

Article

Structure and Electrical Properties of Zirconium-Aluminum-Oxide Films Engineered by Atomic Layer Deposition

Joonas Merisalu , Taivo Jõgiaas , Toomas Daniel Viskus, Aarne Kasikov , Peeter Ritslaid , Tanel Käämbre, Aivar Tarre , Jekaterina Kozlova, Hugo Mändar, Aile Tamm , Jaan Aarik and Kaupo Kukli 

Institute of Physics, University of Tartu, W. Ostwaldi 1, 50411 Tartu, Estonia; taivo.jogiaas@ut.ee (T.J.); toomasdaniel@gmail.com (T.D.V.); aarne.kasikov@ut.ee (A.K.); peeter.ritslaid@ut.ee (P.R.); tanel.kaambre@ut.ee (T.K.); aivar.tarre@ut.ee (A.T.); jekaterina.kozlova@ut.ee (J.K.); hugo.mandar@ut.ee (H.M.); aile.tamm@ut.ee (A.T.); jaan.aarik@ut.ee (J.A.); kaupo.kukli@ut.ee (K.K.)

* Correspondence: joonas.merisalu@ut.ee



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Abstract: Thin films containing either multilayer $\text{ZrO}_2\text{:Al}_2\text{O}_3$ structures or ZrO_2 deposited on $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layers were characterized. The films were grown by atomic layer deposition (ALD) at 300 °C from ZrCl_4 , $\text{Al}(\text{CH}_3)_3$, and H_2O . The multilayer $\text{ZrO}_2\text{:Al}_2\text{O}_3$ structures were grown repeating different combinations of ZrO_2 and Al_2O_3 ALD cycles while the $\text{Zr}_x\text{Al}_y\text{O}_z$ layers were obtained in a novel process using ALD cycles based on successive adsorption of ZrCl_4 and $\text{Al}(\text{CH}_3)_3$, followed by surface reaction with H_2O . The films were grown on TiN electrodes, and supplied with Ti top electrodes, whereby $\text{Zr}_x\text{Al}_y\text{O}_z$ films were exploited as thin buffer layers between TiN and ZrO_2 . The as-deposited ZrO_2 films and $\text{ZrO}_2\text{:Al}_2\text{O}_3$ structures with sufficiently low concentrations of Al_2O_3 were crystallized in the form of cubic or tetragonal ZrO_2 polymorph possessing relative permittivities reaching 35. Notably, multilayered $\text{ZrO}_2\text{:Al}_2\text{O}_3$ films could exhibit resistive switching behavior with ratios between low- and high-resistive-state current values, extending up to five orders of magnitude. Implications of multilevel switching were recorded. In the double-layered $\text{Zr}_x\text{Al}_y\text{O}_z\text{-ZrO}_2$ stacks, the ON/OFF current ratios remained below 40, but the endurance could become extended over 3000 cycles. Remarkably, instabilities, when detected in endurance behavior expressed by reduction in an ON/OFF current ratio could be compensated and the current values restored by real time readjustment of the programming voltage amplitude.

Keywords: atomic layer deposition; zirconium oxide; aluminum oxide; dielectric properties; resistive switching

1. Introduction

Atomic layer deposition (ALD) has enabled the development of ZrO_2 -based capacitor structures for dynamic random-access memories (DRAM) scalable according to the industrial requirements [1–4]. In regard with nonvolatile memory technologies, ZrO_2 has been mentioned among numerous metal oxides investigated as resistively switching (RS) media in recent reviews [5–7]. Several studies have been carried out using ZrO_2 as a single RS medium of memristors [8–12]. An alternative approach, supported with first-principles calculations, has been based on nitrogen-doped ZrO_2 serving as a multilevel RS medium containing oxygen vacancies coupled with nitrogen in ZrO_2 between Pt and TiN electrodes [13]. For analogous reasons, double layers consisting of oxygen deficient ZrO_{2-x} on top of ZrO_2 have been grown and characterized [14]. ZrO_2 films have been also stacked with other metal oxides, such as TiO_2 [10,15], to usefully tune the RS parameters. Notably, in pulsed laser deposited ZrO_2 films embedding Cu nanoparticles, the RS memory window, expressed by the low- to high-resistivity (denoted also as ON/OFF) current ratio ($I_{\text{LRS}}/I_{\text{HRS}}$), has been extended over four orders of magnitude [16].

