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# Holmium and titanium oxide nanolaminates by atomic layer deposition

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ABSTRACT

Nanolaminate (nanomultilayer) thin films of $TiO_2$ and $Ho_2O_3$ were grown on Si(001) substrates by atomic layer deposition at 300 °C from alkoxide and β-diketonate based metal precursors and ozone. Individual layer thicknesses were 2 nm for $TiO_2$ and 4.5 nm for $Ho_2O_3$. As-deposited films were smooth and X-ray amorphous. After annealing at 800 °C and higher temperatures the nanolaminate structure was destroyed by solid-state reaction to form $Ho_2Ti_2O_7$. The films demonstrated diamagnetic or paramagnetic behaviour in the as-deposited state. After annealing, the films possessed net magnetic moment, allowing one to record saturation magnetization and weak coercivity.

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## 1. Introduction

Metal oxide multilayers in the form of superlattices or nanolaminates are of interest as functional thin films possessing advanced electronic, optical and mechanical properties. Nanolaminates may be built up artificially by sequential deposition of different oxides, e.g. $HfO_2$–$Al_2O_3$ [1], $ZrO_2$–$Al_2O_3$ [2–6], $ZrO_2$–$Y_2O_3$ [7], $ZrO_2$–$SiO_2$ [7], $HfO_2$–$Al_2O_3$ [8,9], $TiO_2$–$Al_2O_3$ [10–13], $Al_2O_3$–$Ta_2O_5$ [14–17], $ZrO_2$–$Ta_2O_5$[14,18], $HfO_2$–$Ta_2O_5$ [18,19], $ZrO_2$–$HfO_2$ [18,20], $ZrO_2$–$Er_2O_3$ [21], $ZrO_2$–$Gd_2O_3$ [22], and $TiO_2$–$Cr_2O_3$ [23].

Nanolaminates can assist in tailoring useful physical properties of different chemical compounds, such as band gaps, densities, refractive indexes, elasticity, homogeneity, or to exploit the formation of multiple interfaces as barriers for conduction or diffusion. Such oxide-based nanolaminates have been studied as materials able to provide good compromise between leakage current density and dielectric permittivity, enhancing charge storage capability of capacitor dielectrics while aiming at the improvement of the performance of, e.g., electroluminescent devices [10,14], field effect transistors [2,7,13,18,20], and memories [5,9,16,21,22]. Especially important industrially are the $ZrO_2$–$Al_2O_3$–$ZrO_2$ structures [24] used in dynamic random access memory cells. Nanolaminates may also perform as gas-diffusion barriers for reliable encapsulation of organic electronics [3], show long term durability as corrosion-protective layers [17], and act as optical filters tuning the reflection from silicon substrate [11] or as hard X-ray mirrors [15]. Nanolaminates with a large number of interfaces may also have reduced cross-plane thermal conductivity compared to that in chemically homogeneous films [1]. Alternate layering of different materials also reduces the overall roughness of the coating, compared to the single oxides grown to the same thickness [1,8,24,25].

Nanolaminates of single oxides may be grown using different physical and chemical techniques, such as electron beam evaporation [13], sputtering [4], pulsed laser deposition [6] or, as apparently the most controlled method, atomic layer deposition (ALD) [1–3,5,7,9–12, 14–18,22–24,26]. Studies on ALD-grown nanolaminates containing rare earth oxides have so far been quite scarce [21,22], though, and none has been grown using Ti and Ho oxides as constituents.

This study is devoted to the description of $Ho_2O_3$–$TiO_2$ nanolaminates, grown by atomic layer deposition. Earlier, films consisting of mixtures of $Ho_2O_3$ and $TiO_2$ with variable Ho:Ti ratio have been grown by ALD [27]. The present paper will concentrate on stack of alternate $Ho_2O_3$ and $TiO_2$ films with controlled interlayer thickness. Effects of heat-treatment on the film morphology, crystal structure and magnetic properties are presented and discussed. The study was initially motivated by the interest in the materials which could be deposited at low temperatures in a controlled way as structurally and

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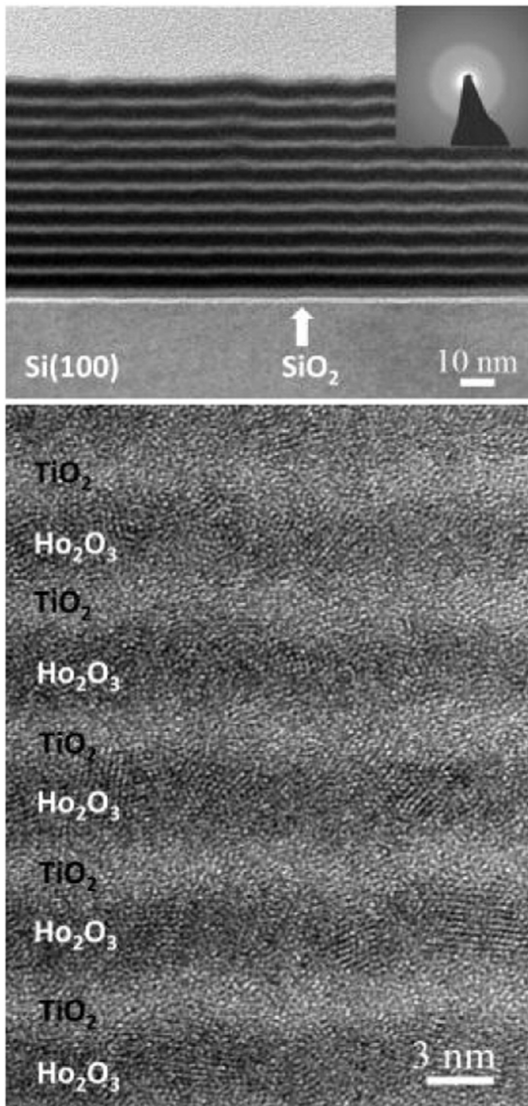
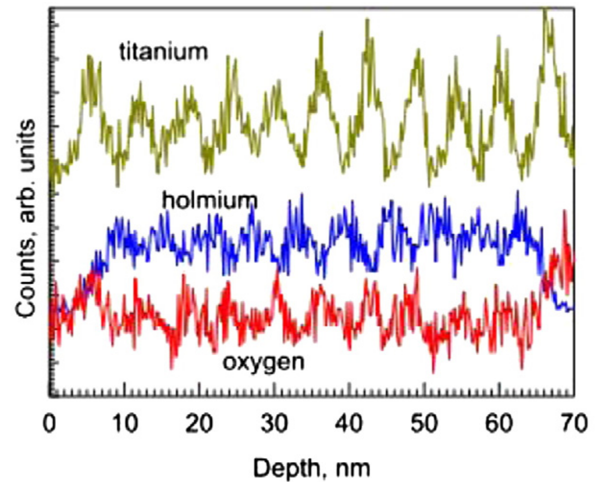



