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Holmium and titanium oxide nanolaminates by atomic layer deposition

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Abstract

Nanolaminate (nanomultilayer) thin films of TiO₂ and Ho₂O₃ 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 TiO₂ and 4.5 nm for Ho₂O₃. 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 Ho₂Ti₂O₇. 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.

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. HfO₂-Al₂O₃ [1], ZrO₂-Al₂O₃ [2-6], ZrO₂-Y₂O₃ [7], ZrO₂-SiO₂ [7], HfO₂-Al₂O₃ [8,9], TiO₂-

Al_2O_3 [10-13], $\text{Al}_2\text{O}_3\text{--Ta}_2\text{O}_5$ [14-17], $\text{ZrO}_2\text{--Ta}_2\text{O}_5$ [14,18], $\text{HfO}_2\text{--Ta}_2\text{O}_5$ [18,19], $\text{ZrO}_2\text{--HfO}_2$ [18,20], $\text{ZrO}_2\text{--Er}_2\text{O}_3$ [21], $\text{ZrO}_2\text{--Gd}_2\text{O}_3$ [22], and $\text{TiO}_2\text{--Cr}_2\text{O}_3$ [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 $\text{ZrO}_2\text{--Al}_2\text{O}_3\text{--ZrO}_2$ 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], act as optical filters tuning the reflection from silicon substrate [11] or as hard X-ray mirrors [15]. Nanolaminates with 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 $\text{Ho}_2\text{O}_3\text{--TiO}_2$ 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 optically well defined layers and, in the

as-deposited state or after post-deposition treatment, exhibit magnetization, possibly 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 N₂ (99.9995 %) as carrier and purging gas. O₃ was used as an oxygen precursor. The O₃ concentration output of the generator was $\sim 100 \text{ g/m}^3$. Ho₂O₃ 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 O₃ [27,29]. TiO₂ films were grown using an ALD process based on titanium *tetra*-isopropoxide, Ti(OCH(CH₃)₂)₄ and ozone, O₃. 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 TiO₂ were 0.5-0.5-1.0-0.5 s, and those for Ho₂O₃ were 1.0-1.5-2.0-2.0 s, denoting the sequence metal precursor pulse – purge – O₃ pulse – purge. TiO₂-Ho₂O₃ nanolaminates were grown using the total sequence of $10 \times [100 \times \text{TiO}_2 + 250 \times \text{Ho}_2\text{O}_3] + 100 \times \text{TiO}_2$ cycles. The substrates were pieces of undoped Si(100) covered with 1.5-2.0 nm thick native SiO₂. Selected samples were annealed at 600, 800 or 1000 °C under a N₂ 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 K α and Ti K α X-ray lines measured with the calibrated beam. The calculations were done with a GMRFILM program [30] assuming a density of 5 g/cm³ for TiO₂ slightly doped and thus densified by holmium.

A Sopra GES-5E variable angle spectroscopic ellipsometer was used to determine the thickness (d) and optical properties (n, k) using ‘Winelli II’ software. Layer thickness and optical constants (n, k) were determined from the ellipsometric $\tan \psi$ and $\cos \Delta$ parameters [40]. All the main parameters, d, n, and k parameters were obtained for each layer using a Levenberg-Marquardt non-linear regression algorithm. Measurements were generally made at incidence and reflectance angle of 75° . Layers of Ho_2O_3 and TiO_2 were modelled as homogeneous mixtures of supposedly dense materials and addition of void content for refractive index, n, and absorption coefficient, k, adjustment. The optical properties of thin films were examined in air at ambient conditions. Optical constants quoted in this paper will further refer to those measured at 633 nm wavelength. In addition, using the same optical model, thicknesses were measured as a matrix laid over an area of 25 cm^2 with steps of 7 mm in X and Y horizontal directions in order to profile the thickness along and across the gas flow direction in the ALD reactor.

The thicknesses of the films were measured and their crystal structure evaluated by X-ray reflectometry (XRR) and by grazing incidence X-ray diffraction (GIXRD), respectively, using a PANalytical X’Pert PRO X-ray diffractometer with Cu K_α source. For the GIXRD, the incidence angle was set at 1 deg. For atomic force microscopy (AFM) studies a MultiMode V equipped with a NanoScope V controller (Veeco Instruments) was used. Tapping mode height and phase images were measured in air using phosphorus-doped silicon probe (RTESP) delivered by Veeco Instruments. Phase imaging detects e.g. variations in composition and it can be applied in order to map different components, such as amorphous and crystalline regions present in the material. Image processing and data analysis were performed with a NanoScope software version 7.30. The scan area was $2 \mu\text{m} \times 2 \mu\text{m}$ and the Z-scale 25 nm in all the AFM images.

