



This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Emara, Jennifer; Kia, Alireza M.; Bönhardt, Sascha; Mart, Clemens; Kühnel, Kati; Haufe, Nora; Puurunen, Riikka L.; Utriainen, Mikko; Weinreich, Wenke

Lanthanum doped hafnium oxide thin films deposited on a lateral high aspect ratio structure using atomic layer deposition: A comparative study of surface composition and uniformity using x-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry *Published in:* 

Applied Surface Science

DOI: 10.1016/j.apsusc.2024.161408

Published: 30/01/2025

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

Published under the following license: CC BY-NC-ND

Please cite the original version:

Emara, J., Kia, A. M., Bönhardt, S., Mart, C., Kühnel, K., Haufe, N., Puurunen, R. L., Utriainen, M., & Weinreich, W. (2025). Lanthanum doped hafnium oxide thin films deposited on a lateral high aspect ratio structure using atomic layer deposition: A comparative study of surface composition and uniformity using x-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry. *Applied Surface Science*, *680*, Article 161408. https://doi.org/10.1016/j.apsusc.2024.161408

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.



Contents lists available at ScienceDirect

# Applied Surface Science



journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

# Lanthanum doped hafnium oxide thin films deposited on a lateral high aspect ratio structure using atomic layer deposition: A comparative study of surface composition and uniformity using x-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry

Jennifer Emara<sup>a,\*</sup>, Alireza M. Kia<sup>a,1</sup>, Sascha Bönhardt<sup>a</sup>, Clemens Mart<sup>a,2</sup>, Kati Kühnel<sup>a</sup>, Nora Haufe<sup>a</sup>, Riikka L. Puurunen<sup>b</sup>, Mikko Utriainen<sup>c</sup>, Wenke Weinreich<sup>a</sup>

<sup>a</sup> Fraunhofer Institute for Photonic Microsystems (IPMS), Center Nanoelectronic Technologies (CNT), An der Bartlake 5, 01109 Dresden, Germany
<sup>b</sup> Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, P.O.Box 16100, FI-00076 Aalto, Finland

<sup>c</sup> Chipmetrics Oy, Yliopistokatu 7, 80130 Joensuu, Finland

#### ARTICLE INFO

Keywords:

Lanthanum doped hafnium oxide X-ray photoelectron spectroscopy Time-of-flight secondary ion mass spectrometry Lateral high aspect ratio PillarHall Atomic layer deposition

# ABSTRACT

Hafnium oxide (HfO<sub>2</sub>) thin films doped with lanthanum (La) can achieve ferroelectricity, making the material applicable in transistor and memory technologies. To downscale future devices in the semiconductor industry, the application of the doped HfO<sub>2</sub> material requires deposition on complex microscopic three-dimensional (3D) structures. A widely used process for the preparation of doped HfO<sub>2</sub> thin films is atomic layer deposition (ALD). With 3D geometries, it is challenging to deposit materials homogeneously and to effectively characterize them. To forego the difficulties in film characterization, two-dimensional (2D) PillarHall lateral high aspect ratio (LHAR) test structures are used. These structures expose a lateral surface to facilitate the conformality analysis of thin films deposited using two different ALD processes. In this work, we aim to further advance the arsenal of analysis techniques used to characterize La doped HfO<sub>2</sub> thin films by using x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to analyze uniformity and composition. The XPS technique can be applied and established as a method for the optimal analysis of thin films deposited on LHAR structures. Both techniques provide a complementary analysis of material formation, elemental distribution, measurement along the LHAR depth range, and can probe differences between deposition processes.

### 1. Introduction

Thin film hafnium oxide (HfO<sub>2</sub>) is a subject of attention due to its high-*k* property, making it a desired material to be used in micro- and opto-electronic devices. The observation of the ferroelectric (FE) effect has made this material promising as an active part of the non-volatile memory, energy storage and sensor fields [1–6]. Doped HfO<sub>2</sub>-based FE thin films are promising materials for FE memory technologies, such as, ferroelectric field-effect transistors (FeFETs), ferroelectric random access memories (FRAM), and ferroelectric tunnel junctions (FTJs) [7,8]. In ferroelectrics, the HfO<sub>2</sub> can be doped with different elements such as lanthanum (La), dysprosium (Dy), aluminum (Al), yttrium (Y), silicon (Si), gadolinium (Gd), etc. [1,9-17]. This material can have several polymorphs, the orthorhombic (Pca2<sub>1</sub>, o-phase), monoclinic (P2<sub>1</sub>/c, mphase), tetragonal (P4<sub>2</sub>/nmc, t-phase), and cubic (Fm3m, c-phase) phases. Using dopants such as La, makes it possible to obtain the o-phase, achieving ferroelectricity in HfO<sub>2</sub> [12,17,18].

Atomic layer deposition (ALD) is a technique that produces highly conformal thin films with nanometer range thickness [19] and it is commonly used to prepare doped  $HfO_2$  thin films. For growing such doped films, two ALD steps, one for the host matrix and one for the dopant, are usually combined. The cycle ratio determines composition and therefore the dopant concentration. However, this classical standard ALD method can lead to poor intermixing of the dopant species in the

\* Corresponding author.

https://doi.org/10.1016/j.apsusc.2024.161408

Received 30 May 2024; Received in revised form 9 September 2024; Accepted 1 October 2024 Available online 2 October 2024 0169-4332/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the

E-mail address: jennifer.salah.emara@ipms.fraunhofer.de (J. Emara).

<sup>&</sup>lt;sup>1</sup> Present address: ams-Osram International GmbH, Leibnitzstraße 4, 93051 Regensburg, Germany.

<sup>&</sup>lt;sup>2</sup> Present address: Infineon Technologies Dresden GmbH & Co. KG, Königsbrücker Straße 180, 01099 Dresden, Germany.

<sup>0169-4332/© 2024</sup> The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

 $HfO_2$  matrix where homogeneous mixing is important to ensure uniformity of stoichiometry and electrical properties. To achieve higher quality films, Mart et. al. [15] have published a modified ALD process (three-step ALD) where the metal–organic precursors are subsequently applied before the co-reactant, for example, water (H<sub>2</sub>O). The HfO<sub>2</sub> films were successfully doped with Al, Si and La, leading to homogenous films with low defect density and reduced internal bias fields.

The application of the doped HfO<sub>2</sub> material in the semiconductor industry requires the deposition of materials in three-dimensional (3D) structures, such as, high aspect ratio (HAR) microstructures, as part of the downscaling of future devices. These types of structures can prove to be a challenge for thin film characterization of doped ferroelectric materials, where changes in low doping concentrations deep inside the trench structures influence the stability of the ferroelectric phase. Due to the micrometer sized dimensions of these structures, it can be difficult to match with the lateral resolution of many techniques. Normally, more complex, and costly cross-sectional preparation and analysis is needed, such as transmission electron microscopy (TEM), where lamella preparation of each trench is required, and light element detection is difficult. During ALD processing, several factors could lead to varying dopant concentration levels throughout the material, such as differences in partial pressure, precursor molar masses and molecular sizes [19]. Dealing with these factors on 3D structures for the elemental characterization of thin films would prove to be challenging. Therefore, to forego the difficulties in film characterization, the two-dimensional (2D) PillarHall lateral high aspect ratio (LHAR) test structures can be used [20]. These structures are fabricated on single-crystal silicon with multiple lateral cavities, and polysilicon pillars, with a defined geometry, holding up a polysilicon membrane roof [20,21]. Removing this membrane exposes a lateral surface, which would help with analyzing the composition and uniformity of the doped material, especially when many device applications require uniformly deposited thin films.

