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Published in:
ACS Applied Materials and Interfaces

DOI:
10.1021/acsami.0c04665

Published: 13/05/2020

Document Version
Publisher's PDF, also known as Version of record

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Flexible $\varepsilon$-Fe$_2$O$_3$-Terephthalate Thin-Film Magnets through ALD/MLD

Anish Philip, Janne-Petteri Niemelä, Girish C Tewari, Barbara Putz, Thomas Edward James Edwards, Mitsuru Itoh, Ivo Utke, and Maarit Karppinen*

ABSTRACT: Pliable and lightweight thin-film magnets performing at room temperature are indispensable ingredients of the next-generation flexible electronics. However, conventional inorganic magnets based on f-block metals are rigid and heavy, whereas the emerging organic/molecular magnets are inferior regarding their magnetic characteristics. Here, we fuse the best features of the two worlds, by tailoring $\varepsilon$-Fe$_2$O$_3$-terephthalate superlattice thin films with inbuilt flexibility due to the thin organic layers intimately embedded within the ferrimagnetic $\varepsilon$-Fe$_2$O$_3$ matrix; these films are also sustainable as they do not contain rare heavy metals. The films are grown with sub-nanometer-scale accuracy from gaseous precursors using the atomic/molecular layer deposition (ALD/MLD) technique. Tensile tests confirm the expected increased flexibility with increasing organic content reaching a 3-fold decrease in critical bending radius ($2.4 \pm 0.3$ mm) as compared to $\varepsilon$-Fe$_2$O$_3$ thin film ($7.7 \pm 0.3$ mm). Most remarkably, these hybrid $\varepsilon$-Fe$_2$O$_3$-terephthalate films do not compromise the exceptional intrinsic magnetic characteristics of the $\varepsilon$-Fe$_2$O$_3$ phase, in particular the ultrahigh coercive force ($\sim 2$ kOe) even at room temperature.

KEYWORDS: flexible magnet, atomic layer deposition, molecular layer deposition, $\varepsilon$-Fe$_2$O$_3$ organic superlattice, thin film

1. INTRODUCTION

Research on flexible magnets is inspired by the strong drive to make consumer electronics thin, lightweight, and wearable; such next-generation flexible electronics should be shapeable into any arbitrary configuration depending on the intended use.\(^1-3\) Progress in the flexible electronics has already opened the door to plethora of advanced applications such as wearable solar cells,\(^4\) flexible transparent electrodes,\(^2\) biocompatible electronic devices,\(^5\) stretchable energy harvesters,\(^6,7\) full color displays,\(^3\) and flexible optoelectronic devices.\(^1\) Because magnets are inevitable components of electronics, development of new types of thin-film magnets with inbuilt flexibility is an urgent challenge.

The pioneering works by Miller et al.\(^5,6\) opened up research on organic/molecular magnets,\(^7-12\) forming the bases for the currently available lightweight and flexible magnets. The organic components in these magnets provide other benefits as well, such as low-temperature processing, critical-element-free composition, and transparency.\(^7,11-13\) For the fabrication of flexible magnetic thin films in particular, two main strategies have been envisioned: (i) nanocomposites comprising traditional inorganic magnetic materials and a polymer substrate\(^14\) or polymeric fillers,\(^15\) and (ii) organic/molecular materials\(^10,11,16\) grown using solution-based\(^7\) or gas-phase\(^10,11,16\) deposition techniques. The multistep and often harsh solution-based reaction pathways used in the first approach are not optimal for the fabrication of conformal, homogeneous, and solvent-free magnetic thin films required in practical applications. The second approach, on the other hand, is more likely to yield high-quality homogeneous thin films, but the organic/molecular magnets based on s- or p-orbital spins typically suffer from weak magnetization/low coercivity field,\(^7,10,11,16\) low magnetic transition temperature,\(^7,9,17\) structural disorder,\(^18\) and/or instability.\(^7,11,19\) In applications such as magnetic storage devices, hard magnets would confer to the better stability of stored data; for this, coercive field values higher than 100 Oe are desirable,\(^8,12\) which has not been achieved with the current organic/molecular magnets.

