Magnetic and Electrical Performance of Atomic Layer Deposited Iron Erbium Oxide Thin Films

Aile Tamm, Kristjan Kalam, Helma Seemen, Jekaterina Kozlova, Kaupo Kukli, Jaan Aarik, Joosep Link, Raivo Stern, Salvador Dueñas, and Helena Castán

INTRODUCTION

Mixtures of rare earth ferrites have been of interest due to their attractive optical, electrical, and magnetic properties. Herewith some hexagonal orthoferrites RFεO₃, where R denotes a trivalent rare earth cation, such as YbFeO₃ or single-crystal LuFeO₃, have been described as materials demonstrating recordable ferroelectric polarization. The latter ternary ferrites below 120 K. Moreover, polarization in both epitaxial or using precursor materials of the highest purity, presumably challenging and has been attempted scarcely. Iron oxide (Er—Fe—O) thin films have been grown earlier by atomic layer deposition (ALD) using either a cyclopentadienyl-type precursor for erbium, carbonyl-type precursor for iron, and ozone for oxygen or β-diketonates of erbium and iron, and ozone. The material to be magnetized has been grown initially in the form of a double layer, comprising a 9 nm thick Er₂O₃ deposited at 200 °C, followed by the deposition of 14 nm thick FeO at 350 °C. The stack was subsequently annealed and recrystallized as ternary solids, e.g., ErFeO₃, ErFe₂O₄, and Er₃Fe₅O₁₂, evidently after solid-state reaction at 850 °C. The appearance of certain ferromagnetic moment in the film at room temperature was recorded. These films were not yet characterized electrically.

In the present study, the thin films containing iron and erbium oxides were grown by atomic layer deposition using ErFeO₃, obtained by sonochemical method from Fe(CO)₅ and rare earth carbonate precursors, exhibited almost insignificant magnetization hysteresis at room temperature. Deteriorating effect on the magnetic coercivity of secondary phases and concurrent reversed domains appearing upon increase in the growth rate was demonstrated in the case of otherwise single-crystal ErFeO₃ grown by the floating-zone method.

Synthesis of thin erbium ferrite films at low temperatures, possessing defined electric and magnetic properties, is thus presumably challenging and has been attempted scarcely. Iron oxide (Er—Fe—O) thin films have been grown earlier by atomic layer deposition (ALD) using either a cyclopentadienyl-type precursor for erbium, carbonyl-type precursor for iron, and ozone for oxygen or β-diketonates of erbium and iron, and ozone. The material to be magnetized has been grown initially in the form of a double layer, comprising a 9 nm thick Er₂O₃ deposited at 200 °C, followed by the deposition of 14 nm thick FeO at 350 °C. The stack was subsequently annealed and recrystallized as ternary solids, e.g., ErFeO₃, ErFe₂O₄, and Er₃Fe₅O₁₂, evidently after solid-state reaction at 850 °C. The appearance of certain ferromagnetic moment in the film at room temperature was recorded. These films were not yet characterized electrically.

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tris(2,2,6,6-tetramethyl-3,5-heptanedionato)erbium (Er(thd)₃) and Fe(C₅H₅)₂ (FeCp₂) as metal precursors, and O₃ as an oxygen precursor. The films were grown both mixtures and laminate-like stacks of iron and erbium oxides using sequential deposition of just a few layers for constituent oxides, or using tens of cycles for every separate layer of erbium and iron oxides. Composition, structure, and magnetic and electrical behavior of the films were examined.

