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The effect of Al substitution on the structural and magnetic properties of epitaxial thin films of epsilon ferrite

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ABSTRACT

Epitaxial growth of aluminum substituted epsilon ferrite by pulsed laser deposition on strontium titanate and yttrium-stabilized zirconium substrates is demonstrated for a wide range of aluminum substitution. Linear decrease of the out-of-plane lattice parameter with aluminum substitution correlates with the decrease of the coercive magnetic field, while the magnetization first increases and then decreases with increasing aluminum concentration. A characteristic inflexion in the hysteresis loops has been attributed to the presence of a small quantity of magnetite. Epitaxial growth on yttrium-stabilized zirconium is technologically significant due to its use as buffer layer for the growth of complex oxides on silicon.

Nanostructured iron oxides have recently drawn a lot of attention given their many potential applications, first based on their inherent magnetic properties, but also in various fields of medicine because of their well-known biochemical characteristics of nontoxicity, biocompatibility, and biodegradability [1–13]. Iron oxides are the most common iron compounds in nature and several of them, such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) occur naturally and are generally easy to synthesize. A notable exception is epsilon ferrite (ε-Fe_2O_3), a ferrimagnetic metastable phase intermediate between maghemite and hematite. The magnetization in ε-Fe_2O_3 arises from a non-fully compensated magnetic moment on the anti-parallel aligned iron atoms (see Fig. 1), in which the tetrahedrally coordinated "D" sites are holding a lower magnetic moment than the other sites. Although being characterized by lower magnetization compared to γ-Fe_2O_3, ε-Fe_2O_3 has received notable attention lately due to its very strong magnetocrystalline anisotropy, which results in a gigantic coercive field [14–17], and also in a natural ferromagnetic resonance (FMR) frequency above 100 GHz, flirting with the low THz range (~0.1–100 THz) at room temperature [18]. This is of particular interest given its potential use in short-range wireless communications (*e.g.* 60 GHz WiFi) [19] and ultrafast non-volatile memories [20]. The origin of such strong magnetocrystalline anisotropy was investigated by X-ray magnetic circular dichroism and found to be due to lattice distortion [21]. Later, first principle calculations supported those experimental findings, by predicting that the magnetic easy axis should lie along the crystal *a* axis direction [22]. Finally, given its crystal structure belonging to the polar space group $Pna2_1$ [23,24] (Fig. 1), ε-Fe_2O_3 is characterized by a spontaneous polarization that, if proved switchable at room temperature, would make it one of the few single phase, room temperature multiferroic materials.

Up until recent years, due to its metastability in ambient condition, epsilon ferrite has mostly been synthesized in the form of nanostructure [15–17,25–27], with size confinement acting as the stabilizing factor. However, in order to further investigate their relatively unexplored magnetic properties and eventually integrate them into devices, synthesis of stable epsilon ferrite thin films and their compounds must be mastered. Recent reports showed that it is indeed possible to grow epsilon ferrite thin films epitaxially directly on single crystalline strontium titanate ($SrTiO_3$) [28] and yttrium stabilized zirconium (YSZ) substrates by pulsed laser deposition (PLD) [29], and on sapphire by using a buffer layer of gallium ferrite ($GaFeO_3$) [30]. Furthermore, presence of reversible spontaneous polarization was reported in layered structure of $SrTiO_3$:Nb/$AlFeO_3$/$SrRuO_3$/ε-Fe_2O_3 [31].

Extensive studies have also been conducted on the effect of metal substitution into epsilon ferrite (ε-$M_xFe_{2-x}O_3$) nanoparticles, in particular regarding its effect on the FMR frequency. Ohkoshi et al. have reported that substitution of Fe^{3+} ions in ε-Fe_2O_3 with metals having a smaller ionic radius, such as Al^{3+} and Ga^{3+}, results in a lowering of the FMR frequency [18,19,32], while through substitution with larger ions like Rh^{3+}, an increase of the FMR is observed [33]. It is interesting to note that $AlFeO_3$ and $GaFeO_3$, which are isostructural to ε-Fe_2O_3, are known room temperature ferroelectrics characterized by spontaneous magnetic ordering at cryogenic temperatures [34–36].