A selection of films was subjected to magnetic measurements. The measurements were performed using the Vibrating Sample Magnetometer option of the Physical Property Measurement System (PPMS) 14T (Quantum Design). Rectangular samples with dimensions of ca. $7 \text{ mm} \times 4 \text{ mm}$ were fixed with GE vanish on commercial quartz sample holders (Quantum Design). The samples were cooled in a magnetic field of 477.6 kA/m parallel to the film surface and the temperature dependence of magnetization was measured in the temperature range from 10 to 310 K in the presence of the same field. The hysteresis measurements were performed by scanning the magnetic fields from -477.6 kA/m to $+477.6$

kA/m at temperatures selected in the range of 10–300 K. Diamagnetic signal arising from the silicon substrate was subtracted from the general magnetization curve for certain samples in which the ferromagnetic-like response was detected.

3. Results and discussion

3.1. Film growth and formation

XRR measurements of thicker binary oxide reference films showed that the growth rate of Ho_2O_3 layers on SiO_2/Si substrates in these experiments was 0.025 nm/cycle. The growth rate of TiO_2 thin films was significantly higher, reaching 0.045 nm/cycle. These growth rates do not exactly correspond to the growth rate during the first few nanometers because the thicknesses of both Ho_2O_3 and TiO_2 single layers in the nanolaminate remained below the values expected on the basis of growth rates of reference films. The difference was more prominent in the case of TiO_2 than with Ho_2O_3 . Figure 1 shows a cross-sectional TEM image taken from the nanolaminate in the as-deposited state. One can clearly see the periodical stack consisting of distinct Ho_2O_3 and TiO_2 layers. The thickness of the constituent layers in the laminate grown using the recipe $10 \times [100 \times \text{TiO}_2 + 250 \times \text{Ho}_2\text{O}_3] + 100 \times \text{TiO}_2$ cycles remained below 5 nm. EDX composition profile (Fig. 2) from the nanolaminate further confirms that the film consists of chemically different alternating layers. Figures 1 and 2 also show that the layer interfaces remain relatively flat up to the top surface with a slightly accumulated roughness limited to less than one individual layer thickness (in the order of 1 nm).

Refractive indices measured from the reference single metal oxide films were 2.39 ± 0.02 and 1.98 ± 0.01 nm, for TiO_2 and Ho_2O_3 , respectively, at the wavelength of 633 nm. Growth rates for single layer films, deposited at temperature of 300 °C, were calculated to be 0.045 nm/cycle and 0.027 nm/cycle for TiO_2 and Ho_2O_3 , matching the values obtained by XRR. Repeated units of the $\text{Ho}_2\text{O}_3/\text{TiO}_2$ bilayer were assumed in constructing a 21 layers optical model for the $\text{Ho}_2\text{O}_3\text{-TiO}_2$ nanolaminate, with an additional capping layer of TiO_2 . The multilayer stack was modelled by fixing refractive index n and absorption coefficient k for each layer to that of the corresponding single-layer reference film allowing variation of the thickness throughout the layers by ~ 1 nm in accord with the TEM results (Fig. 1). Further, by adding void content into each layer, fitting of both thickness and refractive index was accomplished using the standard

three-angle data sets. Fitting of the three-angle data sets and results as thickness (d) and refractive index values (n) for each layer are summarized in Fig. 3.

The values of thicknesses for each layer of TiO₂ and Ho₂O₃ were preliminarily based on calculations taking into account the number of cycles. This kind of approach has also been applied earlier for the TiO₂ and Al₂O₃ layers forming respective nanolaminate structure [12]. Refractive index in TiO₂ layers was basically varying around the corresponding single layer value (2.39 at 633 nm). The refractive index values in both TiO₂ and Ho₂O₃ layers were quite stable throughout the multilayer stack indicating the stability of the growth and uniformity of the constituent layers [12,41]. Moderate variations in the layer thicknesses could be caused by errors in the fitting procedure.