## RESULTS AND DISCUSSION

### Film Growth, Morphology, and Structure.

On planar SiO₂/Si substrates, the Er₂O₃ and Fe₂O₃ reference films were grown to the thicknesses of 4.0 ± 0.5 and 20.9 ± 0.1 nm after 1000 growth cycles, respectively. Thus, the average growth rates of constituent oxides separately were 0.004 and 0.021 nm/cycle for Er₂O₃ and Fe₂O₃ films, respectively. One can note marked differences in the film growth, evidently affected by the choice of reactor conditions, including growth temperature, oxidizing agents, and deposition cycle time parameters. In an earlier study devoted to ALD of Fe₂O₃ from FeCp₂ and O₃, the growth rates reached 0.09–0.12 nm/cycle were measured. In this study, however, the metal precursor and ozone pulse lengths were extended to truly high values, over 40 and 200 s, to achieve saturation in growth rate versus precursor pulse length dependences. The growth temperature was also rather low, 200 °C. Yet, in another process, where very short precursor pulses, i.e., 2 s for ferrocene and only 0.2 s for ozone, were used, the growth rate of iron oxide was 0.022 nm/cycle at 200–220 °C, which is well comparable to the rate observed in our present study. Somewhat surprisingly, the growth rates of the Fe₂O₃ films registered in the present study are inferior to those observed earlier in an ALD process using FeCp₂ and oxygen as Fe₂O₃ precursors under analogous conditions. In the latter study, where the ferrocene and oxygen pulse lengths were 3 and 7 s, respectively, Fe₂O₃ films grew with the rate of 0.14 nm/cycle at temperatures comparable to that applied in the present study. By contrast, a growth per cycle of 0.03–0.04 nm has been obtained for the FeCp₂–O₃ process at 400 °C. Most importantly, it has been revealed that the incubation time that depends on substrate pretreatment might exceed even 200 cycles in this ALD process on the SiO₂/Si substrates. This explains why the growth rates obtained in different experiments and for different kind of structures differ significantly. For instance, the growth rate 0.1 nm per cycle was obtained for the Fe₂O₃ sublayers deposited in the present work by applying 20 FeCp₂–O₃ cycles after 300 Er(thd)₃–O₃ cycles (Table 1). Earlier also, the Er₂O₃ films have been grown with a higher rate, 0.235 nm/cycle, from Er(thd)₃, and O₃ precursors at 300 °C. In the latter study, a deposition reactor enabling higher gas flow rates were exploited, and 2.5 s long ozone pulses after 1.25 s long metal precursor pulses were applied. Thus, depending on the reactor conditions and the choice of cycle time parameters, certain diversity appears concerning the growth rate of the target material. In the case of multicomponent materials, one has to consider the experimental results characteristic of a particular setup, taking into account the largest variations expected to occur during the first deposition cycles of one oxide onto another.

The marked difference in the growth rates of constituent oxides later necessitated the application of much higher amounts of Er₂O₃ growth cycles, compared to those for Fe₂O₃ to deposit multilayer-like structures consisting of distinctive Er₂O₃ and Fe₂O₃ layers. The X-ray fluorescence (XRF) analysis revealed that the cycle ratio of 50:5 or 60:3 resulted in the highest Er/Fe atomic ratios, which were still markedly lower than that for the stoichiometric erbium ferrite FeErO₃ (Table 1). One should consider that, in the case of ALD, few deposition cycles, such as 1–5 applied here for the growth of each Fe₂O₃ layer, do not suffice for the formation of chemically and structurally defined single metal oxide, but result in the growth of a discontinuous submonolayer of metal oxide. As a consequence, this should result in a mixture of oxides rather than a multilayer structure. Further, taking into account that tens of erbium oxide deposition cycles applied between iron oxide deposition cycles resulted in films containing more than 2 times lower amounts of erbium compared to iron, the films deposited cannot be regarded as nanolaminates (multilayers) but rather the mixtures of two different metal oxides. In the case of relatively low amounts of Er₂O₃ applied, the films may even be regarded as those of erbium (oxide) doped iron oxides.

### Table 1. Growth Cycle Ratios, Er/Fe Atomic Ratios Determined by X-ray Fluorescence (XRF), and Thicknesses, Measured with Spectroscopic Ellipsometry, of Er₂O₃:Fe₂O₃ Films Deposited on Planar SiO₂/Si Substrates

| cycle ratio notation | growth cycle sequence | Er/Fe cation ratio | thickness on Si (nm) |
|----------------------|-----------------------|-------------------|----------------------|
| (1:1)                | 500 × (1 × Er₂O₃ + 1 × Fe₂O₃) | <0.002 | 65.1 ± 0.1 |
| (3:1)                | 200 × (3 × Er₂O₃ + 1 × Fe₂O₃) | 0.02 | 56.6 ± 0.1 |
| (60:3)               | 20 × (60 × Er₂O₃ + 3 × Fe₂O₃) | 0.46 | 5.2 ± 0.1 |
| (50:5)               | 22 × (50 × Er₂O₃ + 5 × Fe₂O₃) | 0.30 | 19.5 ± 0.1 |
| (50:1)               | 20 × (50 × Er₂O₃ + 1 × Fe₂O₃) | 0.26 | 14.9 ± 0.2 |
| (30:20)              | 2 × (300 × Er₂O₃ + 20 × Fe₂O₃) + 300 × Er₂O₃ | 0.18 | 5.7 ± 0.1 |