Here, we present a novel approach to the flexible room-temperature magnets; we fabricate inorganic–organic superlattice (SL) thin-film structures using the currently strongly emerging atomic/molecular layer deposition (ALD/MLD) technique,\(^20-25\) which combines the leading ALD (atomic layer deposition)\(^26-28\) technology of advanced inorganic thin films and its less exploited MLD (molecular layer deposition)\(^29,30\) counterpart for purely organic films. Our choice for

Received: March 11, 2020
Accepted: April 23, 2020
Published: April 23, 2020
the inorganic component is ε-Fe₂O₃. This uncommon Fe(III)-
oxide polymorph possesses the most intriguing magnetic
properties, i.e., ferrimagnetism with a Curie temperature as
high as ca. 500 K and a remarkably large coercive field (even
up to 20 kOe at room temperature)²¹,²² and on top of that, strong
magnetoelectric coupling. Moreover, like iron oxides in general, it is nontoxic and biocompatible and consists of Earth-abundant elements only.

The issue with the ε-Fe₂O₃ phase lies in its narrow stability
window; it is nearly nonexistent in nature and challenging to
artificially synthesize except in certain nanoscale samples.²³ The basis for the present work is in our recent success in
developing a facile ALD process for high-quality ε-Fe₂O₃ thin
films, which are free from the other Fe₂O₃ polymorphs, α-
Fe₂O₃ (hematite), β-Fe₂O₃, and γ-Fe₂O₃ and the magnetite
Fe₃O₄. These ε-Fe₂O₃ films grown from FeCl₃ and H₂O
precursors in the temperature range 280–300 °C are perfectly stable in ambient air (even at elevated temperatures) and
against insertion of organic layers through ML processes.²⁴ Here we will demonstrate for the first time the great potential of our
ALD/MLD-grown ε-Fe₂O₃-organic superlattices as flexible thin-film magnets. The regularly inserted organic layers enhance the mechanical properties of the films without compromising their unique magnetic properties. It should be emphasized that similarly to the parent ALD technology, the combined ALD/MLD method yields high-quality ultrathin films with atomic-level thickness control, large-area homogeneity, and conformality. These superior features derive from the way of introducing the gaseous evaporated precursors one after another into the reactor in sequential pulses to achieve the desired surface reactions. The well-controlled surface reactions moreover make the ALD/MLD method uniquely suited to the engineering of inorganic–organic SL structures with the required atomic/molecular level accuracy for the individual layer thicknesses.²⁵–⁴⁰

2. EXPERIMENTAL SECTION

All the thin-film depositions were carried out in a commercial flow-type hot-wall ALD reactor (F-120 by ASM Ltd.) using iron chloride (FeCl₃, Merck, 95%) deionized water and terephthalic acid (TPA; Tokyo Chemical Industry CO., Ltd., > 99.0%) as precursors. The two solid precursors, FeCl₃ and TPA, were placed inside the reactor in open boats and heated at 158 and 180 °C respectively, whereas the deionized water cylinder was placed outside the reactor. Nitrogen (N₂, 99.999%) was used both as the carrier gas and the purge gas between the precursor pulses; the N₂ flow rate was kept at 300 SCCM and the reactor pressure at 3–5 mbar. The depositions were carried out at 280 °C on silicon (100) (Okmetic Oy) substrates cut into 2.0 × 2.0 cm² pieces, washed with ethanol--water mixture and acetone, and dried prior to film deposition. The films for magnetic property studies were deposited on 50 µm thick polyimide substrates (Kapton 200HN) of 4.5 × 4.5 cm² with a total of five precut stripes. The polyimide substrates were washed with isopropyl alcohol and distilled water and dried before taking them for deposition. These substrates were also subjected to a 1 h wait time at 280 °C prior to deposition to outgas the residual water from the polyimide.