A few decades ago, ALD was successfully used for the development of trench DRAMs based on single Al_2O_3 thin insulating dielectric films grown conformally on three-dimensional substrates [17]. Later, amorphous Al_2O_3 as a layered additive in hosting ZrO_2 film turned out to be a useful dopant stabilizing cubic and/or tetragonal polymorphs of ZrO_2 with dielectric permittivity values markedly exceeding that of the monoclinic ZrO_2 . In addition, doping has allowed for the deposition of films with smoother surfaces and concurrent reduction of the leakage currents through the dielectric layers. Such advantages have enabled the development of ZrO_2 - Al_2O_3 stacked structures for DRAMs [1–4].

Some studies have reported RS in oxide films comprising an oxygen-deficient $\text{Al}_2\text{O}_{3-x}$ switching layer deposited on stoichiometric Al_2O_3 [18,19]. In a paper by Huang et al. [19], sputtering and ALD techniques were complementarily applied to fabricate $\text{AlO}_x/\text{Al}_2\text{O}_3$ stacks, whereby $\text{Al}(\text{CH}_3)_3$ and H_2O were exploited as ALD precursors. Multilevel RS was observed in a double-layer $\text{AlO}_x/\text{Al}_2\text{O}_3$ film, both layers grown by ALD from $\text{Al}(\text{CH}_3)_3$ and H_2O [18]. High $I_{\text{LRS}}/I_{\text{HRS}}$ ratios, exceeding four orders of magnitude, were achieved in the case of multilayer devices consisting of thermally grown Al metal and electron beam evaporated Al_2O_3 films [20]. Comparably large $I_{\text{LRS}}/I_{\text{HRS}}$ ratios have been obtained even earlier in devices based on Al_2O_3 films fabricated by plasma oxidation of Al electrodes [21].

In many cases, multilayered RS media have been built up on metal oxide layers characterized either by different defect densities or different valences of metals forming the compounds layered alternately. For example, triple-layered ALD structures consisting of Al_2O_3 films between bottom and top HfO_2 films became functional due to the differences in the oxidation states leading to the formation of energetic barriers, which promoted multilevel switching phenomenon [22]. However, aside of the proven relevance of Al_2O_3 - and ZrO_2 -based DRAM media, reports on RS media built on combinations of ZrO_2 and Al_2O_3 are scarce in general. Only a few research papers have reported the appearance of RS in $\text{ZrO}_2:\text{Al}_2\text{O}_3$ mixtures [23] and periodical multilayers [24] grown by ALD, and in $\text{ZrO}_2/\text{Al}_2\text{O}_3$ double layers sputtered on flexible transparent substrates [25]. It has also been reported that larger $I_{\text{LRS}}/I_{\text{HRS}}$ ratios could be achieved with ZrO_2/AlON double layers, compared to the devices based on single ZrO_2 films [26].

In the present study, RS was investigated in dielectrics containing, first, periodical $\text{ZrO}_2:\text{Al}_2\text{O}_3$ structures and, second, ZrO_2 films deposited on buffer $\text{Zr}_x\text{Al}_y\text{O}_z$ layers in order to obtain new knowledge concerning the influence of the dielectric layer structure on the dielectric properties and RS performance of ZrO_2 -based dielectrics. The RS media were grown to thicknesses of 12–15 nm by ALD at 300 °C, using $\text{Al}(\text{CH}_3)_3$, ZrCl_4 and H_2O as precursors. Dependence of the composition, crystalline structure, RS polarity and stability of $I_{\text{LRS}}/I_{\text{HRS}}$ ratios on the ALD cycle ratios and sequences used for the deposition of $\text{ZrO}_2:\text{Al}_2\text{O}_3$ structures, and application of a novel ALD process for deposition of $\text{Zr}_x\text{Al}_y\text{O}_z$ were addressed.

