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Tailoring of optoelectronic properties of ϵ -Fe₂O₃ thin films through insertion of organic interlayers

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Combined atomic/molecular layer deposition (ALD/MLD) technique enables the engineering of inorganic-organic superlattices with atomic/molecular layer accuracy for the individual layer thicknesses. Here we demonstrate how the optical and electronic properties of ϵ -Fe₂O₃ thin films can be gradually tuned with an insertion of monomolecular organic layers. In our ϵ -Fe₂O₃:benzene superlattice (SL) structures the thickness of individual iron oxide layers varies in the range of 1~17 nm. With decreasing ϵ -Fe₂O₃ layer thickness, i.e. SL period, the films become more transparent. Moreover revealed from the UV-vis spectra is that the indirect optical bandgap increases from ~2.0 eV for ϵ -Fe₂O₃ up to ~2.3 eV for the SL films with the shortest SL period. We foresee that the ALD/MLD approach presented here for the ϵ -Fe₂O₃-benzene thin films could be exploited in fabricating many other interesting hybrid material systems with controlled optoelectronic properties.

In nanoscale many interesting material characteristics including the electrical, magnetic, optical and thermal properties may considerably differ from those of the same material in bulk form.^[1–5] To systematically investigate the effects of decreased dimensions down to nanoscale, superlattice (SL) thin films where ultrathin layers of two mutually different materials alternate along the film-growth direction provide us with an interesting platform. The fundamental advantage of the SL thin-film structures when fabricated using state-of-the-art thin-film techniques is that the individual layer thicknesses can be precisely tailored to a constant value; this is not necessarily possible for other nanostructured materials (e.g. nanoparticles) for which considerably wider dimension variations are typically seen. Indeed, exciting/enhanced material properties and abrupt changes in material characteristics have been reported for various thin-film SL materials owing to interface effects and quantum confinement phenomena.^[6–10]

Creating superlattices with inorganic-organic interfaces is a particularly attractive approach as in such structures the two SL components are mutually extremely different regarding their basic material characteristics. Most interestingly, even dramatic changes in the properties of the inorganic material could be anticipated for superlattices precisely layer-engineered to the desired inorganic-organic sequences. However, very little has been done in practice in this field; this may be due to the difficulties in tailoring the desired layer structures in a controllable fashion with the solution-based synthesis techniques conventionally employed for the inorganic-organic hybrid materials.

The atomic layer deposition (ALD)^[11] thin-film technique combined with its counterpart for the organic materials, i.e. molecular layer deposition (MLD),^[12–14] is uniquely suited to the engineering of carefully designed inorganic-organic hybrid structures owing to its specific film growth mechanism based on self-limiting gas-surface reactions. Namely, the combined ALD/MLD technique allows the precise control of the introduction frequency of the organic layers within the inorganic matrix, and enables the fabrication of inorganic–organic SL structures with a high degree

of controllability over the thickness and composition of individual layers.^[15] The ALD/MLD approach has already been successfully employed for the fabrication of e.g. ZnO:benzene^[16–20] and TiO₂:benzene^[7,21] SL thin films to demonstrate – having the eye on their thermoelectric applications – that the thermal conductivity of these films is efficiently controlled down to ultralow values by the thickness of the individual oxide layers between the monomolecular-thick benzene layers. Here in this work we have fabricated for the first time inorganic-organic SL thin films based on iron oxide and investigated how the optical properties depend on the tailored oxide-layer nano-scale thickness in these SL structures.

Binary iron oxides in their various crystal forms are attractive functional materials as they constitute of earth-abundant low-cost elements only and are thermally and chemically stable, as well as environmentally benign, biocompatible and nontoxic to human; they moreover exhibit an exciting variety of potentially usable magnetic, optical, catalytic and electrochemical properties for applications ranging from electrochromism and photocatalysis to interference filters and photovoltaic and battery systems.^[5,22–25] Here in this work we have focused on the ϵ -Fe₂O₃ phase; it is one of the rarest among the iron oxides (so far only found in nanoscale samples^[26–31]) but of considerable interest due to its unique properties such as room-temperature multiferroics.^[29,32,33] In the non-centrosymmetric (space group *Pna*2₁) ϵ -Fe₂O₃ structure there are four distinct iron sites, three of which are octahedral and one tetrahedral.^[34] At room temperature the phase is ferrimagnetic with a remarkably large coercive field of H_c up to 20 kOe, and also ferroelectric with a polarization of 1 $\mu\text{C cm}^{-2}$.^[29,35]