Each superlattice (SL) deposition consisted of ALD (FeCl₃+H₂O)
cycles for ε-Fe₂O₃, and MLD (FeCl₃+TPA) cycles for the molecular organic layers; the optimized precursor/purge pulse lengths were adopted from our previous work, i.e., 2 s FeCl₃/4 s N₂/1 s H₂O/3 s N₂ for the ALD cycles and 4 s FeCl₃/8 s N₂/25 s TPA/50 s N₂ for the MLD cycles.²⁴²⁵ The pulsing sequence followed the pattern: [(FeCl₃ + H₂O)n + (FeCl₃ + TPA)n] + (FeCl₃ + H₂O)m, where m stands for the number of (FeCl₃ + H₂O) ALD cycles applied for each individual ε-Fe₂O₃ layer, k (=1 in most of the experiments) stands for the number of (FeCl₃ + TPA) MLD cycles applied for each individual organic layer, and n defines the number of the organic/hybrid layer blocks in the SL structure in total; the number of the ε-Fe₂O₃ layer blocks is accordingly n + 1. In our ε-Fe₂O₃-TP (TP = terephthalate) SL samples n varies from 3 to 75 and m from 31 to 1000, see Table 1.

3. RESULTS AND DISCUSSION

We fabricated a series of ε-Fe₂O₃-organic thin films using terephthalic acid (TPA; benzene-1,4-dicarboxylic acid) as the organic precursor, according to the following overall deposition process: [(FeCl₃ + H₂O)n + (FeCl₃ + TPA)n] + (FeCl₃ + H₂O)m, where m stands for the number of (FeCl₃ + H₂O) ALD cycles applied for each individual ε-Fe₂O₃ layer, k (= 1 in most of the experiments) stands for the number of (FeCl₃ + TPA) MLD cycles applied for each individual organic layer, and n defines the number of the organic/hybrid layer blocks in the SL structure in total; the number of the ε-Fe₂O₃ layer blocks is accordingly n + 1. In our ε-Fe₂O₃-TP (TP = terephthalate) SL samples n varies from 3 to 75 and m from 31 to 1000, see Table 1.

3.1. Structural and Chemical Characteristics. All the depositions yielded visually high-quality homogeneous thin films. The expected SL structures were affirmed from the XRR (X-ray reflectivity) patterns, shown in Figure 1A for...
representative \(\varepsilon\)-Fe\(_2\)O\(_3\)-TP samples, and for a parent \(\varepsilon\)-Fe\(_2\)O\(_3\) film for comparison. In Figure 1A, intense regularly appearing SL peaks are clearly seen for all the films containing organic layers \((n > 0)\) but not for the parent \((n = 0)\) \(\varepsilon\)-Fe\(_2\)O\(_3\) film. Moreover, between the SL peaks, smaller oscillations can be seen, the number of which corresponds to the expected value of \(n\) (as far as can be counted before the oscillations start to overlap with each other), thus confirming the excellent controllability of our ALD/MLD process. In Table 1, we also give the film thickness values determined from the XRR data. Because the XRR technique works properly for relatively thin films only, we were not able to directly determine the thickness values for the films thicker than ca. 160 nm. For these thicker films, an approximation was calculated on the basis of the growth-per-cycle (GPC) values calculated for the thinner films (from the experimental thickness value and the number of deposition cycles applied). From XRD (X-ray diffraction) analysis, our \(\varepsilon\)-Fe\(_2\)O\(_3\)-TP SL films are all crystalline (Figure 1B); XRD patterns show the same diffraction peaks (002, 013, 122, 004, 015, 204, 006, and 205) but the intensities of these peaks slowly decrease with increasing \(n\), i.e. with a reduction of individual \(\varepsilon\)-Fe\(_2\)O\(_3\) layer thickness and an increase of organic layers. 34,35

