Tanskanen, A.; Mustonen, O.; Karppinen, Maarit

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Simple ALD process for $\varepsilon$-Fe$_2$O$_3$ thin films

A. Tanskanen, O. Mustonen, and M. Karppinen

Department of Chemistry and Materials Science, Aalto University, FI-00076 Espoo, Finland

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Atomic layer deposition (ALD) is an advanced industrially feasible technique for fabricating functional materials as high-quality thin films. Here we exploit the technique for the first time for growing thin films of the rare $\varepsilon$-Fe$_2$O$_3$ phase that has been found only in nanoscale samples. This single-metal single-valence oxide is receiving increasing interest due to its unusually high coercivity and multiferroic properties. With ALD, polycrystalline thin films of the $\varepsilon$-Fe$_2$O$_3$ phase are achieved on various substrate surfaces at a relatively low deposition temperature (260–300 °C) from FeCl$_3$ and H$_2$O precursors. The films are ferrimagnetic having an $\sim$1.6 kOe coercive field. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

The $\varepsilon$-Fe$_2$O$_3$ phase has attracted considerable interest due to its room-temperature multiferroic properties with high coercivity. This is particularly impressive for a simple single-metal and single-valence compound. Moreover, the phase is based on earth-abundant elements only, and like iron oxide materials in general, is biocompatible and nontoxic to human, and is expected to show reasonable resistance to corrosion.

There are five polymorphs of the iron(III) oxide: the naturally occurring $\alpha$-Fe$_2$O$_3$ (hematite) and $\gamma$-Fe$_2$O$_3$ (maghemite) phases, the high-pressure stabilized $\zeta$-Fe$_2$O$_3$ (Zeta-Fe$_2$O$_3$) phase, and the synthetic $\beta$-Fe$_2$O$_3$ and $\varepsilon$-Fe$_2$O$_3$ phases found in nanoscale samples. The properties of the latter three synthetic polymorphs ($\zeta$, $\beta$, and $\varepsilon$-Fe$_2$O$_3$) are not well-known due to the challenges in stabilization of the phases. $\varepsilon$-Fe$_2$O$_3$ phase was first observed by Forestier and Guioit-Guillain in 1934 and named by Schrader and Buttnner in 1963. Only after several decades, Tronc et al. succeeded in the synthesis of $\varepsilon$-Fe$_2$O$_3$ as a major phase, and Jin et al. enlarged the coercive field up to 2.0 T for $\varepsilon$-Fe$_2$O$_3$ samples with small-sized particles consisting of a single magnetic domain. The $\varepsilon$-Fe$_2$O$_3$ phase is thermally very unstable, which is found upon heating as an intermediate phase between maghemite and hematite. It has only been synthesized in nano-scale as nanoparticles, nanowires, and thin films.

The crystal structure of $\varepsilon$-Fe$_2$O$_3$ is non-centrosymmetric (space group $Pna\overline{2}1$) with four distinct iron sites, three of which are octahedral and one tetrahedral. At room temperature, the phase is ferrimagnetic with moments along the $c$ direction and exhibits an unusually large coercive field ($H_c$) of $\sim$20 kOe. The Curie temperature ($T_C$) is 510 K, but below 110 K the magnetic structure becomes incommensurate. Recently room-temperature ferroelectricity with a polarization of 1 $\mu$C cm$^{-2}$ was observed in epitaxial thin films of $\varepsilon$-Fe$_2$O$_3$. For its potential future application in, e.g., information storage technology or other frontier applications, fabrication of high-quality thin films of the $\varepsilon$-Fe$_2$O$_3$ phase would be vitally important. So far only a few efforts have been reported; in these works, $\varepsilon$-Fe$_2$O$_3$ thin films were grown by electrodeposition (ED) and pulsed laser deposition (PLD) techniques.

Atomic layer deposition (ALD) has been used to fabricate thin films of the most common iron oxide phases, Fe$_2$O$_3$ and Fe$_3$O$_4$ (magnetite),. Here we present for the first time the growth of $\varepsilon$-Fe$_2$O$_3$ thin films with the ALD technique, which is believed to be an inherently superior technology when precise thickness control, large-area homogeneity, and conformity over complex surface

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Author to whom correspondence should be addressed. Electronic mail: maarit.karppinen@aalto.fi
architectures are required.\textsuperscript{34,35} The technique produces polycrystalline thin films but, conversely, does not require a lattice matching substrate for the film growth.