In this work, the La doped HfO<sub>2</sub> thin films were prepared using both standard and three-step ALD on planar Si wafer and PillarHall LHAR test structure chips. We have previously shown that time-of-flight secondary ion mass spectrometry (ToF-SIMS) successfully characterized the elemental distribution of standard ALD deposited Si doped HfO2 thin films in the high aspect ratio structures [22]. Herein, we introduce a second method, x-ray photoelectron spectroscopy (XPS), which in combination with ToF-SIMS, advances the collection of analysis tools used to characterize the doped film in the LHAR structure. Choosing the appropriate technique for elemental analysis depends on the material under study. Widely used techniques for composition analysis such as scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX) spectroscopy, or TEM and electron energy loss spectroscopy (EELS) could be viable for imaging and material characterization. The SEM/ EDX methods can be less costly and more easily accessible, however, they provide semi-quantitative data, and depending on the instrument capabilities and the material matrix, the EDX may not be sensitive to analyze low doping levels or provide a concentration profile [23]. The TEM/EELS methods are complex and time consuming, involving lamella preparation, and provide semi-quantitative results [24]. Herein, the employed ToF-SIMS technique is highly sensitive, making it capable of detecting elements at parts per million (ppm) or even parts per billion (ppb) levels [25,26]. The XPS technique can detect concentrations down to 0.1 – 1 atomic %, is sensitive to heavy elements [27], is quantitative, and provides chemical state information. Furthermore, with XPS, imaging the structured surface of the PillarHall was possible using secondary electron imaging (SXI). Combining imaging and micro area analysis, measurements of the material surface along the lateral deposition depth were made possible. The La and Hf phases and La cationic %(cat. %) doping level throughout the length of the material were analyzed. Both XPS and ToF-SIMS provide a complementary analysis and can distinguish between different deposition processes. Together they probe the penetration depth, elemental distribution, and composition of the La doped HfO2 thin films deposited on the LHAR test structure.

#### 2. Experimental

#### 2.1. ALD thin film deposition of $HfO_2$ on PillarHall test structures

All the 10 nm thin films were fabricated by means of metal–organic atomic layer deposition (ALD) in a Jusung Eureka 3000 warm-wall reactor under vacuum (*ca.* 1 Torr) at a temperature of 280 °C (for lanthanum doped hafnium oxide) and 300 °C (for hafnium oxide and lanthanum hydroxide and buried lanthanum oxide). For the deposition of the films, tetrakis(ethylmethylamino)hafnium (TEMAHf), tris(isopropylcyclopentadienyl)lanthanum (La(iPrCp)<sub>3</sub>), and trimethyl aluminum (TMA) precursors were used with O<sub>3</sub> as an oxidizer. Two different types of ALD deposition were used to prepare differently doped thin films. The standard ALD, where precursors were introduced alternately, and three-step ALD, where metal–organic precursors were applied subsequently (Figure S1). In addition, for XPS analysis, buried lanthanum oxide (with an aluminum oxide capping layer), lanthanum hydroxide and hafnium oxide were prepared (Figure S2).

Fig. 1a shows a PillarHall test chip (LHAR4, 4th generation) before removing the polysilicon membrane roof. Each chip is fabricated with multiple lateral trenches, with lengths (L) ranging 1 µm to 5 mm and aspect ratios (AR) of 2:1 to 10,000:1, respectively, on top of a singlecrystal silicon substrate shielded with a polysilicon membrane that is held up by polysilicon pillars [21]. The lateral gap height (H) of the trenches is 500 nm. A general description of earlier generation test chips with schematic depictions was reported in previous studies [21,22]. One PillarHall test chip contains over 20 different LHAR test structures. Here, we used the  $W = 90 \ \mu m$  structure defined on the chip as a case study for both the XPS and ToF-SIMS analyses; where 90 indicates the open area width in micrometers, at the 1,000 µm length membrane. For analysis, the polysilicon membrane was peeled off using adhesive tape. Fig. 1b shows an optical microscope image of the PillarHall without the polysilicon membrane, exposing the standard ALD deposited La doped hafnium oxide thin film (darker shaded region). The image shows the penetration depth of the material under the membrane, as indicated by the dotted lines.

# 2.2. Time-of-flight secondary ion mass spectrometry

The ToF-SIMS measurements were performed using a ToF-SIMS 300R (IONTOF GmbH, Münster, Germany) to acquire elemental distribution of the thin films. A bismuth (Bi) liquid metal primary ion gun (LMIG) was used as a primary ion source to perform raster scans over the analysis area. The ion beam current was adjusted to ca. 13nA (DC mode). The beam was chopped in 20 ns and focused to a diameter of *ca*. 300 nm. The beam was raster scanned on the sample surface to obtain mass spectra for an analysis area of  $100 \times 100 \ \mu m^2$ . The extraction lens was biased at -30 V to collect and analyze the ejected secondary ions. The secondary ions travelled through a reflection flight tube and were detected using a micro-channel plate (MCP) detector. To sputter the material for profiling, a secondary ion source, an electron impact (EI) gas ion source of oxygen  $(O_2^+)$ , was used. The ion beam energy was adjusted at 1 kV at a fixed current of 250 µA covering a surface area of  $300 \times 300 \ \mu\text{m}^2$  in sawtooth mode. To measure the PillarHall structures, adhesive tape was used to remove the polysilicon membrane and expose the deposited material.

#### 2.3. X-ray photoelectron spectroscopy

Measurements were performed on the PHI Quantes Scanning XPS/ HAXPES Microprobe (Physical Electronics GmbH, MN, US) under ultrahigh vacuum at a base pressure of  $< 6.7 \times 10^{-8}$  Pa. All samples were introduced into the system through ambient atmosphere. The buried lanthanum oxide, lanthanum oxide (exposed to air), hafnium oxide, and



Fig. 1. Optical microscope images of the W90 cavity for (a) a PillarHall structure with membrane and (b) a PillarHall structure with the polysilicon membrane peeled off exposing the La doped hafnium oxide deposited using standard ALD. The image shows the penetration depth of the material under the membrane as indicated by the arrows and dotted lines.

La doped hafnium oxide samples were measured on the same instrument and conditions. An AlK<sub> $\alpha$ </sub> x-ray source ( $h\nu = 1486.6$  eV) with *ca.* a 7.5 µm sized beam diameter was used to excite the samples, ejecting photoelectrons that were detected. The resulting spectra and x-ray induced secondary electron images (SXIs) were taken at a 45° take-off angle. Pass energies ( $E_{pass}$ ) of 280 and 69 eV for the survey and high-resolution scans were used, respectively. The binding energy (BE) scale was calibrated against Au4f<sub>7/2</sub> and Cu2p<sub>3/2</sub> at 83.93 and 932.60 eV, respectively.

For sputtering of the aluminum oxide capping layer, an argon ion (Ar<sup>+</sup>) sputter gun was used. This was performed in the XPS analysis chamber under vacuum. The layer was removed using an ion beam with an energy of 500 eV at a sputter duration of 45 min. The ion beam was rastered over a  $3 \times 3 \text{ mm}^2$  area. The point of measurement was at the center of the sputter crater, so the analysis was performed in an area with uniform sputtering.

The high-resolution elemental spectra were fitted using the CasaXPS software. For all fits, a Gaussian to Lorentian peak shape and Shirley background were used; except for the La3d region, where a Tougaard background was used. Charging effects were accounted for by correcting the BE scale shift to the adventitious C1s signal at 285 eV. For the determination of the metal oxide stoichiometries and the La cationic % (cat. %) concentration, quantification was carried out using the areas under the fit peaks, after background subtraction, and the relative sensitivity factors (RSFs) for each element. The La cat. % concentrations were calculated as {[(La) / (La + Hf)] × 100} [28], where the La and Hf values correspond to the Lad3d<sub>5/2</sub> and Hf4f fitted and RSF corrected areas, respectively. The RSFs were extracted from the MultiPak software developed by Physical Electronics (PHI). The extracted RSFs account and correct for the transmission function of the spectrometer and the x-ray source angle for geometric asymmetry effects.

Throughout this work, the measured elemental core levels were carefully chosen to ensure little to no significant peak overlap of elemental signals and core levels widely studied in the literature for effective comparison. For the planar unstructured samples, four measurement points were analyzed to generate averages and standard deviation errors for the fitted and calculated values. For the PillarHall structured samples, as in ToF-SIMS, the membrane was peeled off using adhesive tape to expose the deposited doped films for measurement. All samples under study were exposed to ambient atmosphere before their introduction into the ultra-high vacuum (UHV) XPS analysis chamber.