The presence of the expected terephthalate moiety in the films was verified by both FTIR (Fourier transform infrared; Figure 1C) and Raman (Figure 1D) spectroscopy analyses. In the FTIR spectra, the well-known carboxylate-group fingerprint, i.e., symmetric \((\nu_s)\) and asymmetric \((\nu_a)\) stretching bands around 1400 and 1510 cm\(^{-1}\), respectively, is clearly seen for all the SL samples, with the intensity of these bands increasing with \(n\). From the splitting between the two bands, i.e., \((1510-1400)\) cm\(^{-1}\) = 110 cm\(^{-1}\), it can be concluded that the TP moieties are bound to the iron atoms in a bidentate binding mode. 42,43 Also seen from the FTIR spectra is that

<table>
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<tr>
<th>Sample</th>
<th>(n)</th>
<th>(k)</th>
<th>(m)</th>
<th>Total no. of ALD/MLD cycles ([m(n[n])]</th>
<th>Total film thickness ((\text{nm}))</th>
<th>Individual (\varepsilon)-Fe(_2)O(_3)-layer thickness ((\text{nm}))</th>
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<td>(n = 0) (62 nm)</td>
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<td>0</td>
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<tr>
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<td>0</td>
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<tr>
<td>(n = 3) (9 nm)</td>
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<td>150</td>
<td>603</td>
<td>39.8</td>
<td>9.3</td>
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<td>150</td>
<td>905</td>
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<td>1</td>
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<td>1207</td>
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<td>(n = 10) (9 nm)</td>
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<td>150</td>
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<tr>
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<td>1</td>
<td>150</td>
<td>2415</td>
<td>157.6</td>
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<tr>
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<td>1000</td>
<td>4003</td>
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<td>1</td>
<td>31</td>
<td>2431</td>
<td>160</td>
<td>2.0</td>
</tr>
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</table>

Table 1. Summary of the \([(\text{FeCl}_3+\text{H}_2\text{O})_m+\text{(FeCl}_3+\text{TPA})_k]_n+\text{(FeCl}_3+\text{H}_2\text{O})_m\) Films Investigated\(^a\)

Figure 1. Structural and chemical characterization data for representative \(\varepsilon\)-Fe\(_2\)O\(_3\)-TP SL films and for a parent \(\varepsilon\)-Fe\(_2\)O\(_3\) film for comparison: (A) XRR patterns, (B) XRD patterns, (C) FTIR spectra, and (D) Raman spectra; each sample is indicated with the number of organic layers \((n)\), and the individual \(\varepsilon\)-Fe\(_2\)O\(_3\)-layer thickness (in parentheses); \(k = 1\) for \(n > 0\), and \(k = 0\) for \(n = 0\).
intensities of the absorption bands due to $\varepsilon$-Fe$_2$O$_3$ in the range of 440–680 cm$^{-1}$ diminish with $n$, as expected.

Raman analysis complemented our understanding of the bonding scheme in our $\varepsilon$-Fe$_2$O$_3$-TP superlattices. The peaks seen in the Raman spectra (Figure 1D) at ca. 1420 and 1606 cm$^{-1}$ are due to the symmetric and asymmetric stretchings of the carboxylate group. The other bands due to the terephthalate group at ca. 290, 860, and 1140 cm$^{-1}$ can be assigned to the out-of-plane ring bending, the C–C stretching of the carboxylate group, and the superposition of ring breathing and in-plane bending of C–H. The band due to in-plane bending of aromatic C–H appears at 1305 cm$^{-1}$. The spectrum for our parent ($n = 0$) sample shows all the features expected for $\varepsilon$-Fe$_2$O$_3$. With an increase in the number of organic layers, the peaks due to $\varepsilon$-Fe$_2$O$_3$ decrease in intensity, whereas those from the organic moiety increase with $n$. We also like to mention that in our previous work, we confirmed with XPS that the films grown with the FeCl$_3$ + TPA process did not contain detectable amounts of elements other than iron, carbon, and oxygen. This rules out the possibility of chlorine contamination in our $\varepsilon$-Fe$_2$O$_3$-TP SL films.