**Fig. 1.** Cross-sectional TEM (upper panel) and HRTEM (lower panel) images of a $Ho_2O_3$–$TiO_2$ nanolaminate in the as-deposited state. The constituent layer materials are indicated by labels.



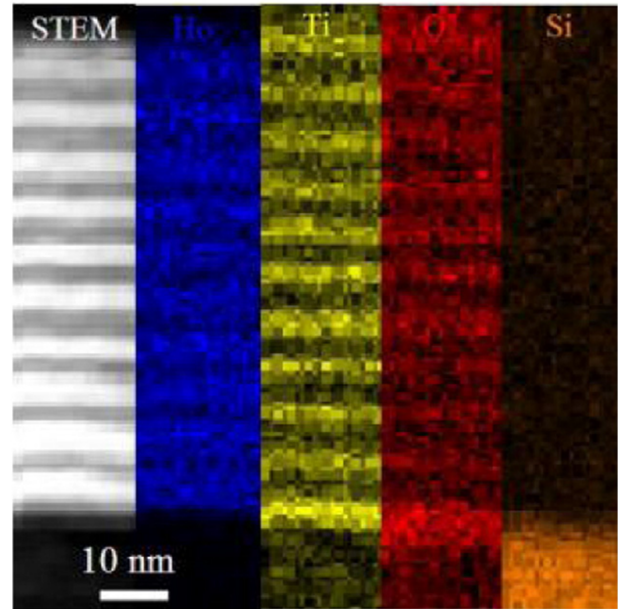




**Fig. 2.** Cross-sectional EDX composition profiling of the $Ho_2O_3$–$TiO_2$ nanolaminate in the as-deposited state. The elements detected are indicated by labels. Due to the higher O concentration in $TiO_2$ compared to that in $Ho_2O_3$, the O profile is following the Ti profile rather than Ho.

optically well defined layers and, in the as-deposited state or after post-deposition treatment, exhibit magnetization, posssibly allowing development of multiferroic materials.

## 2. Experimental details

The films were grown in a commercial flow-type hot-wall reactor F120 (ASM Microchemistry, Ltd.) [28]. The reactor run under a pressure of about 1000 Pa using $N_2$ (99.9995%) as carrier and purging gas. $O_3$ was used as an oxygen precursor. The $O_3$ concentration output of the generator was ~100 g/m$^3$. $Ho_2O_3$ layers were deposited at 300 °C using the ALD process based on $Ho(thd)_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato) and $O_3$ [27,29]. $TiO_2$ films were grown using an ALD process based on titanium *tetra*-isopropoxide, $Ti(OCH(CH_3)_2)_4$ and ozone, $O_3$. The titanium and holmium precursors were evaporated at 35 and 125 °C, respectively, from open boats inside the reactor and transported to the substrates by the carrier gas flow. The cycle times used for $TiO_2$ were 0.5–0.5–1.0–0.5 s, and those for $Ho_2O_3$ were 1.0–1.5–2.0–2.0 s, denoting the sequence metal precursor pulse–purge–$O_3$ pulse–purge. $TiO_2$–$Ho_2O_3$ nanolaminates were grown using the total sequence of 10 × [100 × $TiO_2$ + 250 × $Ho_2O_3$] + 100 × $TiO_2$ cycles. The substrates were pieces of undoped Si(100) covered with 1.5–2.0 nm thick native $SiO_2$. Selected samples were annealed at 600, 800 or 1000 °C under a $N_2$ flow for 30 min.

High-resolution transmission electron microscopy (HRTEM) studies for characterization of the cross-sections of the nanolaminate structure were carried out using a FEI Tecnai G2 TF20 UT instrument with a field emission gun operated at 200 kV with a point resolution of 0.19 nm. The surface morphology images were taken and the film thicknesses measured by a Hitachi S-4800 scanning electron microscope equipped with an Oxford INCA 350 energy dispersive X-ray (EDX) spectrometer. The EDX spectra were measured at 20 keV. The beam current and spectrometer gain were determined from a calibration measurement performed under the same beam conditions. The film thicknesses and ratios of the different metals were calculated from the k ratios of Ho Kα and Ti Kα X-ray lines measured with the calibrated beam. The calculations were done with a GMRFILM program [30] assuming a density of 5 g/cm$^3$ for $TiO_2$ slightly doped and thus densified by holmium.

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