#### 3. Results and discussion

# 3.1. Time-of-flight secondary ion mass spectrometry

The detailed examination of a thin film's chemical composition and interfacial characterization, providing information on the elemental distribution in the range of a few monolayers, is made possible by the ToF-SIMS technique. This method helps obtain information about a material from both the surface and bulk [25,26]. For elemental detection, a lateral resolution of *ca.* 100 nm is feasible using the liquid metal ion gun (LMIG) [29–31]. However, the spatial resolution of the ToF-SIMS technique can be affected by parameters such as the primary ion intensity, instrument transmission, primary ion beam spot size, surface geometry, material concentration and sample matrix [29,32,33]. By combining the PillarHall test structure and the ToF-SIMS technique, the composition, uniformity, and penetration depth of the material can be analyzed.

For analysis, the PillarHall polysilicon membrane was peeled off to expose the deposited material in the W = 90  $\mu$ m structure. The darkened/bright circles in Fig. 2 are the holes left by the pillars after membrane removal. Fig. 2a shows the defined analysis regions. Starting from the area without membrane into the membrane covered area (as indicated by the direction of the green arrows in the figure), the regions of interests (ROIs) were defined as  $2 \times 25 \ \mu$ m<sup>2</sup>, yielding a total of 31 ROIs extracted per sample. Fig. 2b and c show the total ion image spectrum from both the three-step and standard ALD samples. Each elemental signal is color-coded in red, green, and blue for <sup>30</sup>Si<sup>+</sup>, <sup>139</sup>La<sup>+</sup>, and <sup>180</sup>Hf<sup>+</sup>, respectively. The analysis points are situated at the mid-point between the pillars to avoid measurement of the substrate material or voids created by peeling off the membrane.

To assess the elemental distribution and the ratio between the dopant and the oxide material under the membrane, the integrated counts of the total species of <sup>30</sup>Si<sup>+</sup>, <sup>139</sup>La<sup>+</sup>, and <sup>180</sup>Hf<sup>+</sup>, and the calculated La to Hf ratio, from each ROI is plotted in Fig. 3 with respect to the depth in the test structure. The three-step ALD (Fig. 3a) and standard ALD (Fig. 3b) samples show different behavior for each elemental species. For both depositions, the area counts are consistent until 18 µm for the standard ALD and 6 µm for the three-step ALD under the membrane. After this, the area counts decrease, and the counts are measured until a penetration depth of c.a. 73 µm and 74 µm for standard ALD and three-step ALD, respectively, after which the signals disappeared. Along the depth under the membrane, the elements show different profiles. For both depositions,  $^{180}\mathrm{Hf^{+}}$  has less depth range than the  $^{\hat{1}39}\mathrm{La^{+}}$  under the membrane, with values of ca. 35 µm and ca. 70 µm, respectively. The difference of  $^{139}\text{La}^+$  and  $^{180}\text{Hf}^+$  depth range can also be seen by comparing the 2D maps of the three-step and standard ALD from the entire analysis field (bottom of Fig. 3). Another pronounced difference between the two ALD processes is the <sup>139</sup>La<sup>+</sup> area count spike seen for the three-step ALD sample (Fig. 3a). In addition, the  ${}^{30}Si^+$  counts rise around when the <sup>180</sup>Hf<sup>+</sup> counts decrease and <sup>139</sup>La<sup>+</sup> spikes. On the other hand, the standard ALD shows a coupled change in the  $^{139}La^+$  and  $^{180}Hf^+$ area counts throughout, decreasing gradually after 18  $\mu$ m. The  $^{30}Si^+$ counts show a gradual rise. The depth of the constant signal ratio between  $^{139}La^+$  and  $^{180}Hf^+$  for the three-step ALD film is less than that of standard ALD, reaching ca. 6 µm (Fig. 3a) under the membrane versus ca. 18 µm (Fig. 3b), respectively. It should also be noted that the calculated ratio between the <sup>139</sup>La<sup>+</sup> and <sup>180</sup>Hf<sup>+</sup> were not standardized to the sensitivity factors of each element, but they are still comparable



**Fig. 2.** Figure showing the (a) 2D surface matrix ToF-SIMS scan area with defined analysis regions, the ROI, on top of the total analysis area for the standard ALD sample. Each ROI covers an area of  $2 \times 25 \ \mu\text{m}^2$ . The direction of the green arrows indicates the measurement direction. In addition, the superimposed RGB representation of  ${}^{30}\text{Si}^+$ ,  ${}^{139}\text{La}^+$  and  ${}^{180}\text{Hf}^+$  from the deposited area of the (b) three-step and (c) standard ALD deposited La doped hafnium oxide samples are shown.



Fig. 3. Figure showing the ToF-SIMS evaluation of  ${}^{30}$ Si<sup>+</sup>,  ${}^{139}$ La<sup>+</sup> and  ${}^{180}$ Hf<sup>+</sup> for the (a) three-step and (b) standard ALD deposited La doped hafnium oxide samples calculated from the ROIs shown in Fig. 2, and their respective  ${}^{139}$ La<sup>+</sup> and  ${}^{180}$ Hf<sup>+</sup> 2D maps of the analysis area.

regarding the <sup>30</sup>Si<sup>+</sup> counts for each measurement point.

It can be seen in Fig. 3 that the area counts of  $^{139}La^+$  and  $^{180}Hf^+$  differ between the two ALD processes for a given thin film thickness. Although

the higher counts for standard ALD can be partially attributed to a higher overall film thickness, other factors could be involved. Since the experimental deposition processes for both samples are different (Figure S1), this would result in different layer densities and chemical bonds for both samples. The target material properties can significantly affect the sputter yield due to variations in atomic mass, layer density, and binding energy. However, the main difference is in the behavior of the three-step and standard ALD processes. Since the standard ALD consists of full cycles for the lanthanum oxide, it can be concluded that the film morphology is closer to a nano-laminate. Since ALD processes are overly sensitive during the initial growth on a different material than the target material, it can be concluded that the film quality is lower than that of the three-step ALD.

#### 3.2. X-ray photoelectron spectroscopy

Using XPS, the elemental composition and distribution across the deposited doped layers on the PillarHall test structure were examined. Notably, the La and Hf phases, their penetration depth and the La cat. % doping level.

#### 3.2.1. Lanthanum oxide and hydroxide, and hafnium oxide

Before the analysis of the doped thin films, three thin films were studied: lanthanum oxide, lanthanum hydroxide and hafnium oxide. The XPS analysis of these 10 nm ALD films deposited on planar Si (100) blanket wafers developed the optimal parameters for peak fitting of the elements under study, La, Hf and O, to determine the elemental composition in these films and in the doped material.

The lanthanum oxide material is known to be hygroscopic [34], and since the samples in this study are introduced into the XPS chamber through ambient atmosphere, it is subjected to hydration effects. Therefore, a lanthanum hydroxide film was simply formed by exposing a lanthanum oxide film to air. To prepare a lanthanum oxide film, a 5 nm aluminum oxide capping layer was deposited on top to shield it from air (referred to as buried lanthanum oxide). To analyze this layer, the aluminum oxide capping layer was sputtered away using  $Ar^+$  ions at low energy inside the UHV XPS chamber (Figure S3).