Thickness distribution over an area of $5 \times 5 = 25 \text{ cm}^2$ was measured as also shown in Figure 3 (the bottom panel). Obviously, the films grown were quite uniform with thickness deviation not significantly exceeding 10 % of the mean value. The nanolaminates were somewhat thicker close to the leading edge of the substrate and the thickness decreased steadily towards the trailing edge. This kind of thickness profile is common to ALD films grown in our type of flow-type reactors, as observed also in a study on the growth of TiO₂ from TTIP and H₂O [42]. The longitudinal thickness profiles may develop due to incomplete purging of precursors, secondary surface reactions or partial blocking of the surface adsorption sites from the precursors by the reaction byproducts [43].

3.2. Film structure and morphology

The reference 25-45 nm thick Ho₂O₃ and TiO₂ films were crystallized already in the as-deposited state. Ho₂O₃ films were crystallized to the cubic phase as observed earlier using similar precursor chemistry [29] whereas TiO₂ possessed anatase structure, also similarly to that observed before, though using H₂O, then, as the oxygen precursor [42]. A recent study devoted to the mixing of Ho₂O₃ and TiO₂ and doping TiO₂ with Ho₂O₃ revealed that the crystallization temperature was significantly raised together with the Ho:Ti cation ratio approaching 1:1, i.e. that in Ho₂Ti₂O₇ [27].

The average Ho:Ti cation ratio measured by EDX in the TiO₂-Ho₂O₃ nanolaminate was 1.1. The composition of these films thus became close to that of stoichiometric holmium titanate.

Similarly to the TiO_2 - Ho_2O_3 mixture films, the nanolaminates remained X-ray amorphous in the as-deposited state, neither were they crystallized after annealing at 800 °C (Fig. 4). In accord with HRTEM observations (Fig. 1), some crystallization could be detected in Ho_2O_3 interlayers already in the as-deposited state, whereas the TiO_2 layers remained completely disordered. The crystallization in Ho_2O_3 layers was evidently not extensive enough to be recognized by X-ray diffraction. Upon annealing at 1000 °C, the films crystallized into $\text{Ho}_2\text{Ti}_2\text{O}_7$, as determined by XRD (Fig. 4). Signatures of Ho_2O_3 and/or TiO_2 were not detected in the patterns, neither were perovskite HoTiO_3 reflections [44] observed. The patterns were quite similar, regarding the most intense peaks, to those obtained earlier, e.g., for $\text{Ho}_2\text{Ti}_2\text{O}_7$ synthesized via solid state reaction of the component oxides. [45] One can suppose that the ternary pyrochlore structure is energetically the most favored and the easiest one to form, whereas the rest of the material remains amorphous or too weakly crystallized for X-ray diffraction.

In the sample annealed after deposition at temperatures ranging from 800 to 1000 °C the nanolaminate structure was destroyed. The originally distinct TiO_2 and Ho_2O_3 layers were mixed and the elemental composition map became homogeneous throughout the film thickness (Fig. 5). One can see in the TEM images that the distinctive multilayer structure disappeared and, at the same time, round hollow-like features appeared, embedded in the host oxide film. The appearance of hollow regions might be attributed to the Kirkendall effect, i.e. the motion of the boundary layer between two metals or metal oxides due to the difference in diffusion rates of the cations. The Kirkendall effect can arise when two distinct materials are placed in contact to each other and their interdiffusion occurs by a vacancy mechanism. The Kirkendall effect can become observable by the formation of hollow regions, pores or voids during the diffusion process. These voids may accumulate vacancies and expand further in order to restore equilibrium in the material. Kirkendall effect is mostly observed in metal alloys, rather than in other materials such as mixtures of metal oxides. Nevertheless, there is, a study by Yang *et al.* [46], devoted to ALD of Al_2O_3 thin films on ZnO nanorods. After annealing the $\text{ZnO}/\text{Al}_2\text{O}_3$ core-shell layers were mixed and hollow ZnAl_2O_4 tube-like structures formed via Kirkendall process. It is thus reasonable that ternary metal oxides, such as $\text{Ho}_2\text{Ti}_2\text{O}_7$, form as a result of interdiffusion between the initially distinct regions of constituent binary oxides, i.e. Ho_2O_3 and TiO_2 .

