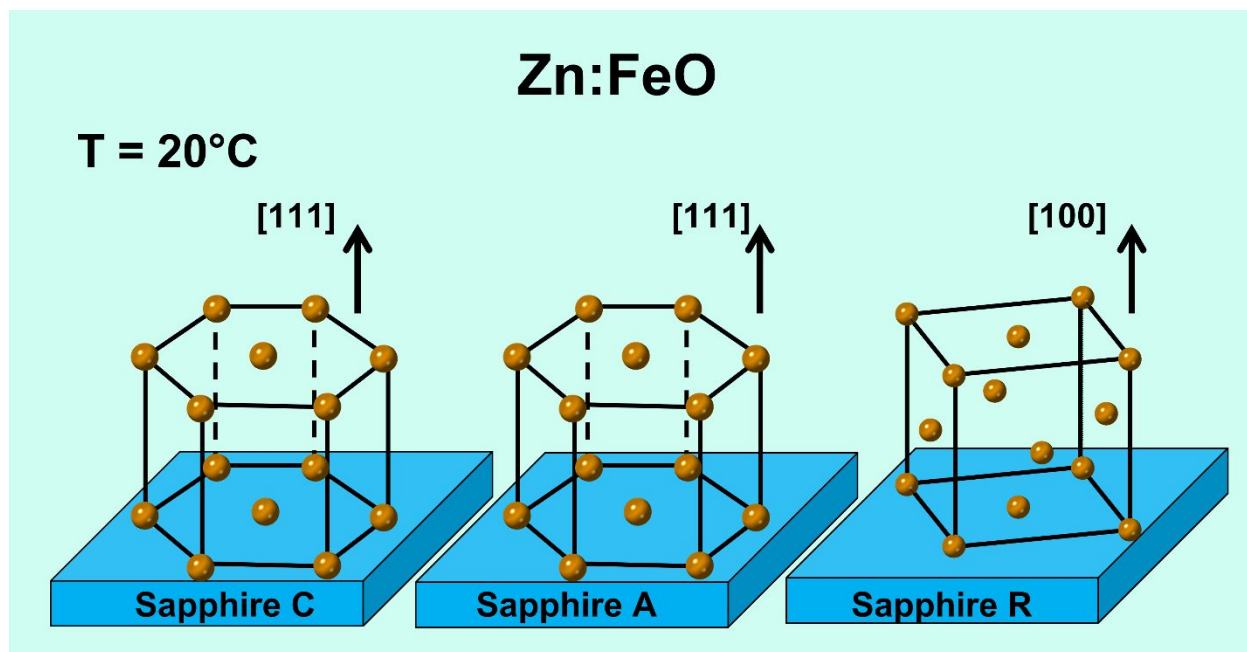
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Room temperature epitaxial growth of Zn-doped iron oxide films on c-, a- and r-cut sapphire substrates

Valérie Demange, Xavier Portier, Sophie Ollivier, Mathieu Pasturel, Thierry Roisnel, Maryline Guilloux-Viry, Christian Hebert, Magdalena Nistor, Christophe Cachoncinlle, Eric Millon, Jacques Perrière



Synopsis: Room-temperature epitaxial growth of Zn doped FeO wüstite thin films on c-cut, a-cut and r-cut sapphire substrates

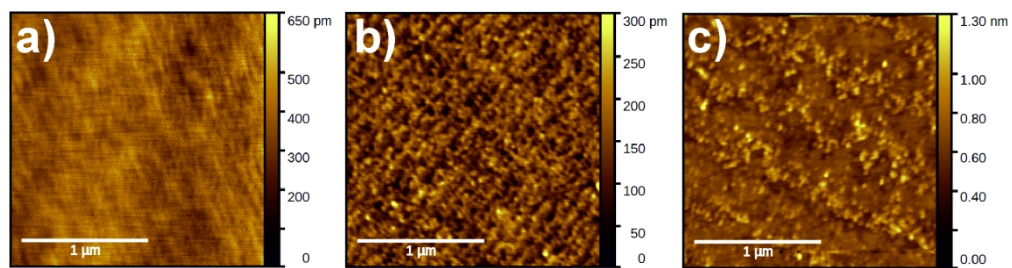


Figure 1. AFM image of c-cut, a-cut and r-cut sapphire substrates without any annealing before the PLD growth.