2. Materials and Methods

The RS films were deposited in an in-house built hot-wall flow-type ALD reactor schematically described in an earlier paper by Arroval et al. [27]. The films were grown at 300 °C on crystalline TiN-covered substrates cut out of Si(100) wafers with a resistivity of 0.014–0.020 $\Omega\cdot\text{cm}$. The Si wafers were boron-doped to concentrations ranging from 5×10^{18} to $1 \times 10^{19} \text{ cm}^{-3}$. A TiN layer of 10 nm was pre-grown by pulsed chemical vapor deposition using a batch $\text{TiCl}_4/\text{NH}_3$ process [28,29] at temperatures of 450–500 °C in an ASM A412 Large Batch 300 mm reactor (Advanced Semiconductor Materials, Almere, The Netherlands). at Fraunhofer IPMS-CNT (Dresden, Germany).

The precursors used for ALD were ZrCl_4 , $\text{Al}(\text{CH}_3)_3$ (TMA) and H_2O . Two different sample sets were prepared with different distributions of Al_2O_3 in the RS layers. The RS media of the first set were grown as nominally periodical $\text{ZrO}_2:\text{Al}_2\text{O}_3$ multilayers (Figure 1a) using ALD cycle sequences $30 \times (1 \times \text{Al}_2\text{O}_3 + 4 \times \text{ZrO}_2)$ and $6 \times (1 \times \text{Al}_2\text{O}_3 + 24 \times \text{ZrO}_2)$. This means that one single Al_2O_3 deposition cycle consisting of sequential exposures of surfaces to $\text{Al}(\text{CH}_3)_3$ and H_2O pulses was performed alternately with 4 or 24 consecu-

tive ZrO_2 deposition cycles consisting of exposures to ZrCl_4 and H_2O . In these samples, the formation of continuous Al_2O_3 layers, intermediating ZrO_2 , was not expected because of the inability of a single ALD cycle to form a full monolayer due to the low nucleation density during the related incubation period [30]. By application of intermediate single Al_2O_3 cycles, doped ZrO_2 layers rather than nanolaminates were targeted. Since the insertion of Al in the ZrO_2 host was realized via surface reactions between $\text{Al}(\text{CH}_3)_3$ and H_2O , the solid film materials eventually formed are to be denoted as $\text{ZrO}_2:\text{Al}_2\text{O}_3$ instead of $\text{Zr}_x\text{Al}_y\text{O}_z$. In addition, binary Al_2O_3 and ZrO_2 films were deposited as reference dielectrics.

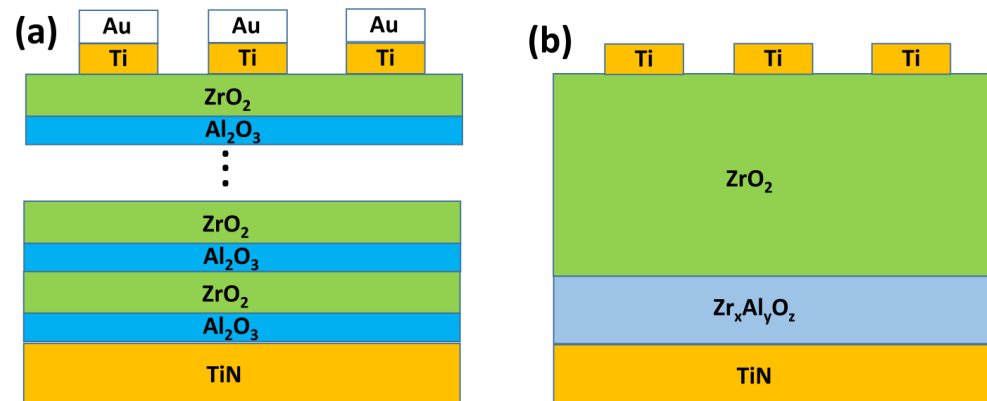


Figure 1. Schematic representation of (a) periodical $\text{ZrO}_2:\text{Al}_2\text{O}_3$ structures and (b) ZrO_2 films grown on buffer $\text{Zr}_x\text{Al}_y\text{O}_z$ layers on bottom TiN electrodes. The component-material layer thicknesses are not to scale.