The depositions were carried out in a commercial flow-type hot-wall ALD reactor (F-120 by ASM Microchemistry Ltd.) using iron chloride (FeCl\textsubscript{3}, Merck, 95\%) and deionized water as precursors; the FeCl\textsubscript{3} powder was set into the reactor in an open precursor boat at 158 °C while the deionized water container was located outside the reactor. Nitrogen (99.999\%) was used as a carrier gas and for purging the reactor after every precursor pulse. The pressure inside the reactor was 2–4 mbar and the N\textsubscript{2} flow rate was 300 SCCM during the depositions. The following precursor/purge pulse lengths were selected based on our preliminary experiments (see the supplementary material): 2 s FeCl\textsubscript{3}/4 s N\textsubscript{2}/1 s H\textsubscript{2}O/3 s N\textsubscript{2}. Silicon(100) (Okmetic Oy) and borosilicate glass (Finnish Special Glass) substrates of the 3.0 × 3.0 cm\textsuperscript{2} size were used as received. The deposition temperature was varied from 210 to 360 °C. Under these conditions, surface saturation was achieved after the precursor pulses and the films were confirmed to grow in a linear manner, i.e., the film thickness linearly increasing with the number of deposition cycles, as expected for a well-behaving ALD process (see Fig. S1 in the supplementary material).

For each thin film, the film thickness, density, and roughness were determined by X-ray reflectivity (XRR) measurements; the data were collected with PANalytical X’Pert PRO Alfa 1 equipment and fitted with X’Pert Reflectivity software. The measurement was carried out within 15 min after taking the sample out from the ALD reactor. The same equipment was used to collect grazing incidence X-ray diffraction (GIXRD) patterns for some of the samples. For the phase composition and crystal structure determination, X-ray diffraction (XRD) measurements were performed with PANalytical X’Pert PRO MPD Alpha 1 (Cu K\textalpha\textsubscript{1} radiation) equipment for ~260 nm thick films with an intention to examine the orientation of the films as well. Transmission electron microscopy (TEM, JEOL JEM-2200FS) was employed to investigate how the crystals were formed through the film. The cross section of the sample was prepared with a focused ion beam (FIB) instrument. Scanning electron microscope (SEM, JEOL JSM-7500FA) images were taken to determine the particle size in the films.

Our depositions yielded homogeneous and crystalline thin films within the entire deposition temperature range investigated; in Fig. 1(a), we display the XRD patterns recorded for representative films deposited at 260–340 °C. It can be seen that at 260 °C the ε-Fe\textsubscript{2}O\textsubscript{3} phase is already formed but the film apparently contains small amounts of a secondary phase seen as some unidentified low-angle peaks and as an additional shoulder for the 013 peak. For the films deposited at 280 and 300 °C, all the diffraction peaks can be readily assigned to the ε-Fe\textsubscript{2}O\textsubscript{3} phase, whereas for the film deposited at 320 °C, peaks due to the hematite phase start to appear and at 340 °C hematite already seems to be the dominant phase with some remains of the ε-Fe\textsubscript{2}O\textsubscript{3} phase. Indications of the γ-Fe\textsubscript{2}O\textsubscript{3}, β-Fe\textsubscript{2}O\textsubscript{3}, and hematite (α-Fe\textsubscript{2}O\textsubscript{3}) phases were not clearly seen in any of the XRD patterns at the lower deposition temperatures (see Fig. S2 in the supplementary material).

We compared the experimental XRD data to simulated patterns based on the structure determined from ε-Fe\textsubscript{2}O\textsubscript{3} nanoparticles by synchrotron X-ray powder diffraction (SXRPD)\textsuperscript{21} (see Fig. 1(b)). It can be seen that most of the diffraction peaks expected can be found but the intensities vary to some extent; also, no apparent impurity peaks are seen. The peaks 002 and 004 seem to be more intense than in the calculated data, and the peaks at ~35° (113 and 200), 36.7° (131), 60.4° (053), and 63.4° (330) that are moderately intense in the calculated data are missing from the data measured for our thin films. These observations indicate a preferred film growth direction perpendicular to the c axis. Similar orientation was observed also for thin films grown by PLD on SrTiO\textsubscript{3} substrates.\textsuperscript{19} The impurity peaks detected at low angles in the sample deposited at 260 °C and as a shoulder at ~30° seem to match to iron chloride and iron hydroxide reflections based on a search of the ICDD database. These peaks disappear for the films deposited at the higher temperatures. The ε-phase could be detected from the samples deposited on the borosilicate glass as well (see Fig. S3 in the supplementary material).