We also investigated the surface morphology and grain size for our $\varepsilon$-Fe$_2$O$_3$-TP SL films in comparison to the parent $\varepsilon$-
Fe$_2$O$_3$ film using top-view SEM analysis (Figure 2). In the parent ε-Fe$_2$O$_3$ thin film the grains are uniform and well-shaped (Figure 2A). The effect of organic layers on the size and distribution of grains is illustrated in Figure S1. With the increasing number of organic layers (and decreasing thickness and distribution of grains is illustrated in Figure S1. With a further increase in $n$ beyond 30, the polydispersity is again reduced, and the grains become more uniform but with a different morphology and size compared to the case in the ε-Fe$_2$O$_3$ film. In the SL films with high organic contents, the grains are fewer and more segregated with nanogaps in between (Figure S2).

3.2. Magnetic Property Characteristics. Magnetic properties of both the parent ε-Fe$_2$O$_3$ and the ε-Fe$_2$O$_3$-TP SL films were investigated using a vibrating sample magnetometer (VSM). The film surface was set parallel to the applied magnetic field (H) during the magnetization (M) measurement, and isothermal $M$–$H$ curves were measured from −50 to +50 kOe at various temperatures from 10 to 300 K, see Figure 3. All the $M$–$H$ curves follow a hysteresis loop typical for ferrimagnetic materials; no perfect saturation is seen up to the magnetic fields measured, though. The magnetic characteristics for the parent ε-Fe$_2$O$_3$ film (e.g., coercivity ca. 2.1 kOe) are similar to those reported earlier.

For the superlattice ε-Fe$_2$O$_3$-TP films, with increasing number of organic layers (and decreasing ε-Fe$_2$O$_3$-layer thickness) the ferrimagnetic behavior is preserved up to $n = 75$ where the individual ε-Fe$_2$O$_3$ layers are as thin as 2 nm, even though the absolute magnetization naturally decreases when the content of nonmagnetic organic layers increases. From Figure 3, both the absolute magnetization and the coercivity field are essentially identical for the two samples, $n = 0$ (248 nm) and $n = 3$ (62 nm), and even up to $n = 20$ (individual ε-Fe$_2$O$_3$-layer thickness 11 nm) the coercivity field remains essentially the same at lower temperatures. However, for higher $n$ values an abrupt change in both magnetization and coercivity at room temperature was observed (Figure S3).

Indeed, our ε-Fe$_2$O$_3$-TP SL thin films retain their room-temperature hard-magnet characteristics (coercive field higher than 100 Oe) very well upon the addition of organic layers, see Figure 4 where we plot the coercivity values at different temperatures. For example, the $n = 20$ (11 nm) sample shows a coercivity field of 260 Oe at 300 K, still clearly above the critical limit. Even for the $n = 75$ (2 nm) sample with extremely thin ε-Fe$_2$O$_3$ layers the ferrimagnetism still exists below ca. 50 K, with significantly lowered coercivity values though.

Finally, we discuss an interesting detail concerning an asymmetry seen in the M–H loops. Namely, the field-cooled (FC) magnetization curves for ε-Fe$_2$O$_3$-TP SL films are shifted toward the negative side (Figure 5A), whereas for ε-Fe$_2$O$_3$, the loops measured under FC and ZFC (zero-field-cooled) conditions are identical and symmetric (Figure 5B). The difference between the positive and negative coercive field values were found to be high for all our ε-Fe$_2$O$_3$-TP SL samples at 10 K when the magnetization curves were measured under FC condition. For example, in case of the $n = 20$ (11 nm) sample, the negative and positive coercive field values with FC were $-10$ and 5.2 kOe, respectively; for the same sample under the ZFC conditions, the coercive field values were $-5.8$ and 5.7 kOe. The observed asymmetry in the FC $M$–$H$ curves could be attributed to an existence of exchange bias, which usually arises from the coupling of ferri-ferromagnetic and antiferromagnetic layers that can cause a unidirectional anisotropy in the ferri/ferromagnetic layer.49 We tentatively assume that the presence of a paramagnetic spacer (Figure S4) between ferrimagnetic ε-Fe$_2$O$_3$ layers might induce an indirect antiferromagnetic coupling of alternating layers, where the conjugate $\pi$ electrons of the terephthalate moieties play an important role.49,50 The interlayer exchange interaction arising from the spin polarization through the bridging terephthalate moieties can also favor antiferromagnetic ordering.50