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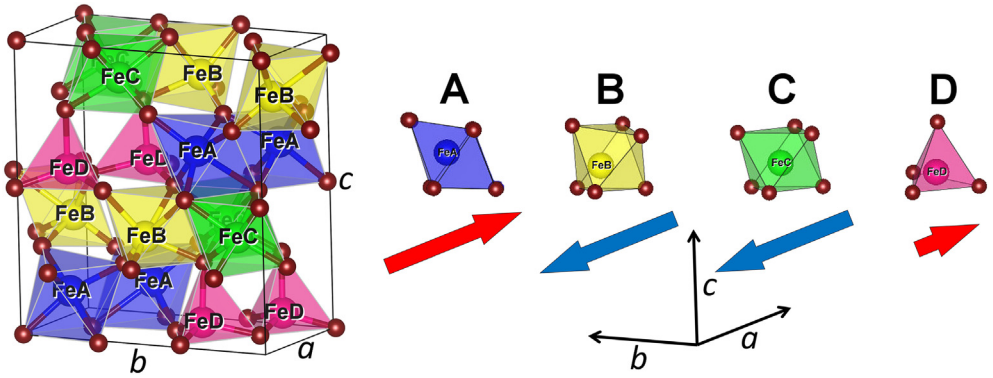

Fig. 1. ε-Fe_2O_3 unit cell and configuration of the magnetic moments on the four different iron sites. It has to be noted that the magnetic moments lie in the *a*–*b* plane. According to recent works, they should be aligned along the a-axis of the crystal unit cell.

In this paper, we report the epitaxial growth by pulsed laser deposition of thin films of Al-substituted epsilon ferrite and the effect of Al substitution on the structural and magnetic properties. Thin films of ε-$Al_xFe_{2-x}O_3$ of thickness of about 50 nm were grown directly on single crystalline (111)-oriented strontium titanate ($SrTiO_3$) and (100)-oriented Yttrium Stabilized Zirconia (YSZ) substrates (no buffer layer was used). While the different symmetry of the two substrates give different epitaxial match and result in different twins formation [29,30], the films grown on both type of substrates exhibited very similar structural and functional properties and the same trends with increasing aluminum substitution. The films were grown following the conditions reported in reference 27; the only peculiarity was that, in order to obtain films with different percentage of Al, the growth was performed by alternatively ablating a standard Fe_2O_3 target and a second target of $AlFeO_3$. Different Al substitution percentages were obtained by changing the ratio of the number of pulses shot on each target. In order to achieve a homogenous distribution of aluminum, the films were grown roughly one monolayer at the time, alternating the targets in order to get the desired composition. Films with Al concentration ranging from pure ε-Fe_2O_3 to ε-$Al_{0.5}Fe_{1.5}O_3$ ($0 < x < 0.5$) were then prepared. Thin films of pure $AlFeO_3$ (*i.e.* $x = 1$) were also prepared (with the same deposition conditions as the epsilon ferrite films) to estimate its growth rate and for comparison with the ε-$Al_xFe_{2-x}O_3$ films. In order to confirm the correctness of our estimation of the composition, which is based on the number of laser pulses on each target and on the growth rate of both $AlFeO_3$ and ε-Fe_2O_3, energy-dispersive X-ray spectroscopy (EDX) was performed on our films. The Al:Fe ratio obtained was in very good agreement with the Al:Fe ratio estimated from the number of pulses shot on each target.