The nanolaminate in the as-deposited state possessed a smooth surface as revealed by AFM (Fig. 6). The surface is clean and homogeneous, i.e. morphologically featureless. The average particle diameter can be estimated to be in the range of 20-30 nm. The rms roughness remains as low as 0.50 nm. As mentioned above, such films required annealing at least at 800 °C in N₂ for 30 min for the initiation of crystallization and were clearly transformed into the ternary crystalline phase upon annealing at 1000 °C. Naturally, the films also roughened upon annealing. Already upon annealing at 800 °C, features resembling particles, crystals or even blisters were observed on the film surface (Fig. 6). These round shaped features may correspond to the voids visible in TEM. The surface features are different in size and shape, with the maximum height of ~30 nm, visible in both height and phase images. The density of these features varied from place to place on the surface causing also the rms roughness to vary between 0.7 and 1.6 nm.

The nanolaminate was also investigated by means of high-temperature X-ray reflectivity (HTXRR) (Fig. 7). Based on the superlattice peak intensity, the laminate structure remains intact up to 425 °C. At higher temperatures up to 725 °C the intensity of that peak decreases indicating layer mixing. When heating further, the intensity drops markedly and the fringes become less defined because of increased roughness most likely caused by the crystallization of the film. This temperature range is well supported by crystallization observed in GIXRD measurements.

3.3. Magnetic behavior

Fig. 8 demonstrates magnetization in the as-deposited Ho₂O₃-TiO₂ nanolaminate on a Si substrate as functions of the measurement temperature and external magnetic field. One can see that the net magnetic moment could be measured in the sample at low temperatures, but it decreased to zero already at about 100 K. In the *M-H* measurements, the nanolaminate did not show ferromagnetic behavior, but exhibited paramagnetic behavior at low temperatures, i.e. at 10 K. At room temperature the diamagnetic response from the sample was dominating. This is not surprising, considering that Ho₂O₃ and TiO₂ are paramagnetic and diamagnetic, respectively, and no additional phases like Ho₂Ti₂O₇ or HoTiO₃ were found in the as-deposited nanolaminates. In the sample annealed at 800 °C, i.e. after conversion of the multilayer to a more homogeneous structure, appearance of voids, and formation of ternary Ho₂Ti₂O₇ phase,

the magnetization tended to saturate apparent in the whole temperature range examined. In accord with the measured magnetization-vs-temperature curve (Fig. 9), the magnetization was measurable in the whole temperature range examined, and remained clearly above the zero around the room temperature as well. Certain transition was observed at 200 K. The transition occurred analogously to that observed earlier in double perovskites, such as epitaxial $\text{Bi}_2\text{CoMnO}_6$ synthesized by a solid state chemical route [47], $\text{La}_2\text{CoMnO}_6$ [48], or in laser ablated epitaxial $\text{La}_2\text{NiMnO}_6$ films [49]. The first magnetic transition at 180-200 K is incomplete as the drop in magnetization is rather weak. In the $M-H$ curves, after subtracting linear para- and diamagnetic components, saturation magnetization below $4.2 \times 10^{-8} \text{ A} \times \text{cm}^2$ could be estimated at 300 K. The magnetization was very soft, with the coercive force not exceeding 4000 A/m. Saturative magnetization probably belongs to the already crystallized $\text{Ho}_2\text{Ti}_2\text{O}_7$, while paramagnetic contribution is due to the remaining amorphous phases. These in-plane magnetization loops were also similar to those observed earlier in double perovskites [47] and holmium titanates [45] in terms of their soft behavior.

Conclusions

$\text{Ho}_2\text{O}_3\text{--TiO}_2$ nanolaminates were grown by atomic layer deposition. Smooth films consisting of distinct metal oxide layers were formed, as recognized by microscopy and ellipsometric measurements. Post-deposition heat-treatment above 800 °C destroyed the multilayer structure and led to the formation of a crystalline ternary phase, $\text{Ho}_2\text{Ti}_2\text{O}_7$. The films with initiated crystallization exhibited magnetic performance with saturative magnetization up to $5 \times 10^{-8} \text{ A} \times \text{cm}^2$ and hysteresis within 3980 A/m in magnetization-versus-external magnetic field curves.

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CAPTIONS TO FIGURES:

Fig. 1

Cross-sectional TEM (upper panel) and HRTEM (lower panel) images of a $\text{Ho}_2\text{O}_3\text{-TiO}_2$ nanolaminate in the as-deposited state. The constituent layer materials are indicated by labels.

Fig. 2

Cross-sectional EDX composition profiling of the $\text{Ho}_2\text{O}_3\text{-TiO}_2$ 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 (color online).