We then performed Le Bail full profile fitting using FULLPROF\textsuperscript{36} software for a GIXRD pattern recorded for a 260 nm thick film deposited at 280 °C; the data are shown in Fig. S2B in the supplementary material. The main ε-Fe\textsubscript{2}O\textsubscript{3} phase in this sample has an orthorhombic crystal structure with space group Pna\textsubscript{2}\textsubscript{1}. The lattice parameters were determined to be \(a = 5.094 \text{ Å}, \ b = 8.789 \text{ Å}, \)
and $c = 9.427 \, \text{Å}$. The TEM images shown in Figs. 2(a)–2(c) for the same sample reveal that the film is formed from oriented crystalline areas. It was however not possible to define the orientations of the crystalline areas by electron diffraction due to overlapping reflections from multiple crystals. In the SEM image for the same sample, multifaced crystals with a width of maximum 120 nm are seen (Fig. 3).
We then investigated the magnetic properties of our ALD-grown $\varepsilon$-$\mathrm{Fe}_2\mathrm{O}_3$ thin films using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL5); DC magnetization curves (M-T) were measured from 5 to 300 K under a field of 1 kOe in both zero-field-cooled (ZFC) and field-cooled (FC) modes. The film surface was set perpendicular to the direction of the applied magnetic field. Additionally, isothermal magnetization curves (M-H) from $-50$ to 50 kOe were measured at several temperatures for the sample deposited at 280 °C. In Fig. 4(a), we display the M-T curves measured for a series of thin-film samples deposited at different temperatures. Both the ZFC and FC curves exhibit a bump around 100 K indicating a magnetic transition. Then comparing the M-T curves for the samples deposited at 260, 280, and 300 °C, it can be seen that the difference between the FC and ZFC curves significantly narrows when the deposition temperature rises to 300 °C.

The M-H curves measured at 100 K and 300 K can be seen in Fig. 4(b) and they display a typical ferro- or ferrimagnetic hysteresis loop. Magnetization does not fully saturate at 50 kOe reaching a value of 96 emu/cm$^3$ at 300 K. This is in good agreement with the 80–100 emu/cm$^3$ room temperature magnetization reported for nanoparticles,\textsuperscript{2,22} at 70 kOe and the 100 emu/cm$^3$ saturation magnetization reported for epitaxial thin films.\textsuperscript{1} The diamagnetic contribution of the silicon substrate has been subtracted from the data point by point. The values for magnetization (emu/cm$^3$) were calculated against the sample volume, estimated from the measured surface area of the sample and the film thickness determined by XRR.

In $\varepsilon$-$\mathrm{Fe}_2\mathrm{O}_3$ nanoparticles, the magnetic transition at 110 K from a high-temperature ferrimagnetic structure to a complex low-temperature incommensurate magnetic structure is associated with a significant decrease in coercivity.\textsuperscript{21,22} At room temperature coercive field, values as high as 20 kOe...
The field-dependent magnetization does not saturate and reaches 96 emu/cm$^3$ on various substrate surfaces without the need for lattice-matching; the as-deposited films are moreover appreciably stable in ambient air. The different growth mechanisms and the precursors employed often lead to dissimilarities in the film properties so far reported for depositing ε-Fe$_2$O$_3$ thin films as well when having the eye on the phase. Also, the deposition temperatures are very different in the two gas-phase deposition techniques, i.e., in the range of 260–300 ºC for our ALD process while ∼800 ºC for the reported PLD process. As for the magnetic characteristics, the RT high-field magnetization of the ALD grown samples (96 emu/cm$^3$) closely matches the saturation magnetization of the epitaxially grown PLD films (100 emu/cm$^3$). $H_C$ was higher for the epitaxial thin film grown on the lattice-matching SrTiO$_3$(100) substrate by PLD (3–8 kOe) than for our only slightly oriented polycrystalline ALD ε-Fe$_2$O$_3$ films grown on silicon (∼1.6 kOe). All in all, the most important notion is that ALD enables much milder deposition conditions than PLD and does not require a lattice matching substrate; ALD is moreover already widely used in industry which makes it a highly feasible deposition technique for ε-Fe$_2$O$_3$ films as well when having the eye on the potential applications.