181x47mm (300 x 300 DPI)

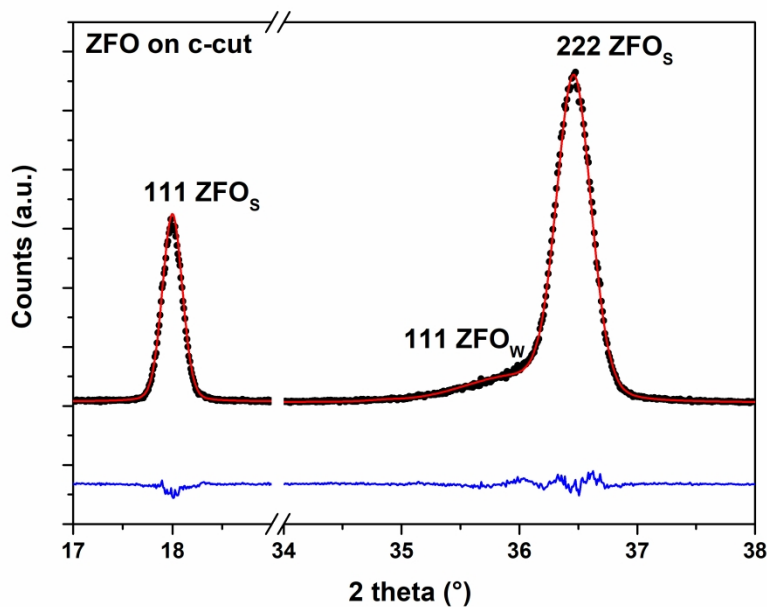


Figure 2. Experimental θ - 2θ XRD pattern (black symbols) of the ZFO film grown on c-cut sapphire substrate showing a peak at about 18° corresponding to the 111 Bragg reflection of the spinel phase and a broad peak around 36° corresponding to the 111 reflection of wüstite and the 222 reflection of spinel phases, respectively. This pattern has been refined using the Le Bail method and calculated and difference patterns are shown as red and blue lines, respectively.

288x201mm (300 x 300 DPI)