3.3. Mechanical Property Characteristics. In order to corroborate the positive influence of the organic layers on the mechanical flexibility of our ferrimagnetic ε-Fe$_2$O$_3$-TP SL thin films, we deposited few representative SL samples and reference samples in parallel on both polyimide (for mechanical tests) and silicon (for basic characterization). For reference, we deposited both ε-Fe$_2$O$_3$ ($n = 0$) and pure iron-terephthalate (Fe-TP) films; for the latter film, the deposition processes consisted only of (FeCl$_3$+TPA)$_k$ cycles and they thus completely lacked the ε-Fe$_2$O$_3$ layers ($n = 0$).51 For the SL samples, we deposited two samples; first a film with $n = 20$ and $k = 1$. Then with another sample, we wanted to test the effect of making each organic layer thicker, in other words, we set $k = 10$ instead of $1$ in the deposition process, $(\text{FeCl}_3+\text{H}_2\text{O})_m+(\text{FeCl}_3+\text{TPA})_m+(\text{FeCl}_3+\text{H}_2\text{O})_m$. Note that, in both our $k = 1$ and 10 SL samples, the individual ε-Fe$_2$O$_3$ layer thickness expected is 15 nm; we named these samples as, $n = 20-1$ (15 nm) and $n = 20-10$ (15 nm), respectively.

To confirm the expected chemical and structural state of these samples, we characterized the ε-Fe$_2$O$_3$ and the two SL films by FTIR, XRD (Figure S5) and cross-sectional SEM (Figure 6). Compared to the $k = 1$ case, the $k = 10$ SL sample exhibits stronger TP IR bands but less intense XRD peaks, as expected. Cross-sectional SEM images in Figure 6 and Figure S6 confirm the intended layer structures for the SL films. The thickness calculated from the SEM data was 423, 454, 663, and 263 nm for the ε-Fe$_2$O$_3$, $n = 20-1$ (15 nm), $n = 20-10$ (15 nm) and Fe-TP films, respectively. The pore type pattern observed only in case of $n = 20-10$ (15 nm) suggests that the pores most likely are located in the organic layers; similar pattern was observed also for a film grown on silicon substrate (Figure S7).

The surface morphology changes such that the homogeneous grains of the size of ca. 130 nm in ε-Fe$_2$O$_3$ start to aggregate but not grow for $n = 20-1$ (15 nm). For $n = 20-10$ (15 nm), the
Grains are considerably bigger (ca. 800 nm) and more isolated, having a carbon-coated appearance (Figure S8).

The $M-T$ curves measured from 100 to 400 K for the three samples deposited on polyimide substrates are displayed in Figure 7. Magnetization decreases with increasing temperature in a way typical for a ferrimagnet; the $T_C$ is apparently higher than the upper limit of our measurement, i.e., 400 K, for all the samples, in accordance with the clear hysteresis loops seen for these samples at 400 K. The absolute magnetization naturally decreases with increasing portion of organic layers but—most importantly—the coercivity field remains essentially the same at lower temperatures, i.e., ca. 5 kOe at 10 K for all the samples.

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**Figure 5.** Magnetization versus magnetic field curves measured at 10 K in both FC and ZFC modes: (A) SL sample $n = 20$ (11 nm) with $k = 1$ and (B) $\varepsilon$-Fe$_2$O$_3$ with both $n$ and $k$ are 0. Diamagnetic contribution from the substrate subtracted from the data.

**Figure 6.** Cross-section SEM images for: (A) $\varepsilon$-Fe$_2$O$_3$, (B) $n = 201$ (15 nm), and (C) $n = 20-10$ (15 nm) samples grown on polyimide (PI) substrates. The scale bar is 500 nm in each image.