Fig. 3

Spectroscopic ellipsometry results of the $\text{Ho}_2\text{O}_3\text{-TiO}_2$ nanolaminate in the as-deposited state. Upper panels depict the Δ and ψ curves measured together with the fitting results. The 3rd panel from the top represents the multilayer schematics with the thicknesses and refractive indexes giving the best fit with measured spectra. The bottom panel demonstrates total multilayer thickness map over a Si(100) substrate with an area of $5 \times 5 \text{ cm} \times \text{cm}$.

Fig. 4

X-ray diffraction patterns from the $\text{Ho}_2\text{O}_3\text{-TiO}_2$ nanolaminate in the as-deposited state, and after annealing at 800 and 1000 °C in N_2 for 30 min. Miller indexes assigned after crystallization to the pyrochlore phase $\text{Ho}_2\text{Ti}_2\text{O}_7$ are indicated.

Fig. 5

HRTEM images in two different scales (top and middle panels) and compositional EDX map (bottom panel) from the $\text{Ho}_2\text{O}_3\text{-TiO}_2$ nanolaminate annealed at 1000 °C in N_2 for 30 min. (color online)

Fig. 6

Atomic force microscopy height (left column) and phase (right column) images of the $\text{Ho}_2\text{O}_3\text{-TiO}_2$ nanolaminate in the as-deposited state (upper row) and after annealing at 800 °C in N_2 for 30 min (lower row).

Fig. 7

X-ray reflectivity patterns from Ho₂O₃-TiO₂ nanolaminate at different annealing temperatures under nitrogen atmosphere in three-dimensional (a) and conventional (b) mode.

Fig. 8

Magnetization vs. measurement temperature (the 1st and 2nd panels from top) and magnetic moment vs. external magnetic field (***M-H***) curves (the 3rd and 4th panels) for the Ho₂O₃-TiO₂ nanolaminate after annealing at 800 °C in N₂ for 30 min. The temperatures for the ***M-H*** curves are indicated by labels.

Fig.1 Kukli et al.

Fig. 2 Kukli et al.

TiO ₂	d= 2.18 ± 0.06 nm	n=2.39 ± 0.01
Ho ₂ O ₃	d= 4.36 ± 0.09 nm	n=1.99 ± 0.02
TiO ₂	d= 1.97 ± 0.07 nm	n=2.38 ± 0.01
Ho ₂ O ₃	d= 4.32 ± 0.08 nm	n=1.98 ± 0.03
TiO ₂	d= 1.88 ± 0.03 nm	n=2.43 ± 0.04
Ho ₂ O ₃	d= 4.37 ± 0.05 nm	n=2.02 ± 0.01
TiO ₂	d= 1.89 ± 0.01 nm	n=2.42 ± 0.02
Ho ₂ O ₃	d= 4.35 ± 0.06 nm	n=2.01 ± 0.01
TiO ₂	d= 1.89 ± 0.04 nm	n=2.38 ± 0.01
Ho ₂ O ₃	d= 4.38 ± 0.09 nm	n=2.03 ± 0.02
TiO ₂	d= 1.87 ± 0.05 nm	n=2.36 ± 0.04
Ho ₂ O ₃	d= 4.39 ± 0.05 nm	n=2.01 ± 0.03
TiO ₂	d= 1.92 ± 0.04 nm	n=2.38 ± 0.01
Ho ₂ O ₃	d= 4.38 ± 0.07 nm	n=1.99 ± 0.01
TiO ₂	d= 1.87 ± 0.09 nm	n=2.42 ± 0.03
Ho ₂ O ₃	d= 4.37 ± 0.05 nm	n=2.03 ± 0.04
TiO ₂	d= 1.81 ± 0.05 nm	n=2.43 ± 0.04
Ho ₂ O ₃	d= 4.39 ± 0.02 nm	n=2.01 ± 0.02
TiO ₂	d= 1.82 ± 0.08 nm	n=2.39 ± 0.01
Ho ₂ O ₃	d= 4.42 ± 0.08 nm	n=2.02 ± 0.01
TiO ₂	d=2.53 ± 0.03 nm	n=2.52 ± 0.03
SiO ₂	d=1.42 ± 0.01 nm	n=1.45 ± 0.01
Si(100) substrate

Fig. 3 Kukli et al.

Fig. 4 Kukli et al.

Fig. 5 Kukli et al.

Fig. 6 Kukli et al.

Fig. 7 Kukli et al.

Fig. 8 Kukli et al.