Recently we reported straightforward ALD (FeCl₃+H₂O)^[36] and MLD ((FeCl₃+TPA; TPA = terephthalic acid)^[37] processes to deposit ϵ -Fe₂O₃ and iron terephthalate (Fe-TP) thin films in a highly controllable atomic or molecular layer-by-layer fashion. Here in this work we fabricate the SL thin films by combining these two deposition processes to yield structures where ϵ -Fe₂O₃ layers of a certain thickness are separated with monomolecular-thick benzene layers bonded to the ϵ -Fe₂O₃

layers via the carboxylate groups of the TPA precursor, see **Figure 1**. The deposition process can be described as $[(\text{FeCl}_3+\text{H}_2\text{O})_m+(\text{FeCl}_3+\text{TPA})]_n+(\text{FeCl}_3+\text{H}_2\text{O})_m$ where the selected number m of the $(\text{FeCl}_3+\text{H}_2\text{O})$ ALD cycles controls the thickness of the individual $\epsilon\text{-Fe}_2\text{O}_3$ layers and the number n tells the number of the $(\text{FeCl}_3+\text{TPA})$ MLD cycles applied in total and thus the number of the organic (benzene) monolayers in the SL structure; the number of the $\epsilon\text{-Fe}_2\text{O}_3$ layers in the superlattice is accordingly $n+1$. We deposited a series of SL structures where n varied from 3 to 24 and m from 20 to 250, as summarized in Table 1. Additionally, thin films of the pure $\epsilon\text{-Fe}_2\text{O}_3$ phase ($m=1000$, $n=0$) and the Fe-TP hybrid ($m=0$, $n=100$) were deposited for reference.

Figure 1. Schematic illustration of the Fe₂O₃:benzene superlattice structure and examples of XRR patterns recorded for our SL (~70 nm) thin films to confirm the intended layer sequences; XRR patterns for plain oxide ($n=0$; ~65 nm) and hybrid ($n=100$; ~110 nm) thin films are shown as well for comparison.

Table 1. The $[(\text{FeCl}_3+\text{H}_2\text{O})_m+(\text{FeCl}_3+\text{TPA})]_n+(\text{FeCl}_3+\text{H}_2\text{O})_m$ thin-film structures deposited in this work.

Film type	n	m	Expected Fe_2O_3 -layer thickness (nm)	Number of cycles $(n \times (m+1) + m)$	Film thickness (nm)	Average GPC ($\text{\AA}/\text{cycle}$)
$\epsilon\text{-Fe}_2\text{O}_3$	0	1000	65.0	1000	65.0	0.65
SL	3	250	16.3	1003	69.6	0.69
SL	4	200	13.0	1004	70.8	0.71
SL	5	165	10.7	995	71.4	0.72
SL	6	143	9.3	1007	72.2	0.72
SL	11	83	5.4	1007	73.5	0.73
SL	17	30	2.0	557	72.6	1.3
SL	24	20	1.3	524	78.7	1.5
Hybrid	100	0	0	100	112	11

In Table 1 we also summarize the growth-per-cycle (GPC) values, calculated from the total film thickness values determined by XRR. For the end members, $\epsilon\text{-Fe}_2\text{O}_3$ and Fe-TP, the GPC values are 0.65 and 11 $\text{\AA}/\text{cycle}$, respectively, in accordance with our previous studies.^[36,37] For the SL thin films the GPC value increases with increasing frequency of the organic layers as expected. The intended SL structures were readily confirmed from the XRR data as well; in Figure 1 we display representative patterns for the SLs with $n = 3, 4, 5$ and 6. In each case the periodicity of the XRR interference pattern showing the more intense SL peaks regularly separated with n less intense oscillation peaks is fully explained by the expected SL structure.

Figure 2. FTIR spectra for representative thin films deposited through the $[(\text{FeCl}_3+\text{H}_2\text{O})_m+(\text{FeCl}_3+\text{TPA})]_n+(\text{FeCl}_3+\text{H}_2\text{O})_m$ process with different n values (see Table 1 for the corresponding m values).

To verify the presence of the intended organic moieties/bonds in the SL films we measured FTIR spectra for the films with different numbers of organic layers ($n = 4, 11$ and 17) and also for the plain $\epsilon\text{-Fe}_2\text{O}_3$ ($n=0$) and Fe-TP hybrid ($m=0$) films for reference; the spectra are shown in **Figure 2**. It can be seen that already for the $n=4$ SL film the bands of asymmetric (ν_{as}) and symmetric (ν_{s}) stretches of the carboxylate groups of the terephthalate moiety appear at ~ 1508 and $\sim 1396\text{ cm}^{-1}$, respectively. With increasing n also the features due to the benzene ring become visible at $740\text{-}830\text{ cm}^{-1}$ whereas the weak absorption bands from $\epsilon\text{-Fe}_2\text{O}_3$ at the lower wave numbers gradually disappear.