Scanning electron microscopy (SEM) images demonstrated that the surfaces of Er₂O₃:Fe₂O₃ films were quite smooth without significant features referring to a polycrystalline structure (Figure 1). The morphology of the films obviously depended somewhat on the growth recipe. High relative amounts of Er₂O₃ growth cycles (Er₂O₃:Fe₂O₃ cycle ratios of 60:3 and 50:1) resulted in amorphous and, consequently, smoother films compared to those grown using low amounts of Er₂O₃ growth cycles (1:1). The bird-eye SEM images visually implied certain tiny grainlike features on the surface of the films grown using cycle ratios 50:1 and 50:5. These are not, however, to be taken as direct indications of the crystal growth, but rather small-sized agglomerations of disordered material often visible on the images taken from X-ray amorphous film surfaces. As will later be seen from the X-ray diffraction (XRD) data, the crystal structure is not fully formed in these films. It should also be taken into account, that the film thicknesses are not to be necessarily and directly compared to each other based just on the numbers of constituent oxide cycles because the nucleation delays for the constituents and their corresponding growth rates at the early growth stages may differ considerably. The detailed and, thus, extensive studies of these effects remained beyond the scope of this work. However, an amorphous film
was grown to a relatively high thickness exceeding 50 nm using the Er2O3:Fe2O3 cycle ratios of 3:1 specifically to examine the possibility to grow oxides, using that particular precursor chemistry, onto three-dimensionally (3D) designed silicon-based substrates. As one can see in Figure 1, the film could be grown along the depth of ca. half micrometer in trenches built into a silicon wafer substrate with the aspect ratio 20:1, with certain amount of the growing material reaching the bottom of the trenches, although the nucleation of the solid layer was apparently not uniform throughout the whole depth.

X-ray diffraction studies on the films with very low Er content, i.e., on the films grown using Er2O3:Fe2O3 cycle ratios of 1:1 on SiO2/Si, clearly revealed a crystal growth (Figure 2). For this film, the reflections can be indexed considering only the rhombohedral hematite phase of iron oxide (PDF card 033-0664). One may actually consider also multiphase, more disordered, nature of the film with contribution from iron oxide phases with similar stoichiometry but different lattice, such as that of the hexagonal Fe2O3 with reflections 017, 116, and 204 at 24.6, 33.8, and 36.46°, respectively (PDF card 040-1139), which actually more precisely coincide with the centers of the gravity of the reflection peaks registered. Trace reflections from orthorhombic Fe2O3 with 020 at 36.19° (PDF card 047-1409) may be considered as well. However, it is worth noting that the same films grown on ca. 5 nm thick TiN layer (Figure 2) were also crystallized, whereas the locations of the reflections gave better fit with those of hematite. The iron-free Er2O3 film grown to the thickness of 4 nm was obviously not entirely amorphous but exhibited a nanocrystalline nature with a broad peak around 29.5−30° (Figure 2). Small thickness of the film was evidently the main reason for the small size of crystallites leading to this kind of diffraction pattern. Further, the films grown with cycle ratios allowing larger, measurable, erbium-to-iron cation ratios occurred essentially amorphous. Exceptionally, the film grown with the Er2O3:Fe2O3 cycle ratio of 50:5 demonstrated a pattern with a broad peak at around 33.2°, which just may be attributed to the 112 reflection from ErFeO3 (PDF card 047-0072), and thus allowing one to consider partial formation of the nanocrystalline erbium ferrite phase. The phase determination here remains ambiguous and, in fact, incomplete. The broad band formed between 30 and 35° in the diffractionogram of the film grown with the cycle ratio of 50:5 allows one to consider the formation of a multiphase nanostructure and nucleation of iron-rich ErFe2O4 and/or Er2Fe5O12 (ICPDS card 023-0240) phases. This may occur possibly also because of the excess of iron content in accord with the measured Er/Fe atomic ratio (see Table 1). The appearance of the latter iron-rich phases was considered possible also in the ALD-grown Er–Fe–O films earlier.8