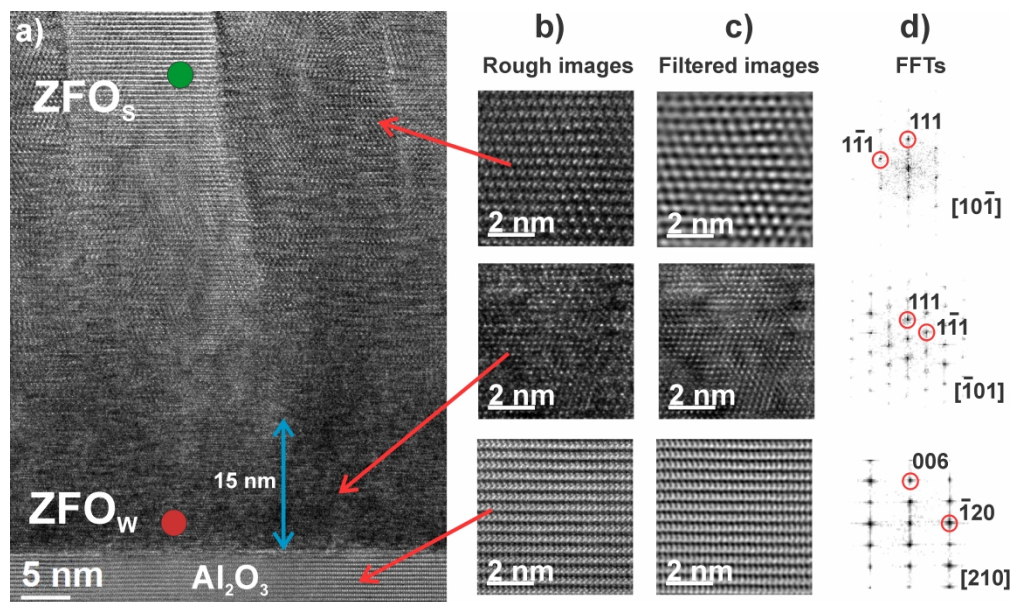


Figure 3. a) HREM image of a cross section of a ZFO film on c-cut sapphire substrate showing a thin region of ZFO_W at the bottom of the film; b) and c) are enlarged regions of the different parts of the film and the Al₂O₃ sapphire substrate corresponding to rough and filtered images respectively; d) FFTs of the previous mentioned images leading to the identification of the structures.

385x229mm (300 x 300 DPI)

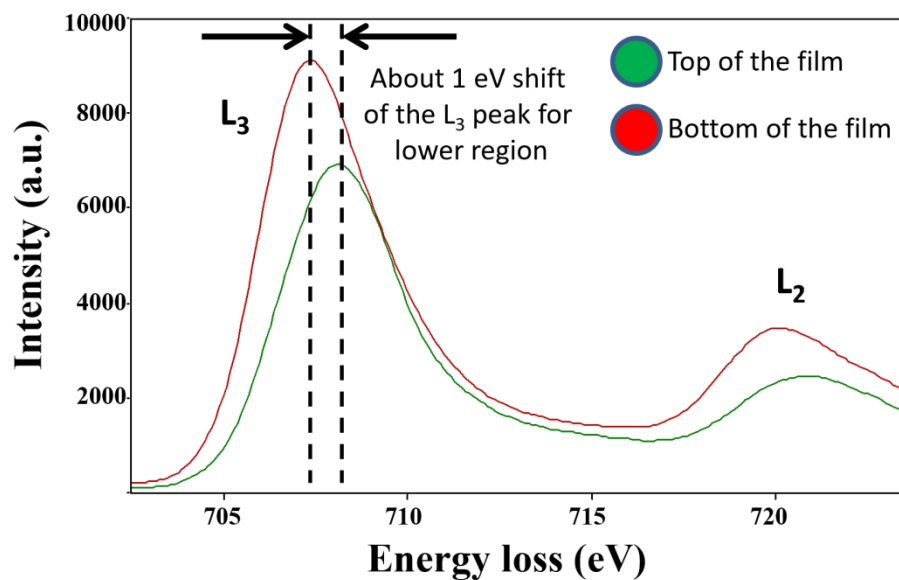


Figure 4. EELS spectra of the L₃ and L₂ energy thresholds of Fe. A 1 eV shift of the L₃ peak confirms the lowering of the valence state of Fe and thus the presence of wüstite at the bottom of the film.

141x90mm (330 x 330 DPI)