Fig. 4a shows the La3d and O1s high resolution scans for the lanthanum hydroxide and the buried lanthanum oxide films. The La3d region exhibits multiplet splitting for the La3d<sub>5/2</sub> and La3d<sub>3/2</sub> spin orbit peaks [34–36]. Seven Gaussian components can be fit in the La3d region, adopted from Mullica *et. al.* [35,36]. Based on the peak fitting analysis, both the oxide and hydroxide films' La3d high resolution scans showed spectral differences that distinguish between them: peak position, energy separation, full width half maximum (FWHM), intensity ratios, in addition to the binding energy positions in the O1s region (Figure S4). The La3d<sub>5/2</sub> peak for the hydroxide is found at a higher BE (834.61  $\pm$  0.06 eV) compared to the buried oxide (833.55  $\pm$  0.09 eV)

(Fig. 4 and Table S1) [37–41]. The main O1s peak is found at  $531.75 \pm 0.04$  and  $528.69 \pm 0.08$  eV for the hydroxide and buried oxide, respectively [32,35,37–39]. There are multiple possible contributions to the smaller O1s peaks, which are discussed in more detail in the supporting data.

The atomic ratio of La:O for the hydroxide and buried oxide is 1:2.80  $\pm$  0.10 and 2:3.02  $\pm$  0.02, respectively (Table S3), indicating that the oxide phase is indeed La<sub>2</sub>O<sub>3</sub> and the hydroxide La(OH)<sub>3</sub> with a slight oxygen defect due to dehydration effects in the analysis chamber. Therefore, the spectral differences between lanthanum hydroxide and oxide can be differentiated using XPS.

Fig. 4b shows the Hf4f and O1s high resolution scans of the hafnium oxide film. The Hf4f region was fit with two components corresponding to the Hf4f<sub>7/2</sub> and Hf4f<sub>5/2</sub> doublet at 17.36  $\pm$  0.04 eV and 19.02  $\pm$  0.04 eV, respectively (Table S1), with an energy separation of 1.66  $\pm$  0.00 eV (Table S2). The peak positions and energetic separation are indicative of the HfO<sub>2</sub> phase [42–47]. The O1s region was fit with two components, a main peak at 530.72  $\pm$  0.02 eV corresponding to O<sup>2-</sup> (oxygen bound to hafnium) [42,45,47–50], and a small peak at a higher BE of 532.45  $\pm$  0.02 eV possibly corresponding to oxygen bound to carbon (C-O), hydroxide species and/or oxygen vacancies based on literature reports [48,49,51]. In addition, a Hf4s signal occurs around 538 eV [52,53] in the O1s region, but it is safely omitted from the O1s fit. Based on the total peak area fits of Hf4f and O1s, the Hf:O atomic ratio is 1:2.03  $\pm$  0.05 (Table S3).

#### 3.2.2. Lanthanum doped hafnium oxides deposited on planar silicon wafers

The ALD prepared La doped hafnium oxides deposited on planar silicon wafers resemble the area uncovered by the membrane in the PillarHall structure. Fig. 5 shows an example of the La3d<sub>5/2</sub>, O1s and Hf4f high resolution scans of La doped hafnium oxide on the planar Si wafer for the three-step ALD sample. An adequate fitting of the entire La3d region was not possible since it has a low signal to noise (S/N) ratio and low intensity; particularly the La3d<sub>3/2</sub> peak had significant scattering, and therefore, could not be fit. The better resolved La3d<sub>5/2</sub> peak was deconvoluted into three components (cf<sup>0</sup>, cf<sup>1</sup>L bonding, and cf<sup>1</sup>L antibonding) (Fig. 5), with their BEs listed in Table 1.

The BEs of the La3d<sub>5/2</sub> components are found at higher values of the energy scale (Fig. 5 and Table 1), shifted by *c.a.* + 1 eV with respect to the measured lanthanum hydroxide (Table S1). The occurrence of this peak at higher BEs was also observed in the literature [35,36,54,55]. The highest La oxidation state that can be reached is + 3, therefore, this BE shift could be due to a change in chemical environment (and not a change to higher oxidation state) since the lanthanum here acts as a dopant incorporated into a foreign matrix.



Fig. 4. High resolution XPS spectra of (a) the La3d and O1s regions of the 10 nm buried lanthanum oxide layer (after sputtering) and the 10 nm lanthanum hydroxide layer (lanthanum oxide exposed to air) on planar Si wafer, and (b) the O1s and Hf4f regions of the 10 nm hafnium oxide layer on planar Si wafer.



Fig. 5. High resolution XPS spectra of the La3d, O1s, Si2s and Hf4f regions of the three-step ALD deposited 10 nm La doped hafnium oxide thin film on planar Si wafer.

#### Table 1

XPS fit data for the La doped hafnium oxide thin films deposited on planar Si wafer. The values listed are averages of four different measurement points, with the error given in standard deviation.

	Peak Position / eV	
	Three-step ALD	Standard ALD
La3d <sub>5/2</sub> (cf <sup>0</sup> )	$835.38\pm0.05$	$835.19\pm0.14$
La3d <sub>5/2</sub> bonding (cf <sup>1</sup> L)	$839.31 \pm 0.13$	$839.42\pm0.23$
La3d <sub>5/2</sub> antibonding (cf <sup>1</sup> L)	$837.59 \pm 0.23$	$837.79\pm0.14$
O1s (main peak)	$530.55\pm0.09$	$530.74\pm0.04$
O1s (small peak)	$532.36 \pm 0.11$	$532.58\pm0.08$
Hf4f <sub>7/2</sub>	$17.20\pm0.08$	$17.36\pm0.04$
Hf4f <sub>5/2</sub>	$18.86\pm0.09$	$19.02\pm0.04$
La doping level (cat. %)	$1.60\pm0.13$	$\textbf{3.05} \pm \textbf{0.43}$

Table 2 lists the calculated energy separation and FWHM of the components. The energetic difference between the La3d<sub>5/2</sub> (cf<sup>0</sup>) and La3d<sub>5/2</sub> (cf<sup>1</sup>L bonding) for the three-step and standard ALD samples are  $3.93 \pm 0.10$  and  $4.19 \pm 0.08$  eV, respectively and between the La3d<sub>5/2</sub> cf<sup>1</sup>L bonding and antibonding satellites for the three-step and standard ALD samples are  $1.71 \pm 0.17$  and  $1.61 \pm 0.17$  eV, respectively. The FWHM of La3d<sub>5/2</sub> (cf<sup>0</sup>) for the three-step and standard ALD samples are 2.43 and 2.42, respectively. All the values are similar to the ones of the measured lanthanum hydroxide (Table S2) and reported in the literature

#### Table 2

Table listing the energy separation for La3d and Hf4f, and FWHM of La3d<sub>5/2</sub>, for the La doped hafnium oxide thin films deposited on planar Si wafer. The values listed are averages of four different measurement points, with the error given in standard deviation.

	Three-step ALD	Standard ALD
$La3d_{5/2}$ (cf <sup>0</sup> ) – $La3d_{5/2}$ bonding (cf <sup>1</sup> L)	$\begin{array}{c} 3.93 \pm 0.10 \\ eV \end{array}$	$\begin{array}{c} 4.19 \pm 0.08 \\ eV \end{array}$
$La3d_{5/2}$ bonding (cf <sup>1</sup> L) – La3d <sub>5/2</sub> antibonding	$1.71\pm0.17$	$1.61 \pm 0.17$
La3d <sub>5/2</sub> bonding (cf <sup>1</sup> L) to La3d <sub>5/2</sub> (cf <sup>0</sup> ) intensity	ev 0.72 ± 0.14	$ev$ $0.62\pm0.03$
ratio		
La3d <sub>5/2</sub> (cf <sup>0</sup> ) FWHM	2.43	2.42
$Hf4f_{7/2} - Hf4f_{5/2}$	$1.66\pm0.00$	$1.66\pm0.00$
	eV	eV

[41,55–57]. The La3d<sub>5/2</sub> bonding (cf<sup>1</sup>L) to La3d<sub>5/2</sub> (cf<sup>0</sup>) intensity ratio for the three-step and standard ALD are 0.72  $\pm$  0.14 and 0.62  $\pm$  0.03 eV, respectively. For the standard ALD sample, the value is lower than what is expected for the measured lanthanum hydroxide film (Table S2). Since the satellite intensity is strongly dependent on the surrounding ligands and chemical environment [58], adding to that the larger scatter and noise associated with the signal, this could lead to the difference in calculated intensity ratios. A comparison of the La3d<sub>5/2</sub> and O1s highresolution scans between the standard and three-step ALD samples shows that there are no significant differences in peak shape or binding energy values (Tables S6 and S7), or in the energy separation and intensity ratios of the La3d<sub>5/2</sub> region (Tables S8 and S9). Therefore, a significant difference in the hydroxylation behavior of the lanthanum oxide between the two ALD processes cannot be seen from the XPS results. Overall, it can be concluded that the lanthanum dopant is present in the hydroxide phase, which is likely since the planar samples were introduced into the XPS instrument through air.