**Figure 7.** Magnetization versus field ($M-H$) curves measured at various temperatures from 10 to 400 K, for films deposited on polyimide substrates: (A) $\varepsilon$-Fe$_2$O$_3$, (B) $n = 20-1$ (15 nm), and (C) $n = 20-10$ (15 nm), and the magnetization versus temperature ($M-T$) curves measured for: (a) $\varepsilon$-Fe$_2$O$_3$, (b) $n = 20-1$ (15 nm), and (c) $n = 20-10$ (15 nm) under FC and ZFC conditions (D). The magnified $M-H$ curves for coercive fields between $-15$ and $+15$ kOe are given in the insets.
The mechanical properties of $\varepsilon$-$\text{Fe}_2\text{O}_3$, the two types of $\varepsilon$-$\text{Fe}_2\text{O}_3$-TP SLs, and Fe-TP (all grown on stretchable polyimide substrates) were addressed through tensile testing,\textsuperscript{52–54} these measurements yield the crack onset strain (COS) and the closely related critical bending radius (for a given film/substrate bilayer) as the metrics for the stretchability and flexibility, respectively. The measurements were uniaxial tensile experiments coupled with in situ optical microscopy. Channel cracks were observed to form perpendicular to the straining axis above the crack onset strain for all the samples investigated. The visual appearance of the film surfaces is illustrated in Figure 8 for the $\varepsilon$-$\text{Fe}_2\text{O}_3$ and Fe-TP references for various tensile-strain values corresponding to various crack-density values.

From Figure 8 and Table 2, above the crack onset strain, the number density of cracks (along the straining axis) increases rapidly with increasing strain up to a saturation value for $\varepsilon$-$\text{Fe}_2\text{O}_3$, $n = 20\text{-}1$ (15 nm), and $n = 20\text{-}10$ (15 nm), while for Fe-TP the complete saturation is not reached in the studied strain range of 0–10%. The saturation crack density is directly proportional to adhesive strength, and therefore provides us with an indication of the adhesion of the films to the substrate. The first three films exhibit saturation crack density values of the same order, which indicates that the adhesion of the two SL films is governed by the $\varepsilon$-$\text{Fe}_2\text{O}_3$ layer at the film–substrate interface.\textsuperscript{47} In contrast, the crack density (approaching saturation) for the Fe-TP film is order-of-magnitude higher, reflecting its better adhesion to the polyimide substrate.\textsuperscript{41} Therefore, Fe-TP could potentially serve as an interface layer to enhance adhesion of $\varepsilon$-$\text{Fe}_2\text{O}_3$ (and the SLs) to the polyimide substrate. Most importantly, with increasing portion of organic layers the COS value of the films increases progressively from 0.33% for $\varepsilon$-$\text{Fe}_2\text{O}_3$ to 1.07% for $n = 20\text{-}10$ (15 nm) (Table 2), where the decrease in crystallinity seen for the SLs could moreover contribute to the enhanced mechanical performance.\textsuperscript{55} It should be emphasized that the relative increase is as high as 220%.

From the COS values, we calculated the critical bending radii as $R_c = (h_f + h_i)/(2\text{\ COS})$, where $h_f$ and $h_i$ are the thicknesses of the substrate and the film, respectively. The $R_c$ values for our $\varepsilon$-$\text{Fe}_2\text{O}_3$-TP SL films indicate considerably enhanced flexibility compared to the parent $\varepsilon$-$\text{Fe}_2\text{O}_3$ film, being increased by 32% for $n = 20\text{-}1$ (15 nm) and by 69% for $n = 20\text{-}10$ (15 nm) (Table 2).