In the second set of samples, asymmetric double-layer structures were devised by depositing, at first, a $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layer on the bottom TiN electrode, creating a chemically mixed and, presumably, structurally more defective starting layer between the bottom TiN electrode and the host ZrO_2 medium (Figure 1b). The $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layers were deposited using ALD cycles consisting of consecutive exposures of the surface to ZrCl_4 , $\text{Al}(\text{CH}_3)_3$, and H_2O pulses, that is, without the application of a water pulse after the ZrCl_4 pulse. The amount of such cycles, applied successively, varied from 1 to 5. The deposition of $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layers was always followed by the deposition of the main medium consisting of ZrO_2 . The ZrO_2 layer was deposited applying 80 ALD cycles consisting of sequential exposure of the surface to ZrCl_4 and H_2O pulses. Additionally, a 11 nm thick $\text{Zr}_x\text{Al}_y\text{O}_z$ reference film was deposited applying 80 ALD cycles consisting of successive ZrCl_4 , $\text{Al}(\text{CH}_3)_3$, and H_2O pulses. Unfortunately, the results of comparative composition analysis performed for the reference film and the $\text{Zr}_x\text{Al}_y\text{O}_z$ - ZrO_2 stacks indicated that, probably because of an incubation period typical for chloride-based ALD processes [31], the composition of the $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layers obtained after 1–2 ALD cycles could not be controlled with sufficient accuracy. Therefore, these samples were not used in the further studies described in this paper.

Useful knowledge, gained before the present experiments on either Al-doped ZrO_2 , or sandwiched Al_2O_3 and ZrO_2 films, allowed one to expect the formation of metastable cubic or tetragonal phase of ZrO_2 , highly stable against heat-treatments [32,33]. Overall, an insulating material with bandgap likely lower than that characteristic of stable bulk ZrO_2 would form [34,35]. It has also been found earlier that defect clusters, consisting of Al atoms associated with oxygen vacancies, should form as a result of Al doping in the cubic phase of ZrO_2 , whereas the concentration of such clusters should remain negligible in the monoclinic, i.e., stable ZrO_2 [36]. Thus, the $\text{Zr}_x\text{Al}_y\text{O}_z$ interfacial layer could perform as a reservoir of defects below the host ZrO_2 and, possibly, be a source of ionic current. Application of a similar interface layer has recently been reported in studies of TiN/ HfO_2 :Al/ HfO_2 /Pt [37] and Pt/ Al_2O_3 / HfO_2 / HfAlO_x /TiN [38] RRAM stacks. In the present study, the content of aluminum in the $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layer was expected to be lower than that of zirconium,

because in the successive exposures of surface to ZrCl_4 and $\text{Al}(\text{CH}_3)_3$ without intermittent supply of oxygen precursor, the incorporation of zirconium into the film material was more likely than that of aluminum. In order to enable convenient elemental analysis of the film material, a reference 11 nm thick $\text{Zr}_x\text{Al}_y\text{O}_z$ film was deposited applying 80 deposition cycles consisting of ZrCl_4 , $\text{Al}(\text{CH}_3)_3$, and H_2O consecutive pulses.

In order to determine the film thickness, optical measurements of the structures were performed with a spectroscopic ellipsometer GES-5E (Semilab Co., Budapest, Hungary) using a microspot option. The spot size was about 0.35×0.8 mm at an incidence angle of 65° , and the converging angle of a beam was about 4° . Fitting was performed using SEA software. The fitting quality was characterized using a correlation function R^2 reaching unity for ideal correspondence between the measured and computed spectra.