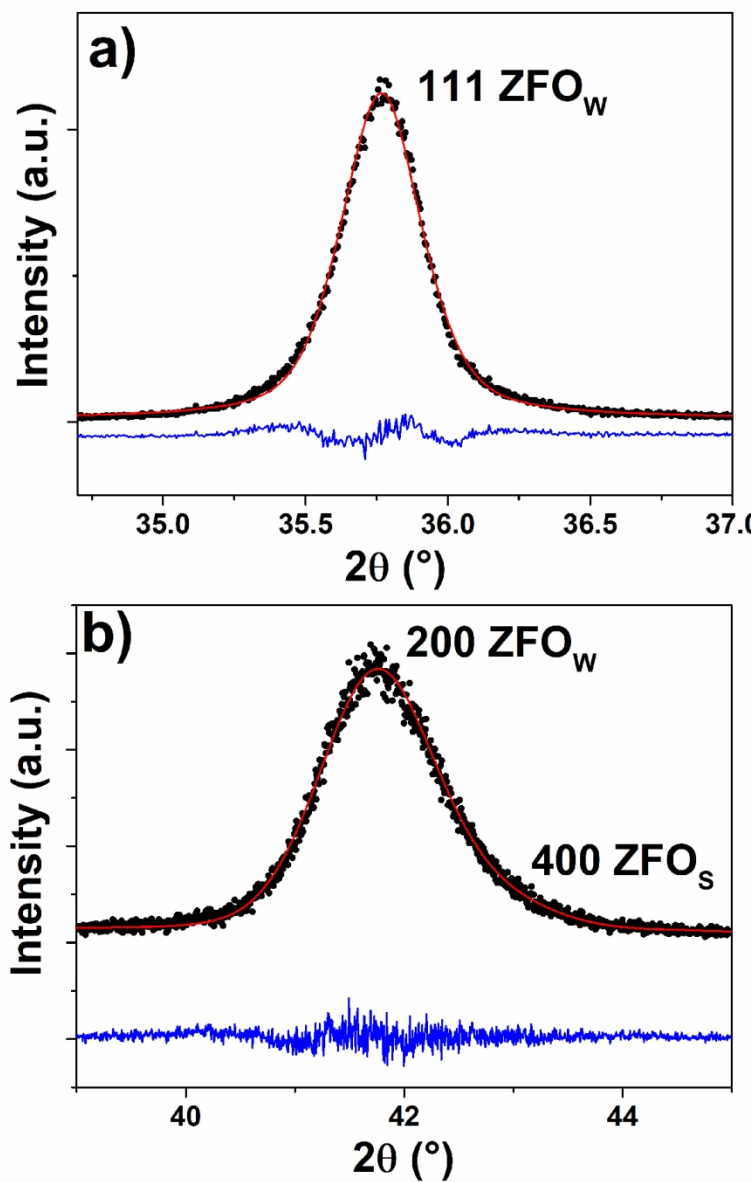
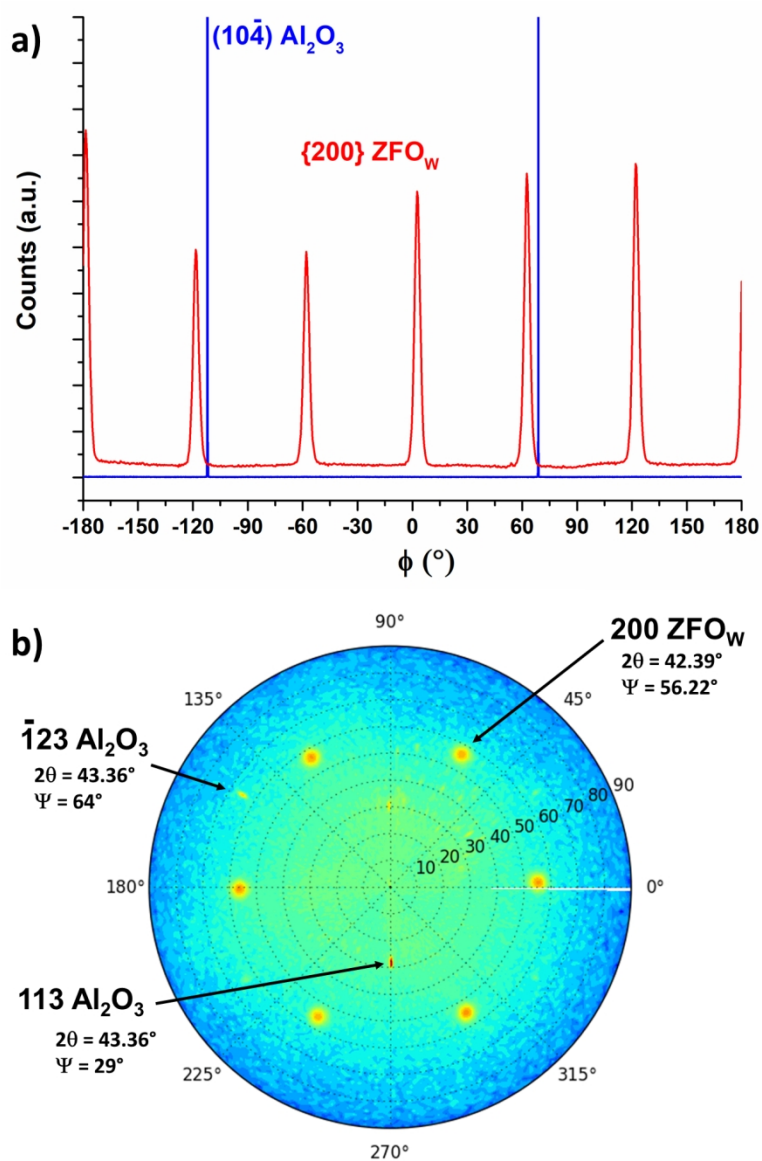