For the XRD measurements we deposited similar but thicker films (ca. 4000 cycles in total). Representative XRD patterns are displayed in **Figure 3**. All the samples are polycrystalline, consisting of no other phase except the $\epsilon\text{-Fe}_2\text{O}_3$ phase; the pattern for the $n=0$ sample is essentially identical to those obtained for the plain $\epsilon\text{-Fe}_2\text{O}_3$ films grown by ALD in our earlier study.^[36] With increasing number n of organic layers (and decreasing thickness of the individual iron oxide layers) the SL films remain crystalline and the $\epsilon\text{-Fe}_2\text{O}_3$ structure otherwise unaffected but the degree of crystallinity seems to gradually decrease, as indicated by the gradually broadened diffraction peaks. This is an expected outcome of the reduction of the $\epsilon\text{-Fe}_2\text{O}_3$ layer dimension, i.e. nanostructuring.

Figure 3. XRD patterns for ϵ -Fe₂O₃ and representative (thicker) SL thin films with the individual ϵ -Fe₂O₃-layer thicknesses of 52 nm ($m=800$, $n=4$), 26 nm ($m=400$, $n=9$) and 6.5 nm ($m=100$, $n=39$); the smaller peaks due to the silicon substrate are indicated by SS.

The measured UV-Vis transmittance (T) and reflectance (R) spectra and the calculated absorbance ($A=1-(R+T)$) curves for all the thin films listed in Table 1 are shown in **Figure 4**. The 65 nm thick ϵ -Fe₂O₃ ($n=0$) film is of a rusty orange color, whereas the 112 nm thick Fe-TP hybrid ($m=0$) film in the other end of the sample series is nearly transparent. From Figure 4(A) the transmittance for the latter film is nearly 90 % and almost the same as for the borosilicate glass substrate in the wavelength range from 465 to 800 nm. With decreasing number of organic layers within the ϵ -Fe₂O₃ matrix the transmittance gradually decreases such that for the pure ϵ -Fe₂O₃ film transmittance is less than 50 % in the visible range. Also the SL films with $n = 17$ and 24 with the thinnest ϵ -Fe₂O₃ layer thicknesses are highly transparent as was clearly seen by naked eye as well.

The reflectance data shown in Figure 4B reveal that for the ϵ -Fe₂O₃ film the reflectance maximum (at ~ 610 nm) is 47 % whereas for the Fe-TP hybrid it is 10 % or less; for the SL films the reflectance curves are located in between those of the two end members. Similarly, the absorption spectra for the SL films are intermediates of those of ϵ -Fe₂O₃ and Fe-TP (Figure 4C). For ϵ -Fe₂O₃ the absorption maximum is at ~ 376 nm. For the SLs, due to the increase in transmittance and decrease in reflectance the absorption maximum increases with increasing n to ~ 408 nm for $n=11$,

and simultaneously the absorption edge moves from ~ 588 to ~ 604 nm. From all the Figures 4 A-C, it is clear that the SL films with $n = 3$ to 11 resemble the ϵ -Fe₂O₃ film while those with $n = 17$ and 24 are closer to the Fe-TP film.

Figure 4. UV-Vis data for representative thin films deposited through the $[(\text{FeCl}_3 + \text{H}_2\text{O})_m + (\text{FeCl}_3 + \text{TPA})]_n + (\text{FeCl}_3 + \text{H}_2\text{O})_m$ process: (A) transmittance, (B) reflectance, (C) absorbance, (D) the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ relation to determine the indirect optical bandgap, (E) the bandgap value against the individual ϵ -Fe₂O₃ layer thickness.

Finally we estimated the optical bandgaps (E_g) for our SL thin films based on the data in Figure 4. To the best of our knowledge no experimental bandgap values have been reported for ϵ -Fe₂O₃ but a theoretical study finds the indirect bandgap of ϵ -Fe₂O₃ at 1.6 eV.^[38] Thus assuming an indirect