The Hf4f region was fit with two components. The BEs of the Hf4f<sub>7/2</sub> and Hf4f<sub>5/2</sub> are 17.20  $\pm$  0.08 and 18.86  $\pm$  0.09 eV, respectively, for the three-step ALD sample, and 17.36  $\pm$  0.04 and 19.02  $\pm$  0.04 eV, respectively, for the standard ALD sample (Table 1). The energy separation between the doublet pair is 1.66  $\pm$  0.00 eV for both three-step and standard ALD (Table 2). Both the BE positions and the peak separation is consistent with the measured HfO<sub>2</sub> thin film (Fig. 4b and Table S1) [42–47].

The O1s region (Fig. 5) shows mainly character belonging to the HfO<sub>2</sub> phase (as seen in Fig. 4b), with comparable peak shape. The BE of the O1s main peak is at  $530.55 \pm 0.09$  and  $530.74 \pm 0.04$  eV for the three-step and standard ALD samples respectively, which corresponds to oxygen bound to hafnium as observed for the HfO<sub>2</sub> phase (Table S1) [42,45,47–50]. The fitted small O1s peak lies at  $532.36 \pm 0.11$  and  $532.58 \pm 0.078$  eV for the three-step and standard ALD samples respectively. The position of this peak corresponds to that fitted for the measured HfO<sub>2</sub> (Table S1) [48,49,51].

To calculate the doping level of La (cat. %), the Lad3d<sub>5/2</sub> and Hf4f fitted areas corrected to RSF were used. The La cat. % for the three-step and standard ALD samples are 1.60  $\pm$  0.13 and 3.05  $\pm$  0.43 %, respectively (Table 1).

# 3.2.3. Lanthanum doped hafnium oxides deposited on the PillarHall test structure

The elemental composition, distribution, and penetration depth along the deposited doped thin films on the PillarHall LHAR structure, in addition to the doping level of La (cat. %) and the La and Hf phases, is presented here. Similar to the measurement procedure employed by ToF-SIMS, the polysilicon membrane was peeled off to expose the underlying material. An x-ray induced secondary electron image (SXI) example for the three-step ALD sample is shown in Fig. 6. The bright circles are the holes left behind after membrane removal. The zoomed in image in the figure shows the analysis points starting from the area with no membrane into the membrane covered area (as shown by the direction of the green arrows). The analysis points were positioned between the pillars to evade the measurement of the holes left behind by the pillars due to peeling off the membrane. The x-ray beam size used for analysis was tuned to ca. 7.5 µm. Thanks to this small area capability, micro area analysis of the space between the pillars on the structured sample was possible. A total of 18 analysis points per sample were measured, with a lateral offset of 10 µm. The membrane covered region starts between points 6 and 7. Point 7 is regarded as the zero position, in order to align the depth distances closely with ToF-SIMS for direct comparison. From point 1 to 7, the distances are given in negative values, and from point 7 to 18, in positive values.

The La3d<sub>5/2</sub>, O1s, Si2s and Hf4f high resolution scans are plotted in Fig. 7 for both the three-step and standard ALD samples. To follow the spectra, the curves start at the bottom of the plot (starting from the no membrane leading into the membrane covered area) as indicated by the direction of the dotted arrow on the right. To show the elemental distribution of the material under the membrane, the La3d<sub>5/2</sub> and Hf4f fitted peak areas, extracted and corrected to RSF, from each measurement point is plotted in Fig. 8 with respect to the depth in the structure.

In Fig. 8, for both depositions, the La3d<sub>5/2</sub> and Hf4f corrected peak areas are consistent starting from the first analysis point in the no membrane area until the membrane covered area is reached. Under the membrane, the La3d<sub>5/2</sub> and Hf4f peaks were measured until a depth of *c. a.* 70  $\mu$ m, after this, their signals disappeared. Along this 70  $\mu$ m depth, each element shows a different profile, and the depth range of Hf, for both depositions, gradually decreased until *c.a.* 40  $\mu$ m before reaching values near zero (Table S4 and S5). These observations are in agreement with ToF-SIMS. For the three-step ALD deposition, the Hf4f corrected peak area decreases after 20  $\mu$ m in the membrane covered section, and for the standard ALD deposition after the zero position.

For the three-step ALD deposition, the high-resolution scans of  $La3d_{5/2}$  show a spike in the peak intensity (Fig. 7a), and correspondingly a spike in the  $La3d_{5/2}$  extracted and corrected peak areas (Fig. 8a). In contrast, the standard ALD deposition showed a relatively consistent La intensity (Fig. 7b), and correspondingly a consistent peak area (Fig. 8b) throughout. Both trends were also confirmed by ToF-SIMS.

Tables S6 and S7 list the fitted peak positions of the spectra in Fig. 7. The peak positions of the La3d<sub>5/2</sub>, O1s and Hf4f components in the no membrane area in the structured PillarHall are similar to that measured on the planar wafers (Table 1). For both the three-step and standard ALD, the BEs of the La3d<sub>5/2</sub> and Hf4f components increase gradually by *c.a.* 0.50 eV across the measured distance. This could be attributed to the change in composition and the gradual appearance of the substrate signal that can in turn affect the nature of bonding between the elements.

At the start of the measurement, the Si substrate signal was not detected. Measuring further along the structure, a Si substrate signal arises in the Si2s region, with two main components corresponding to Si-Si and Si-O (Fig. 7). Fig. 8a and b indicate that the Si substrate signal starts to show from 40 and 20  $\mu$ m for the three-step and standard ALD samples, respectively. This coincides with the decrease in the Hf4f and spike in the La3d<sub>5/2</sub> profile, a trend confirmed by ToF-SIMS.

In Fig. 7, for both samples, both the O-Hf and HO-La components are present in the O1s region as indicated by the position and direction of the dotted arrows. At the start of the measurements, the O1s region shows mainly character belonging to the HfO<sub>2</sub> phase. As the amount of La, with respect to Hf increases, the O-Hf peak gradually decreases relative to the HO-La peak. As the Si substrate signal (Si-Si and Si-O) appears in the Si2s region, the O1s region shows the gradual rise of a third component (O-Si) at higher BE (values listed in Tables S6 and S7), for both three-step and standard ALD. Eventually when the La and Hf signals disappear, the O1s region has predominantly O-Si character.

Tables S8 and S9 list the calculated energy separation and intensity ratio parameters of the spectra in Fig. 7. The calculated energy separation between the La3d<sub>5/2</sub> (cf<sup>0</sup>) – La3d<sub>5/2</sub> bonding (cf<sup>1</sup>L) and La3d<sub>5/2</sub> bonding (cf<sup>1</sup>L) – La3d<sub>5/2</sub> antibonding (cf<sup>1</sup>L) components, for both structured samples, are similar to that calculated for the doped planar samples. Here too, as with the doped planar samples, the intensity ratio of the La $3d_{5/2}$  bonding (cf<sup>1</sup>L) to La $3d_{5/2}$  (cf<sup>0</sup>) components is lower than what was measured for the lanthanum hydroxide thin film (Table S2), due to the larger noise and scatter of the signal and because the satellite peak intensities are dependent on the surrounding ligands and chemical environment [58]. The energetic difference between  $Hf4f_{7/2}$  and  $Hf4f_{5/2}$ corresponds to Hf in HfO2. Towards the last Hf4f measurement points, the signal diminishes, the peaks are broadened, and the intensity is low, therefore the energy separation value changes. It can be concluded that, in the structured samples, La is present in the hydroxide phase and Hf in the oxide phase.