Figure 5. Le Bail refined θ - 2θ XRD patterns of ZFO films grown on a-cut (a) and r-cut (b) sapphire substrates. Black symbols display the experimental data, red lines represent the theoretical patterns and blue curves show the difference between them.

102x161mm (300 x 300 DPI)



45 Figure 6. a) Phi-scan of the $\{200\}$ planes of the (111) ZFO_W film (red) and of the (10-4) planes of the a-cut
46 sapphire substrate (blue). b) Pole figure of the $\{200\}$ planes of the (111) ZFO_W film showing 6 poles.

47 230x346mm (150 x 150 DPI)

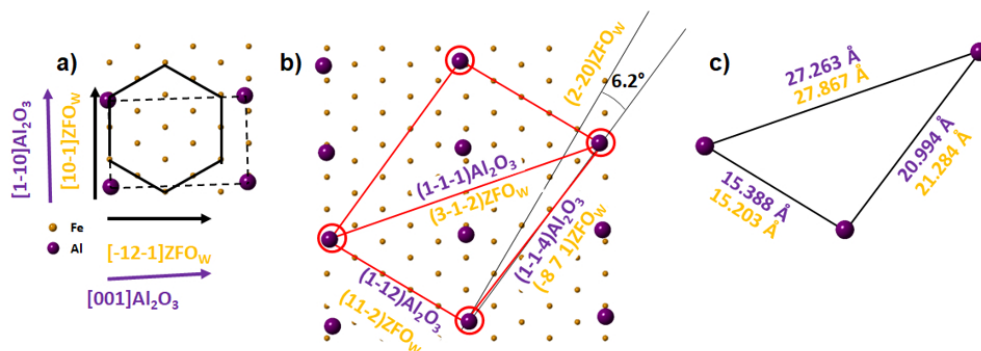


Figure 7: a) Scheme of the epitaxy of (111) ZFO_W grown on the a-cut sapphire substrate, determined by phi-scans measurement. b) Scheme of the domain matching epitaxy of (111) ZFO_W grown on the a-cut sapphire substrate, showing the site coincidences between the two lattices. The 6.2° rotation between the (2-20) ZFO_W plane and the (1-1-4) sapphire plane highlighted in the phi-scans is shown. c) Interatomic distances of the two lattices reported on the scheme.