bandgap, we determined the E_g values by extrapolating the linear regions of the $(\alpha hv)^{1/2}$ vs. hv plots, where α is the absorption coefficient (calculated from the T and R data) and hv is the photon energy, see Figure 4D. For our ϵ -Fe₂O₃ film this results in a bandgap value of 1.98 eV. From Figure 4E where the bandgap values for our SL films are plotted against the SL period n (and decreasing ϵ -Fe₂O₃ layer thickness) it can be seen that the E_g of ϵ -Fe₂O₃ is blue shifted having an onset in the region of $n=17$ (ϵ -Fe₂O₃ layer thickness ~ 2 nm). For the Fe-TP hybrid film the bandgap value is 2.95 eV. This increase in the bandgap could be important from an application point of view, as for example for the use of the semiconductor in water photolysis the bandgap should exceed the value of 2.46 eV.^{39,40} It is interesting to note that for different binary iron oxide phases in bulk samples, the indirect bandgap values reported in literature typically vary between 1.9-2.2 eV.⁴¹ In the literature in general, the increase in bandgap energy with decreasing total film thickness for various homogeneous oxide thin films has been attributed to the quantum confinement effect.^{42,43} In particular for hematite-structured Fe₂O₃ thin films the quantum confinement effect has been seen when the film thickness is decreased below 20 nm.⁴ For TiO₂ nanoparticles and superlattice thin films the onset of the blueshift has been addressed to dimensions smaller than 3 nm.^{44,45} Here it is intriguing to emphasize that for our superlattice ϵ -Fe₂O₃:benzene films we may achieve the increases in the bandgap value by cutting the ϵ -Fe₂O₃ matrix into thinner sublayers while keeping the overall film thickness much larger. While the experimental finding is clear, we definitely need to clarify the fundamental mechanism behind the increased bandgap in our future studies. In particular, we plan to extend our work to a series of ultrathin ALD-grown ϵ -Fe₂O₃ films with varied film thicknesses for comparison to the present SL thin films. It is interesting to note that in a very recent computational paper by Ahamed et al.,⁴⁶ the authors modeled ultrathin ϵ -Fe₂O₃ films with different terminations but did not observe bandgap values higher than 2 eV.

In conclusion, we have demonstrated an exciting new approach to nanostructurize ϵ -Fe₂O₃ thin films; our ALD/MLD fabrication enables superlattice structures in which precisely thickness-controlled ultrathin layers of ϵ -Fe₂O₃ alternate with monomolecular organic layers in a regular

manner. This superlattice approach was shown to be an effective way to tune the optoelectronic properties of ϵ -Fe₂O₃, such as the transparency of the films. Most importantly, with decreasing ϵ -Fe₂O₃-layer thickness the indirect optical bandgap was shown to considerably increase when the layer thickness was reduced below 2 nm; at the same time the overall film thickness can be kept at any desired value in the scale of appr. 10 to 100 nm. This should be an attractive option for a number of applications, and moreover, easily transformable to other related oxide-organic systems.

Experimental Section

Sample preparation: Superlattice iron oxide:benzene thin films were deposited using a commercial flow-type hot-wall ALD reactor (F-120 by ASM Microchemistry Ltd) from iron chloride (FeCl₃, Merck, 95%) and terephthalic acid (TPA, Tokyo Chemical Industry CO., Ltd, >99.0 %); these precursor powders were placed in open precursor boats inside the reactor and heated to 158 and 185 °C, respectively. Deionized water was used as the oxygen source for the iron oxide layers and the container was located outside the reactor. The precursor pulses were separated by pulsing nitrogen (99.999 %) that was also used as a carrier gas. The pressure was between 2 and 4 mbar and the N₂ flow 300 sccm during the depositions. The deposition temperature was set to 280 °C and the pulsing sequences were selected to be 2 s FeCl₃/4 s N₂/1 s H₂O/3 s N₂ for the ALD cycle (iron oxide) and 4 s FeCl₃/8 s N₂/25 s TPA/50 s N₂/2 s FeCl₃ for the MLD cycle, following our previous works for the ϵ -Fe₂O₃ and hybrid Fe-TP films, respectively.^[36,37] Silicon(100) substrates (3.0 x 3.0 cm², Okmetic Oy) were used as such. Samples for the UV-Vis characterization were deposited on borosilicate glass (3.5 x 3.5 cm², Finnish special glass) washed with ethanol-water solution prior to the use.

Characterization: X-ray reflectivity (XRR) patterns were measured with X'Pert MPD PRO Alfa 1, PANalytical equipment. The XRR measurements were carried out within 15 min after taking the samples out from the ALD reactor. From the XRR curves (X'Pert Reflectivity software by PANalytical) the film thicknesses were determined manually measuring the average distance

between the smaller oscillations. Moreover, the curves confirmed the targeted superlattice periods. The same diffractometer was used to collect the X-ray diffraction (XRD) patterns for the samoles; the XRD measurements were performed with incidence angle from 5 to 65 °. Organic molecules were detected with Fourier transform infrared (FTIR; Nicolet magma 750) spectroscopy. Dry air was used for purging the chamber during the measurements. A spectrum of blank Si was subtracted from the spectra to compensate the interference caused by the substrate. Ultraviolet-Visible spectroscopy (UV-VIS-NIR Agilent Cary 5000) was used to characterize the change in the optical properties of the films when the content of organic molecular layers was increased. For these measurements the thin films (ca. 70 nm) were deposited only on the top surface of the borosilicate glass.

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Table of contents entry

This communication reports the possibility to tailor the optoelectronic properties of ϵ -Fe₂O₃ thin films through insertion of monomolecular organic interlayers. This is achieved by using the combined atomic/molecular layer deposition (ALD/MLD) technique which enables the engineering of inorganic-organic superlattices with atomic/molecular layer accuracy for the individual layer thicknesses.