In conclusion, we have successfully developed a simple ALD process to fabricate magnetic ε-Fe$_2$O$_3$ thin films at relatively low temperatures around 100 K, the strong reduction in the coercive field was not detected in the M-H curves measured. Even though the M-T curve showed a sign of a magnetic transition around 100 K, the strong reduction in the coercive field was not detected in the M-H curves measured. This might be due to the relatively large particle size of ∼120 nm in the films or other factors such as differences in film thickness, roughness, or impurities. $H_C$ at 300 K was ∼1.6 kOe which is much lower than the values (3–8 kOe) reported for epitaxial thin films grown by PLD. For our thin films, the coercive field was found to increase towards lower temperatures (Fig. 4(b), inset), which is typical for ferrimagnetic materials. In earlier studies, the asymmetry in the M-H loops was taken as an indication and measured for the γ-Fe$_2$O$_3$ impurity in the thin-film and nanoparticle samples. Here, for our ALD thin films, the hysteresis loops are very symmetric and thus it seems that the samples are of the essentially pure ε-Fe$_2$O$_3$ phase.

In Table I, we compare our ALD process with the two other thin-film processes, i.e., ED and PLD, so far reported for depositing ε-Fe$_2$O$_3$ thin films. Unlike ED, ALD and PLD are both gas-phase processes where no solvent is needed. The main difference between ALD and PLD is the way the films are formed; in PLD the material growth starts with the laser excited material condensation, whereas in ALD the gas-surface reactions between the precursor molecules form new chemical bonds. The different growth mechanisms and the precursors employed often lead to dissimilarities in the end products, such as in the crystal structure. With the PLD process, it was not possible to deposit ε-Fe$_2$O$_3$ films on Si(100), MgO, or yttria-stabilized zirconia substrates but only on SrTiO$_3$ with the better lattice parameter match with the ε-Fe$_2$O$_3$ phase. Also, the deposition temperatures are very different in the two gas-phase deposition techniques, i.e., in the range of 260–300 ºC for our ALD process while ∼800 ºC for the reported PLD process. As for the magnetic characteristics, the RT high-field magnetization of the ALD grown samples (96 emu/cm$^3$) closely matches the saturation magnetization of the epitaxially grown PLD films (100 emu/cm$^3$). $H_C$ was higher for the epitaxial thin film grown on the lattice-matching SrTiO$_3$(100) substrate by PLD (3–8 kOe) than for our only slightly oriented polycrystalline ALD ε-Fe$_2$O$_3$ films grown on silicon (∼1.6 kOe). All in all, the most important notion is that ALD enables much milder deposition conditions than PLD and does not require a lattice matching substrate; ALD is moreover already widely used in industry which makes it a highly feasible deposition technique for ε-Fe$_2$O$_3$ films as well when having the eye on the potential applications.

In conclusion, we have successfully developed a simple ALD process to fabricate magnetic ε-Fe$_2$O$_3$ thin films at relatively low temperatures around 260–300 ºC from low-cost precursors, FeCl$_3$, and water. Our ALD process yields high-quality polycrystalline ε-Fe$_2$O$_3$ films in a reproducible manner on various substrate surfaces without the need for lattice-matching; the as-deposited films are moreover appreciably stable in ambient air. The field-dependent magnetization does not saturate and reaches 96 emu/cm$^3$ at 50 kOe at room temperature in line with previous studies. The magnetic coercive field value of ∼1.6 kOe measured for the films perpendicular to the thin-film plain is reasonable for polycrystalline films. We believe that our results are of interest in both a fundamental scientific
and a more practical sense, as the type of synthesis routes for the rare but exciting ε-Fe₂O₃ phase have been very much limited. In particular, considering the fabrication of ε-Fe₂O₃ in the thin-film form, we like to emphasize that the industrially feasible ALD technique could indeed provide us with a number of advantageous features to be explored in future studies.

See supplementary material for the process optimization and XRD analysis.

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