The COS value of 0.33% for our ca. 400 nm $\varepsilon$-$\text{Fe}_2\text{O}_3$ film extrapolates to a value of 0.68% for a 100 nm film thickness ($\text{COS} \propto h_f^{-1/2}$).\textsuperscript{41} This is comparable to the COS value of ca. 0.5% reported for 100 nm ALD-Al$_2$O$_3$ films on polyimide substrates;\textsuperscript{52} hence, $\varepsilon$-$\text{Fe}_2\text{O}_3$ exhibits behavior typical for brittle metal oxide materials. From the other end, the COS value for our Fe-TP film (0.99%) is slightly lower than that reported for ALD/MLD-grown Al-ethylene glycol films of similar thickness (1.8%),\textsuperscript{54} where the difference could be due to differences in crystallinity and/or the rigidity of the organic component. For Al$_2$O$_3$/Al-ethylene glycol superlattices/nanolaminates with large organic concentrations (ALD:MLD cycle ratios of 1:1 and 3:1), Jen et al.\textsuperscript{52} reported critical strain values of around 0.9%.\textsuperscript{52} Our result for the $n = 20\text{-}10$ (15 nm) SL film is on the same order but with a lower concentration of the organic layers.

### Table 2. Results of Tensile Experiments\textsuperscript{a}

<table>
<thead>
<tr>
<th>sample</th>
<th>critical bending radius (nm)</th>
<th>crack onset strain (COS) (%)</th>
<th>saturation crack density (mm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$-$\text{Fe}_2\text{O}_3$</td>
<td>7.7 ± 0.3</td>
<td>0.33 ± 0.02</td>
<td>32 ± 4</td>
</tr>
<tr>
<td>$n = 20\text{-}1$ (15 nm)</td>
<td>5.3 ± 0.2</td>
<td>0.48 ± 0.02</td>
<td>39 ± 9</td>
</tr>
<tr>
<td>$n = 20\text{-}10$ (15 nm)</td>
<td>2.4 ± 0.3</td>
<td>1.07 ± 0.13</td>
<td>66 ± 8</td>
</tr>
<tr>
<td>Fe-TP</td>
<td>2.5 ± 0.2</td>
<td>0.99 ± 0.08</td>
<td>&gt;317</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The given error margins are standard deviations over 3–5 measurements.

4. CONCLUSION

We have demonstrated the potential of the ALD/MLD technique in the fabrication of new types of flexible inorganic–organic thin-film magnets. This technique allows for the introduction of monomolecular organic layers or thicker metal–organic layer blocks between nanoscale inorganic layers in any predefined frequency into advanced superlattice structures. Our reproducible ALD/MLD process yielded high-quality, visually homogeneous thin films with appreciable stability under ambient conditions.

In this work, our inorganic component was the ferrimagnetic $\varepsilon$-$\text{Fe}_2\text{O}_3$ phase, with exceptionally high coercive field even at room temperature. This was possible, as we had recently developed a facile ALD process for fabricating high-quality and stable thin films of this rare but attractive iron oxide phase. Now we have shown in this work that by introducing thin,
organic-rich layers, either in the form of separate monomolecular terephthalate layers or relatively thin-terephthalate layer blocks, it is possible to considerably improve the flexibility of the otherwise relatively rigid ε-Fe$_2$O$_3$ thin films. Most importantly, the enhancement in mechanical properties was achieved with reasonably low organic-to-inorganic ratios such that the functionality of the inorganic layers, here the “hard” high-coercive-field room-temperature ferrimagnetism of ε-Fe$_2$O$_3$, was not compromised. In other words, we were able to bring together the functional properties of the inorganic layers and the mechanical flexibility of the organic layers in one single superlattice thin-film material.

Both the magnetic and mechanical properties of our novel flexible magnets were unambiguously presented through an extensive investigation of coercivity, magnetization, and tensile properties including critical bending radius, crack onset strain and saturation crack density. We are convinced that our novel mechanically flexible room-temperature magnetic thin films have high potential in next-generation applications where hard magnets in the form of flexible, lightweight, metal-sparing, and nonpoisonous thin films/coatings, possibly applied on challenging surface architectures, are desired. Moreover, our work could open up new horizons for any future application requiring the fusion between an important material functionality of inorganics and the mechanical flexibility only provided by organics.

**ASSOCIATED CONTENT**

Electronic Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsami.0c04665.

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c04665

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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