Structural analysis was performed by X-ray diffractometry with a PANalytical X'Pert MRD PRO diffractometer using the Cu K_α radiation ($\lambda = 1.54056$ Å). Goniometer (θ/2θ) scans confirmed that ε-$Al_xFe_{2-x}O_3$ grows epitaxially both on $SrTiO_3$ (111) and YSZ (100). The films are (001)-oriented as shown by the diffraction patterns of pure ε-Fe_2O_3, ε-$Al_{0.1}Fe_{1.9}O_3$, and pure $AlFeO_3$ grown on $SrTiO_3$ (111) (Fig. 2a). A shift towards higher 2θ angles with increasing Al concentration is observed, which was expected given the smaller ionic radius of Al^{3+} (53.5 pm) compared to Fe^{3+} (64.5 pm).

The out-of-plane lattice parameter "*c*" was calculated from the measured goniometer scans, averaging the values found utilizing the inter-planar distances corresponding to the two detectable *00l* peaks ($l = 2$ and 6). A linear decrease in the out-of-plane lattice parameter with increasing aluminum content was found, as shown in the graph in Fig. 2b, in agreement with previous studies [19].

The magnetic properties of our films were measured using a Vibrating Sample Magnetometer (VSM - model EV9 from ADE Technologies). The hysteresis loops were recorded at room temperature for all the samples, with the magnetic field applied both parallel (in-plane) and perpendicular (out-of-plane) to the film surface. In order to obtain solely the signal arising from the thin films, the contribution of the vibrating rod holding the samples and of the substrates were measured and subtracted from the measured hysteresis loops. The resulting magnetic moment was divided by the volume of the thin film. The measured magnetic hysteresis loops of films with $x = 0$, $x = 0.1$, and $x = 0.5$ are shown in Fig. 3. We observe an inflexion at low applied fields in all loops, which we attribute to the presence of a secondary soft magnetic phase that was identified as magnetite (Fe_3O_4) by detailed XRD and magnetic analysis [29]. Presences of these inflections were also recorded

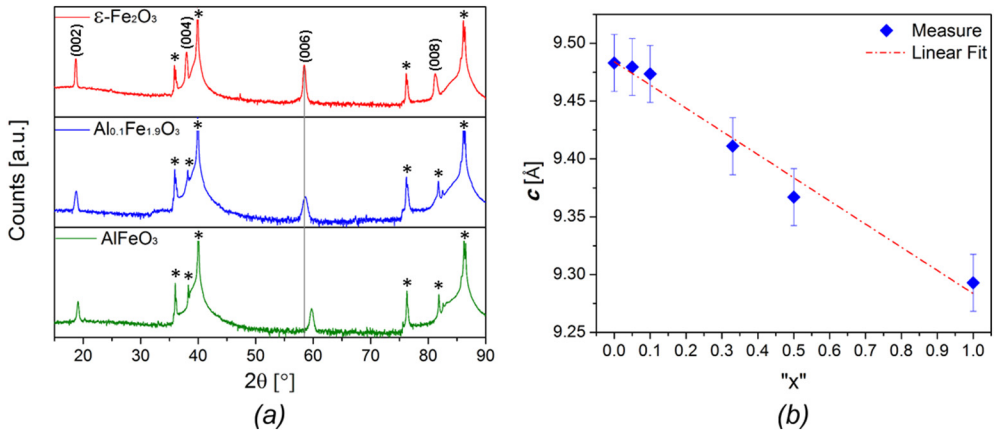

Fig. 2. (a) θ/2θ scans of (100)-oriented ε-Fe_2O_3, ε-$Al_{0.1}Fe_{1.9}O_3$, and $AlFeO_3$ thin films, revealing how all the three materials grow epitaxially on (111)-oriented $SrTiO_3$. The line drawn in grey helps visualizing the shift in position of the (006) peak in the Al-substituted films in comparison to pure ε-Fe_2O_3. The peaks noted by asterisks belong to the $SrTiO_3$ (111) substrates and its secondary lines. (b) Evolution of the lattice parameter "*c*" with increasing Al concentration "x".