Figure S5, and Tables S4 and S5, show the change in the La cat. % values for the three-step and standard ALD samples along the measured distance. For both samples, the La cat. % is consistent in the no membrane area until the membrane covered area is reached. The calculated La cat. % in the no membrane area until *ca*. 10  $\mu$ m under the membrane falls within the expected average and error calculated for the doped



Fig. 6. An example of an SXI image taken inside the UHV XPS analysis chamber of the W90 structure of the three-step ALD deposited La doped hafnium oxide sample showing a total of 18 XPS analysis points. The arrows indicate the measurement direction.



**Fig. 7.** High resolution XPS spectra of the La3d, O1s, Si2s and Hf4f regions of the 10 nm La doped hafnium oxide thin film deposited on the LHAR structure for the (a) three-step and (b) standard ALD samples. A total of 18 analysis points, with a lateral offset of 10  $\mu$ m, for each sample is shown. The location of analysis points can be seen in the SXI (Fig. 6).



**Fig. 8.** The La3d<sub>5/2</sub> and Hf4f peak areas corrected to RSF measured using XPS plotted with respect to the measured distance on the LHAR structure are shown for the (a) three-step and (b) standard ALD samples. The shaded area corresponds to the region covered by the membrane.

films deposited on the planar wafers (Table 1). After *ca.* 10  $\mu$ m under the membrane, the cat. % values increase for both the three-step and standard ALD depositions, suggesting a relative change in the amount of La and Hf.

# 3.3. Thin film behavior in the PillarHall test structure

Both measurement techniques are complementary and have probed the La and Hf profiles along the measured lateral depth. Under the membrane, the Hf penetration depth is larger for the three-step than for standard ALD. This difference is attributed to the longer Hf pulse time for the depositions, which for the three-step ALD was twice that of standard ALD (6 versus 3 s, Figure S1) to reach a higher penetration depth. In Fig. 8, the Hf4f corrected peak area plotted against the measured distance along the structure is halved under the membrane in the range of  $30 - 40 \,\mu\text{m}$  for three-step ALD and  $20 - 30 \,\mu\text{m}$  for standard ALD. With a ratio of c.a. 1.4 that matches the general expectation from the kinetic step coverage modelling [59] which found the penetration depth to be proportional to the square root of the precursor exposure time. In addition, the La penetration depth is ca. 70 µm for both depositions with a spike in the La profile for the three-step ALD. A Langmuir model for competitive single-site adsorption could explain the spike [60]. The expected behavior for the three-step ALD is, that after the reaction of the larger Hf precursor is saturated, there are still unreacted sites between the adsorbed Hf precursor fragments because of steric hindrance. After purging, the smaller La precursor may still reach these sites for adsorption. This leads to a well-defined mixture of target elements even at extremely low concentrations. The spike in La concentration occurs at the adsorption front [20] where the Hf concentration decreases. Here, the La precursor meets a high fraction of unreacted sites and reacts with them until the La precursor runs out. To avoid the

spike, the La precursor exposure time could be reduced in future experiments.

#### 4. Conclusions

Both XPS and ToF-SIMS have been demonstrated as complementary and viable for the analysis of the La doped HfO2 thin films deposited on the PillarHall LHAR test structure, and for the analysis of the differences between the two ALD deposition processes. Using both techniques, combined information about the elemental composition and distribution, La (cat. %) doping level, phases and thin film penetration depth profile can be acquired. The focus of this work was to develop a way to measure and analyze the ALD films deposited with different processes on an LHAR structure using XPS. For future experiments, different geometries of the PillarHall test structure could be studied, for example, slit width and height, pillar geometry, and changing the ALD pulse times could be experimented on to further study the effects on film penetration depth and changes in elemental profiles. Since the Al<sub>2</sub>O<sub>3</sub> capping layer proved viable in protecting the underlying lanthanum oxide from phase transformation into hydroxide, this capping layer could be further used for protecting the La doped HfO2 films for future studies without exposure to air.

#### CRediT authorship contribution statement

Jennifer Emara: Writing – review & editing, Writing – original draft, Validation, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Alireza M. Kia: Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Sascha Bönhardt: Writing – review & editing, Visualization, Conceptualization. **Clemens Mart:** Methodology, Conceptualization. **Kati Kühnel:** Validation, Resources, Investigation, Data curation. **Nora Haufe:** Writing – review & editing, Supervision, Project administration. **Riikka L. Puurunen:** Writing – review & editing, Visualization, Resources. **Mikko Utriainen:** Writing – review & editing, Resources. **Wenke Weinreich:** Writing – review & editing, Supervision, Project administration.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

# Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2024.161408.

#### References

- T.S. Böscke, J. Müller, D. Bräuhaus, U. Schröder, U. Böttger, Ferroelectricity in hafnium oxide thin films, Appl. Phys. Lett. 99 (2011) 102903, https://doi.org/ 10.1063/1.3634052.
- [2] K. Kühnel, M. Czernohorsky, C. Mart, W. Weinreich, High-density energy storage in Si-doped hafnium oxide thin films on area-enhanced substrates, J. Vacuum Sci. & Technol. B. 37 (2019) 21401, https://doi.org/10.1116/1.5060738.
- [3] J. Müller, T.S. Böscke, U. Schröder, S. Mueller, D. Bräuhaus, U. Böttger, L. Frey, T. Mikolajick, Ferroelectricity in Simple Binary ZrO2 and HfO2, Nano Lett. 12 (2012) 4318–4323, https://doi.org/10.1021/nl302049k.
- [4] M.H. Park, H.J. Kim, Y.J. Kim, T. Moon, K.D. Kim, C.S. Hwang, Thin HfxZr1-xO2 films: A new lead-free system for electrostatic supercapacitors with large energy storage density and robust thermal stability, Adv. Energy Mater. 4 (2014) 1400610, https://doi.org/10.1002/aenm.201400610.
- [5] T. Ali, P. Polakowski, S. Riedel, T. Buttner, T. Kampfe, M. Rudolph, B. Patzold, K. Seidel, D. Lohr, R. Hoffmann, M. Czernohorsky, K. Kuhnel, P. Steinke, J. Calvo, K. Zimmermann, J. Muller, High endurance ferroelectric hafnium oxide-based FeFET memory without retention penalty, IEEE Trans. Electron Devices. 65 (2018) 3769–3774, https://doi.org/10.1109/TED.2018.2856818.
- [6] C. Mart, T. Kämpfe, S. Zybell, W. Weinreich, Layer thickness scaling and wake-up effect of pyroelectric response in Si-doped HfO 2, Appl. Phys. Lett. 112 (2018) 52905, https://doi.org/10.1063/1.5019308.
- [7] A. Chernikova, M. Kozodaev, A. Markeev, D. Negrov, M. Spiridonov, S. Zarubin, O. Bak, P. Buragohain, H. Lu, E. Suvorova, A. Gruverman, A. Zenkevich, Ultrathin Hf0.5Zr0.5O2 Ferroelectric Films on Si, ACS Appl. Mater. & Interf. 8 (2016) 7232–7237, https://doi.org/10.1021/acsami.5b11653.
- [8] A. Chouprik, A. Chernikova, A. Markeev, V. Mikheev, D. Negrov, M. Spiridonov, S. Zarubin, A. Zenkevich, Electron transport across ultrathin ferroelectric Hf0.5Zr0.502 films on Si, Microelectronic Eng. 178 (2017) 250–253, https://doi. org/10.1016/j.mee.2017.05.028.
- [9] A.G. Chernikova, D.S. Kuzmichev, D.V. Negrov, M.G. Kozodaev, S.N. Polyakov, A. M. Markeev, Ferroelectric properties of full plasma-enhanced ALD TiN/La:Hf02/ TiN stacks, Appl. Phys. Lett. 108 (2016) 242905, https://doi.org/10.1063/ 1.4953787.
- [10] M. Hoffmann, U. Schroeder, T. Schenk, T. Shimizu, H. Funakubo, O. Sakata, D. Pohl, M. Drescher, C. Adelmann, R. Materlik, A. Kersch, T. Mikolajick, Stabilizing the ferroelectric phase in doped hafnium oxide, J. Appl. Phys. 118 (2015) 72006, https://doi.org/10.1063/1.4927805.
- [11] J. Müller, U. Schröder, T.S. Böscke, I. Müller, U. Böttger, L. Wilde, J. Sundqvist, M. Lemberger, P. Kücher, T. Mikolajick, L. Frey, Ferroelectricity in yttrium-doped hafnium oxide, J. Appl. Phys. 110 (2011) 114113, https://doi.org/10.1063/ 1.3667205.
- [12] U. Schroeder, C. Richter, M.H. Park, T. Schenk, M. Pešić, M. Hoffmann, F.P. G. Fengler, D. Pohl, B. Rellinghaus, C. Zhou, C.-C. Chung, J.L. Jones, T. Mikolajick, Lanthanum-doped hafnium oxide: A robust ferroelectric material, Inorg. Chem. 57 (2018) 2752–2765, https://doi.org/10.1021/acs.inorgchem.7b03149.