254x93mm (96 x 96 DPI)

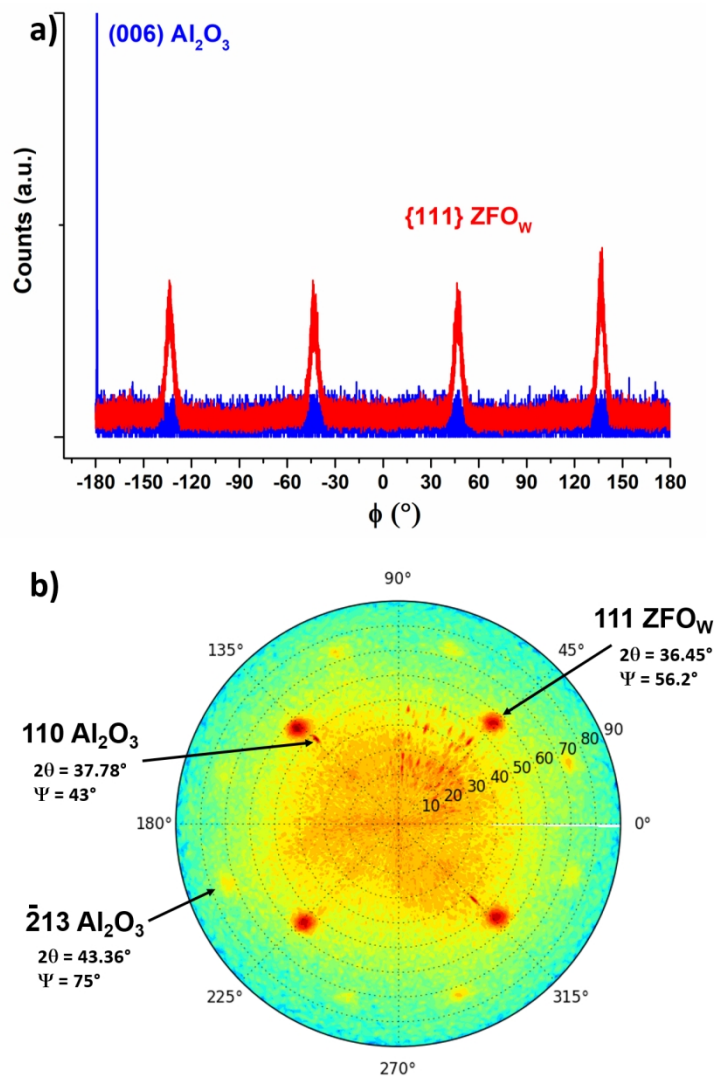


Figure 8: a) Phi-scan of the {111} planes of the (100) ZFO_w film (red) and of the (006) plane of the r-cut sapphire substrate (blue). b) Pole figure of the {111} planes of the (100) ZFO_w film showing 4 poles.

251x376mm (150 x 150 DPI)

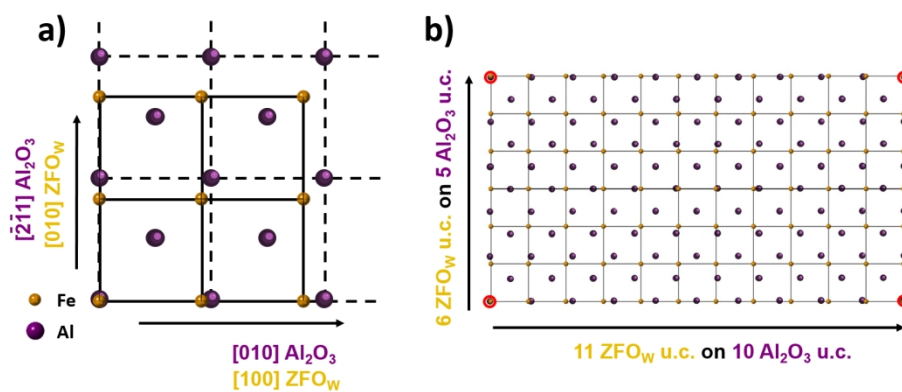


Figure 9: a) Scheme of the epitaxy of (100) ZFO_w grown on r-cut sapphire substrate. b) Scheme of domain matching epitaxy of (100) ZFO_w grown on r-cut sapphire substrate.

309x138mm (150 x 150 DPI)