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**Figure 1.** Bird-eye scanning electron microscopy images of as-deposited Er2O3:Fe2O3 films with cycle ratios of 1:1, 50:5, 50:1, and 300:20, indicated by labels, and cross-sectional image of the as-deposited Er2O3:Fe2O3 films with cycle ratio 3:1 into a three-dimensionally configured substrate with the trench aspect ratio of 20:1.

**Figure 2.** Grazing incidence X-ray diffraction (GIXRD) patterns of Er2O3:Fe2O3 films on SiO2/Si substrate (upper panel), and on TiN/Si substrate (lower panel). Also shown is the pattern measured from the 4 nm thick reference Er2O3 film (upper panel). The cycle ratios (Er2O3:Fe2O3) are denoted by labels (see Table 1). The reflections are denoted with Miller indexes corresponding to hematite, cubic Er2O3, and orthorhombic ErFeO3.
Magnetic and Electric Behavior. Magnetic measurements were performed with the magnetic field applied in plane of the surface of the substrate for the Er$_2$O$_3$:Fe$_2$O$_3$ films. The structures demonstrated a ferromagnetic-like behavior at room temperature with saturation magnetization (Figure 3).

![Figure 3](Image)

The capacitance–voltage (C–V) curves are, in a satisfactory approximation, characteristic of those commonly seen with metal–insulator–metal (MIM)-like structures with quite leaky dielectric layers, i.e., with certain plateau tending to appear around zero bias voltages, and further deviations in the effective capacitance with increase in the absolute bias values. In the present case, the decrement of capacitance at larger biases is obvious, especially in the films with relatively low thicknesses, i.e., those grown with the cycle ratios 300:20, 60:3, or 50:1. One can propose that capacitance is in obvious, especially in the films with relatively low thicknesses, i.e., those grown with the cycle ratios 300:20, 60:3, or 50:1. One can propose that capacitance is in

One could see that the films containing Er$_2$O$_3$ and Fe$_2$O$_3$ layers deposited using relatively large amounts of growth cycles separately for constituent oxides, i.e., 300 cycles for Er$_2$O$_3$ and 20 cycles for Fe$_2$O$_3$, demonstrated a markedly stronger magnetization than the more homogeneously mixed Er–Fe–O films. The saturation magnetization in the film denoted with the cycle ratio (300:20) was 5.3 emu/m$^2$, i.e., 10 times higher than that in the mixed/doped Er$_2$O$_3$:Fe$_2$O$_3$ films, regardless of the lower thickness compared to that of the films with a more uniform distribution of erbium.

It is known that the magnetic properties of nanostructures can, besides chemical composition, markedly depend on defects, morphology, phase, and growth recipe. The magnetization in the composites or mixtures containing iron oxide could be enhanced by increasing the relative content of iron oxide in the materials deposited, as we have observed, for instance, in Bi$_2$O$_3$–Fe$_2$O$_3$ films grown by ALD or Fe$_3$O$_4$–MgO by ALD. It is likely that in our most strongly magnetized sample, the Fe$_2$O$_3$ interlayers, despite their X-ray amorphous nature, were still formed as stoichiometric iron oxides, although in a short-range order only, thereby giving the most prominent magnetic response in this sample series. It is to be noted that in ErFeO$_3$ films with a defined structure grown by pulsed laser deposition, certain magnetization-field hysteresis was registered at 130 K at the highest. Further, in the films grown in the present study, the monotonic relationship between the Er/Fe cation ratio and the magnetization was not recognized (see Figure 3). The Er–Fe–O films deposited by ALD earlier have demonstrated a somewhat analogous magnetization-field behavior with saturation magnetization not exceeding 30% from that of iron oxide. In the latter study, however, the coercivity was somewhat better defined, approaching 1 T.