- [13] S. Mueller, J. Mueller, A. Singh, S. Riedel, J. Sundqvist, U. Schroeder, T. Mikolajick, Incipient Ferroelectricity in Al-Doped HfO2 Thin Films, Adv. Funct. Mater. 22 (2012) 2412–2417, https://doi.org/10.1002/adfm.201103119.
- [14] C. Mart, K. Kühnel, T. Kämpfe, S. Zybell, W. Weinreich, Ferroelectric and pyroelectric properties of polycrystalline La-doped HfO2 thin films, Appl. Phys. Lett. 114 (2019) 102903, https://doi.org/10.1063/1.5089821.
- [15] C. Mart, K. Kühnel, T. Kämpfe, M. Czernohorsky, M. Wiatr, S. Kolodinski, W. Weinreich, Doping ferroelectric hafnium oxide by in-situ precursor mixing, ACS Appl. Electron. Mater. 1 (2019) 2612–2618, https://doi.org/10.1021/ acsaelm.9b00591.
- [16] C. Adelmann, V. Sriramkumar, S. van Elshocht, P. Lehnen, T. Conard, S. de Gendt, Dielectric properties of dysprosium- and scandium-doped hafnium dioxide thin films, Appl. Phys. Lett. 91 (2007) 162902, https://doi.org/10.1063/1.2798498.
- [17] M.H. Park, Y.H. Lee, H.J. Kim, Y.J. Kim, T. Moon, K.D. Kim, J. Müller, A. Kersch, U. Schroeder, T. Mikolajick, C.S. Hwang, Ferroelectricity and antiferroelectricity of doped thin HfO2-based films, Adv. Mater. (Deerfield Beach Fla.) 27 (2015) 1811–1831, https://doi.org/10.1002/adma.201404531.
- [18] R. Batra, T.D. Huan, G.A. Rossetti, R. Ramprasad, Dopants promoting ferroelectricity in hafnia: insights from a comprehensive chemical space exploration, Chem. Mater. 29 (2017) 9102–9109, https://doi.org/10.1021/acs chemmater.7b02835.
- [19] R.L. Puurunen, Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process, J. Appl. Phys. (2005) 121301, https://doi.org/ 10.1063/1.1940727.
- [20] J. Yim, O.M.E. Ylivaara, M. Ylilammi, V. Korpelainen, E. Haimi, E. Verkama, M. Utriainen, R.L. Puurunen, Saturation profile based conformality analysis for atomic layer deposition: aluminum oxide in lateral high-aspect-ratio channels, Phys. Chem. Chem. Phys. PCCP. 22 (2020) 23107–23120, https://doi.org/ 10.1039/d0cp03358h.
- [21] M. Ylilammi, O.M.E. Ylivaara, R.L. Puurunen, Modeling growth kinetics of thin films made by atomic layer deposition in lateral high-aspect-ratio structures, J. Appl. Phys. 123 (2018) 205301, https://doi.org/10.1063/1.5028178.
- [22] A.M. Kia, N. Haufe, S. Esmaeili, C. Mart, M. Utriainen, R.L. Puurunen, W. Weinreich, ToF-SIMS 3D analysis of thin films deposited in high aspect ratio structures via atomic layer deposition and chemical vapor deposition, Nanomaterials (Basel Switzerland) 9 (2019), https://doi.org/10.3390/ nano9071035.
- [23] A.S.H. Makhlouf, M. Aliofkhazraei (Eds.), Handbook of Materials Failure Analysis with Case Studies from the Oil and Gas Industry, Butterworth-Heinemann, 2016.
- [24] R.F. Egerton, Electron energy-loss spectroscopy in the TEM, Rep. Prog. Phys. 72 (2009) 16502, https://doi.org/10.1088/0034-4885/72/1/016502.
- [25] C. John Riviere, Sverre, Myhra, Handbook of Surface and Interface Analysis: Methods for Problem-Solving, 2nd ed., CRC Press, Boca Raton, FL, USA, 2017.
- [26] A. Benninghoven, F.G. Rudenauer, H.W. Werner, Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications, and Trends, 1st ed., J. Wiley, New York, NY, USA, 1987.
- [27] A.G. Shard, Detection limits in XPS for more than 6000 binary systems using Al and Mg Kα X-rays, Surf. & Interf. Anal. 46 (2014) 175–185, https://doi.org/10.1002/ sia.5406.
- [28] M.H. Park, Y.H. Lee, H.J. Kim, Y.J. Kim, T. Moon, K.D. Kim, J. Müller, A. Kersch, U. Schroeder, T. Mikolajick, C.S. Hwang, Ferroelectricity and antiferroelectricity of doped thin HfO2-based films, Adv. Mater. 27 (2015) 1811–1831, https://doi.org/ 10.1002/adma.201404531.
- [29] B. Hagenhoff, High Resolution Surface Analysis by TOF-SIMS, Mikrochim Acta. 132 (2000) 259–271, https://doi.org/10.1007/s006040050019.
- [30] L. Tortora, M. Urbini, A. Fabbri, P. Branchini, L. Mariucci, M. Rapisarda, M. Barra, F. Chiarella, A. Cassinese, F. Di Capua, A. Aloisio, Three-dimensional characterization of OTFT on modified hydrophobic flexible polymeric substrate by low energy Cs+ ion sputtering, Appl. Surf. Sci. 448 (2018) 628–635, https://doi. org/10.1016/j.apsusc.2018.04.097.
- [31] J. Sameshima, T. Sugahara, T. Ishina, S. Nagao, K. Suganuma, 3D imaging of backside metallization of SiC-SBD influenced by annealing, J. Mater. Sci.: Mater. Electron. 30 (2019) 10848–10856, https://doi.org/10.1007/s10854-019-01428-4.
- [32] S. Siljeström, Single Fluid Inclusion Analysis Using ToF-SIMS Implications for Ancient Earth Biodiversity and Paleoenvironment Studies., Ph.D. Thesis,. Stockholm University, Stockholm, Sweden (2011).
- [33] D.J. Graham, L.J. Gamble, Dealing with image shifting in 3D ToF-SIMS depth profiles, Biointerphases. 13 (2018) 06E402, https://doi.org/10.1116/1.5041740
- [34] M.F. Sunding, K. Hadidi, S. Diplas, O.M. Løvvik, T.E. Norby, A.E. Gunnæs, XPS characterisation of in situ treated lanthanum oxide and hydroxide using tailored charge referencing and peak fitting procedures, J. Electron Spectrosc. Related Phenomena. 184 (2011) 399–409, https://doi.org/10.1016/j.elspec.2011.04.002.
- [35] D.F. Mullica, C.K.C. Lok, H.O. Perkins, V. Young, X-ray photoelectron final-state screening in La(OH)3: A multiplet structural analysis, Phys. Rev. B. 31 (1985) 4039, https://doi.org/10.1103/PhysRevB.31.4039.
- [36] D.F. Mullica, H.O. Perkins, C. Lok, V. Young, The X-ray photoemission spectra of La (OH)3, J. Electron Spectrosc. Related Phenomena. 61 (1993) 337–355, https://doi. org/10.1016/0368-2048(93)80024-G.
- [37] Y. Uwamino, T. Ishizuka, X-ray Photoelectron Spectroscopy of Rare-Earth Compounds, J. Electron Spectrosc. Related Phenomena. 34 (1984) 67–78, https:// doi.org/10.1016/0368-2048(84)80060-2.
- [38] D.D. Sarma, C. Rao, XPES studies of oxides of second- and third-row transition metals including rare earths, J. Electron Spectrosc. Related Phenomena. 20 (1980) 25–45, https://doi.org/10.1016/0368-2048(80)85003-1.
- [39] V.V. Atuchin, A.V. Kalinkin, V.A. Kochubey, V.N. Kruchinin, R.S. Vemuri, C. V. Ramana, Spectroscopic ellipsometry and x-ray photoelectron spectroscopy of

 $La_2O_3$  thin films deposited by reactive magnetron sputtering, J. Vacuum Sci. & Technol. A: Vacuum, Surfaces, and Films. 29 (2011) 021004-1–021004-5, https://doi.org/10.1116/1.3539069.

- [40] K. Kim, D. Kim, T. Kim, B.-G. Kim, D. Ko, J. Lee, Y. Han, J.C. Jung, H.B. Na, Synthesis of mesoporous lanthanum hydroxide with enhanced adsorption performance for phosphate removal, RSC Adv. 9 (2019) 15257–15264, https://doi. org/10.1039/C9RA00895K.
- [41] A. de Asha, J. Critchley, R. Nix, Molecular adsorption characteristics of lanthanum oxide surfaces: the interaction of water with oxide overlayers grown on Cu(111), Surf. Sci. 405 (1998) 201–214, https://doi.org/10.1016/S0039-6028(98)00044-2.
- [42] G. He, M. Liu, L.Q. Zhu, M. Chang, Q. Fang, L.D. Zhang, Effect of postdeposition annealing on the thermal stability and structural characteristics of sputtered HfO2 films on Si (100), Surf. Sci. 576 (2005) 67–75, https://doi.org/10.1016/j. susc.2004.11.042.
- [43] S. Sayan, E. Garfunkel, T. Nishimura, W.H. Schulte, T. Gustafsson, G.D. Wilk, Thermal decomposition behavior of the HfO2/SiO2/Si system, J. Appl. Phys. 94 (2003) 928–934, https://doi.org/10.1063/1.1578525.
- [44] O. Renault, D. Samour, D. Rouchon, P. Holliger, A.-M. Papon, D. Blin, S. Marthon, Interface properties of ultra-thin HfO<sub>2</sub> films grown by atomic layer deposition on SiO<sub>2</sub>/Si, Thin Solid Films. 428 (2003) 190–194, https://doi.org/10.1016/S0040-6090(02)01198-7.
- [45] S. McDonnell, A. Azcatl, G. Mordi, C. Floresca, A. Pirkle, L. Colombo, J. Kim, M. Kim, R.M. Wallace, Scaling of HfO<sub>2</sub> dielectric on CVD graphene, Appl. Surf. Sci. 294 (2014) 95–99, https://doi.org/10.1016/j.apsusc.2013.12.115.
- [46] D. Gu, K. Tapily, P. Shrestha, G. Celler, H. Baumgart, Experimental Study of ALD HfO2 Deposited on Strained Silicon-on-Insulator (sSOI & xsSOI) and SOI, ECS Trans. 11 (2007) 421–429, https://doi.org/10.1149/1.2779578.
- [47] L.-G. Wang, X. Qian, Y.-Q. Cao, Z.-Y. Cao, G.-Y. Fang, A.-D. Li, Di Wu, Excellent resistive switching properties of atomic layer-deposited Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> trilayer structures for non-volatile memory applications, Nanoscale Res. Lett. 10 (2015) 135, https://doi.org/10.1186/s11671-015-0846-y.
- [48] J.C. Hackley, T. Gougousi, Properties of atomic layer deposited HfO2 thin films, Thin Solid Films. 517 (2009) 6576–6583, https://doi.org/10.1016/j. tsf.2009.04.033.
- [49] G. Park, H. Yang, J.H. Lee, G. Lee, J. Kwak, U. Jeong, Polymer-assisted deposition of Al-Doped HfO2 thin film with excellent dielectric properties, Adv. Mater. Interf. 6 (2019) 1900588, https://doi.org/10.1002/admi.201900588.

- [50] J. Fan, H. Liu, Q. Kuang, B. Gao, F. Ma, Y. Hao, Physical properties and electrical characteristics of H<sub>2</sub>O-based and O3-based HfO<sub>2</sub> films deposited by ALD, Microelectronics Reliability. 52 (2012) 1043–1049, https://doi.org/10.1016/j. microrel.2012.01.010.
- [51] J.-C. Dupin, D. Gonbeau, P. Vinatier, A. Levasseur, Systematic XPS studies of metal oxides, hydroxides and peroxides, Phys. Chem. Chem. Phys. 2 (2000) 1319–1324, https://doi.org/10.1039/a908800h.
- [52] A. Ohta, H. Murakami, S. Higashi, S. Miyazaki, Determination of Energy Band Alignment in Ultrathin Hf-based Oxide/Pt System, J. Phys.: Conf. Ser. 417 (2013) 12012, https://doi.org/10.1088/1742-6596/417/1/012012.
- [53] T. Bertaud, M. Sowinska, D. Walczyk, S. Thiess, A. Gloskovskii, C. Walczyk, T. Schroeder, In-operando and non-destructive analysis of the resistive switching in the Ti/HfO<sub>2</sub> /TiN-based system by hard x-ray photoelectron spectroscopy, Appl. Phys. Lett. 101 (2012) 143501, https://doi.org/10.1063/1.4756897.
- [54] K. Bolwin, W. Schnurnberger, G. Schiller, Influence of valence band states on the core hole screening in lanthanide perovskite compounds, Z. Physik B - Condensed Matter. 72 (1988) 203–209, https://doi.org/10.1007/BF01312136.
- [55] H.C. Siegmann, L. Schlapbach, C.R. Brundle, Self-restoring of the active surface in the hydrogen sponge LaNi5, Phys. Rev. Lett. 40 (1978) 972–975, https://doi.org/ 10.1103/PhysRevLett.40.972.
- [56] V. Bondarenka, S. Grebinskij, V. Lisauskas, S. Mickevičius, K. Šliužienė, XPS Study of Epitaxial LaNiO3-x Films, Lithuanian J. Phys. 46 (2006) 95–99, https://doi.org/ 10.3952/lithjphys.46114.
- [57] P. Burroughs, A. Hamnett, A.F. Orchard, G. Thornton, Satellite Structure in the X-Ray Photoelectron Spectra of some Binary and Mixed Oxides of Lanthanum and Cerium, J. C. S. Dalton (1976) 1686–1698, https://doi.org/10.1039/ DT9760001686.
- [58] H. Berthou, C.K. Jørgensen, Influence of the Ligands on 3d photoelectron spectra of the first four lanthanides, Chem. Phys. Lett. (Chem. Phys. Lett.) 38 (1976) 199–206, https://doi.org/10.1016/0009-2614(76)85135-4.
- [59] R.G. Gordon, D. Hausmann, E. Kim, J. Shepard, A kinetic model for step coverage by atomic layer deposition in narrow holes or trenches, Chem. Vapor. Deposition. 9 (2003) 73–78, https://doi.org/10.1002/cvde.200390005.
- [60] J.R. Ommen, A. Goulas, R.L. Puurunen, Atomic Layer Deposition, in: I. John Wiley & Sons (Ed.), Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, 2000, pp. 1–42.