In Figure 4, the capacitance–voltage curves measured from the metal–insulator–metal (MIM)-type capacitor structures are depicted.

Figure 4. Capacitance–voltage curves of Al/Ti/Er$_2$O$_3$:Fe$_2$O$_3$/TiN/Ti/Si capacitor structures containing Er$_2$O$_3$:Fe$_2$O$_3$ films deposited using constituent oxide cycle ratios indicated by labels, measured at 100 kHz.

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via a sequential deposition of the constituent compound materials.

Assuming that the oxide film does form the thickest part of capacitive stack of layers and thus dominates in the series of capacitors, it is still possible to roughly estimate the average permittivity of the oxide-based films, taking into account the capacitance values recorded at alternating current component of the applied voltage at zero bias. The relative permittivity of the stacked material can then simply be calculated taking into account the parallel-plate capacitor model. It is thereby also to be considered that the permittivity calculated in this manner does not reflect the physical property of the metal oxide layer alone, but it is deviated by the charge-polarized and concurrent fields built up at the interface layers. Therefore, the permittivity calculated from the capacitance measured must be lower than the one truly characteristic of the metal oxide layer, and the detrimental effect of the interfaces must increase with decrease in film thickness. Nevertheless, the estimated permittivities for the 5, 19.5, and 14.9 nm thick films grown using the cycle ratios of 300:20, 50:5, and 50:1 (see Figure 5) were as high as 9.4, 20.6, and 25.3, respectively, at zero bias and 100 kHz. In these films, the relative content of erbium was high enough to allow at least partial formation of the iron-rich ferrite phases (see Figure 2). Of course, one cannot exclude the interference of leakage, as was noted above, which may, as opposed to the permittivity, deviate from the charge-polarized fields built up at the interface layers. Therefore, the permittivity calculated from the capacitance measured must be lower than the one truly characteristic of the metal oxide layer, and the detrimental effect of the interfaces must increase with decrease in film thickness. Nevertheless, the estimated permittivities for the 5, 19.5, and 14.9 nm thick films grown using the cycle ratios of 300:20, 50:5, and 50:1 (see Figure 5) were as high as 9.4, 20.6, and 25.3, respectively, at zero bias and 100 kHz. In these films, the relative content of erbium was high enough to allow at least partial formation of the iron-rich ferrite phases (see Figure 2). Of course, one cannot exclude the interference of leakage, as was noted above, which may, as opposed to the effect of interface layers, give rise to the apparent capacitance as measured. Further, the permittivity of the amorphous 5.2 nm thick film grown with the cycle ratio of 60:3 was only 2.3. Note, that the currents through the stacks are to be considered as factors able to affect the charge polarization at the layer interfaces.

Polarization charge vs applied voltage (P–V) characteristics measured on Al/Ti/Er2O3:Fe2O3/TiN/Ti/Si/Al structures in Sawyer–Tower circuit are shown in Figure 7.
the effectively measurable polarization in the material deposited, is drifting in the material under external field and becomes trapped at the interfaces between metal oxide and the electrode layers, causing interfacial polarization. Consequently, the electrical charge becomes carried to and trapped at the interface layer under certain polarity, and an opposite polarity with increasing, oppositely directed, field is required to release the charge from the traps, which is the main cause for the apparently spontaneous charge polarization between 0.8 and 1.8 nC over an electrode with an area of 0.024 mm². On the other hand, somewhat analogous polarization-field behavior has been observed and recorded for pulsed laser-deposited hexagonally structured ErFeO₃ films and, together with magnetization behavior, was designated as a signature of the multiferroic performance of that material.

**CONCLUSIONS**

In summary, the atomic layer deposition of Er₂O₃:Fe₂O₃ thin films with Er/Fe atomic ratios up to 0.46 was realized. All of the samples exhibited saturation magnetization and charge polarization measured at room temperature. Promising results in terms of the simultaneous appearance of internal magnetization and certain electrical charge polarization were demonstrated in planar Er₂O₃:Fe₂O₃ structures. Further electrical and magnetic modeling and analysis will be needed to elaborate the phenomenon and optimize the material structure for magnetoelectric performance.

**EXPERIMENTAL SECTION**

The films were deposited in a flow-type in-house built hot-wall ALD reactor using Er(thd)₃ and FeCp₂ as metal precursors and O₃ as an oxygen precursor. N₂ (99.999%) was used as the carrier and purge gas. In all of the cases, an ALD cycle was started with a metal precursor pulse and continued with a purge of the reaction zone with pure carrier gas, followed by oxygen precursor pulse and another purge. To obtain sufficient precursor pressures, the Er(thd)₃ source temperature was set at 160 °C and FeCp₂ source was set at 60 °C. The Er₂O₃:Fe₂O₃ films and laminate structures were grown at 375 °C by applying certain numbers of constituent binary oxide growth cycles alternately (Table 1). The cycle times were 5−5−5−5 s for the sequence of metal precursor pulse−purge−ozone pulse−purge. To obtain films with different composition starting with very light doping and ending with almost laminated structures, the ratio of the cycle numbers used for the deposition of Er₂O₃ and Fe₂O₃ was varied keeping the total number of cycles approximately at the same level for all of the samples. The substrate temperature of 375 °C was chosen to achieve appreciable compromise between the temperatures suited to both metal precursors. β-Diketonates are expected to decompose thermally rather intensely at 400 °C and higher temperatures, whereas the reactivity of ferrocene and, concurrently, the growth rate of iron oxide would decrease notably with the decrease in substrate temperature below 350 °C.

The mass thickness and elemental composition of the films were measured by X-ray fluorescence spectroscopy method using ZSX400 (Rigaku) spectrometer. For the calibration of the measurement procedure, we used binary Er₂O₃ and Fe₂O₃ films with known thicknesses and densities determined by the X-ray reflection (XRR) method. Grazing incidence X-ray diffraction (GIXRD) was applied for structural studies, and all of the XRD and XRR studies were carried out with Smartlab (Rigaku) X-ray analyzer using Cu Kα radiation. In addition, thicknesses of a series of films with different compositions were determined using GESSE (Sopra-Semilab) spectroscopic ellipsometer. The morphology of nanostructures on the Si substrate and on three-dimensional (3D) substrates were investigated by scanning electron microscopy (SEM) using a Dual BeamVR equipment Helios NanoLab 600 (FEI) equipped with a focused ion beam (FIB) module. The FIB was employed for the preparation of samples on the 3D-configured substrate stack.

The films grown on Si substrates (Table 1) were subjected to magnetic measurements. The measurements were performed by using a vibrating sample magnetometer option of a physical property measurement system 14 T (Quantum Design). Rectangular samples with dimensions of around 5 × 4 mm² were fixed with general electric varnish on the commercial quartz sample holders (Quantum Design). The magnetization was measured at room temperature (350 K) and in the presence of a magnetic field of 79.6 kA/m parallel to the film surface. Magnetization isotherms were measured by scanning the magnetic fields from −4800 to +4800 kA/m. The films subjected to magnetometry were grown on nondoped silicon without an additional TiN electrode layer. This was to avoid possible interferences by magnetization signal and noise from the substrates. The diamagnetic signal arising from the pure silicon substrate was subtracted from the general magnetization curve for all of the samples in which ferromagnetic-like response was detected.

To carry out the electrical measurements, metal−insulator−metal (MIM) structures were prepared. Silicon substrates with 5 nm thick TiN layers grown by chemical vapor deposition were used as bottom electrodes. Top electrodes with an area of 0.204 mm² were formed by the electron beam evaporation of 30 nm thick Ti layers directly in contact with Er–Fe–O film, followed by the evaporation of 120 nm thick Al on Ti through a shadow mask. The electrical characterization techniques used were capacitance−voltage (C−V) and current−voltage (I−V) measurements. The electrical measurements were done by means of an Agilent DSO-X 3104 digital oscilloscope with a built-in wave generator. The standard Sawyer−Tower experiment was carried out by applying a periodic triangular stimulus and recording the voltage loops data from the oscilloscope. The charge values were obtained from the sensed voltage across a stated capacitance.

**AUTHOR INFORMATION**

Corresponding Author
E-mail: aile.tamm@ut.ee.

ORCID
Aile Tamm: 0000-0002-0547-0824

Notes
The authors declare no competing financial interest.

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