Elemental composition of the films was, in general, measured by wavelength dispersive X-ray fluorescence spectroscopy (XRF) using a spectrometer ZSX-400 (Rigaku, Tokyo, Japan). The growth cycle sequences, thicknesses and elemental compositions of both $\text{ZrO}_2:\text{Al}_2\text{O}_3$ and selected $\text{Zr}_x\text{Al}_y\text{O}_z$ - ZrO_2 sample sets are presented in Tables 1 and 2. In addition, X-ray photoelectron spectra (XPS) were collected from selected $\text{Zr}_x\text{Al}_y\text{O}_z$, ZrO_2 and Al_2O_3 reference samples using a Gammatdata/Scienta SES100 hemispherical photoelectron energy analyser (in constant transmission mode) and a non-monochromatic $\text{Mg-K}\alpha$ ($h\nu = 1253.6$ eV) X-ray excitation source, a Thermo VG Scientific XR3E2 non-monochromatic dual Al/Mg anode X-ray gun (East Grinstead, West Sussex, UK) at an overall spectral resolution of approximately 0.8 eV. The minor sample charging was corrected for by adjusting the adventitious carbon (assumed to contain mainly sp^3 -hybridised carbon species, typically present in ex situ measured samples) C 1s peak to 285.1 eV. Spectral components were fitted, and elemental content from survey spectra was estimated using CasaXPS software (version 2.3.19) [39], taking into account the photoionization cross-sections at the excitation energy used and the measurement geometry. To estimate the (kinetic energy dependent) depth range of origin of detected photoelectrons, their inelastic mean free path (IMFP) was estimated using the TPP2M formula [40] and also weighed into the XPS sensitivity factor of each core level.

Table 1. ALD cycle sequence, thickness, and elemental composition measured by XRF for $\text{ZrO}_2:\text{Al}_2\text{O}_3$ films designed as periodical multilayers with uniform distribution of Al_2O_3 layers throughout the thickness of the host ZrO_2 medium. The measurement uncertainty ranges for atomic percentages express the differences between measurement results obtained on different locations of samples on substrate holder, due to the lateral thickness and composition profile.

ALD Cycle Sequence	Thickness, nm	Al, at. %	Zr, at. %	O, at. %	Cl, at. %
$6 \times (1 \times \text{Al}_2\text{O}_3 + 24 \times \text{ZrO}_2)$	14.6	1.8 ± 0.1	37.1 ± 1.3	60.8 ± 1.4	0.39 ± 0.02
$30 \times (1 \times \text{Al}_2\text{O}_3 + 4 \times \text{ZrO}_2)$	14.3	8.9 ± 0.2	28.7 ± 2.8	62.1 ± 2.6	0.43 ± 0.02
$150 \times \text{Al}_2\text{O}_3$	20.0	39.9 ± 0.2	-	60.1 ± 0.2	-
$120 \times \text{ZrO}_2$	12.2	-	37.1 ± 2.1	62.5 ± 2.0	0.44 ± 0.0

Table 2. ALD cycle sequence, together with thickness and elemental composition, measured by XRF for $\text{Zr}_x\text{Al}_y\text{O}_z$ - ZrO_2 films deposited on TiN substrates, applying first consecutive exposures of substrate surface to metal precursors without oxidizing steps between ZrCl_4 and $\text{Al}(\text{CH}_3)_3$ pulses in order to form $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layer prior to the main ZrO_2 layer.

ALD Cycle Sequences	Thickness, nm	Al, at. %	Zr, at. %	O, at. %	Cl, at. %
$3 \times (\text{ZrCl}_4 + \text{Al}(\text{CH}_3)_3 + \text{H}_2\text{O}) + 80 \times \text{ZrO}_2$	13.0	0.5 ± 0.4	27.4 ± 1.4	71.3 ± 1.0	0.8 ± 0.4
$4 \times (\text{ZrCl}_4 + \text{Al}(\text{CH}_3)_3 + \text{H}_2\text{O}) + 80 \times \text{ZrO}_2$	12.1	1.3 ± 0.4	32.1 ± 1.4	65.8 ± 1.0	0.8 ± 0.4
$5 \times (\text{ZrCl}_4 + \text{Al}(\text{CH}_3)_3 + \text{H}_2\text{O}) + 80 \times \text{ZrO}_2$	14.6	1.2 ± 0.4	31.0 ± 1.4	67.0 ± 1.0	0.8 ± 0.4
$80 \times (\text{ZrCl}_4 + \text{Al}(\text{CH}_3)_3 + \text{H}_2\text{O})$	10.7	7.4 ± 0.4	26.8 ± 1.4	64.8 ± 1.0	1.0 ± 0.4

The crystal structure was evaluated by grazing incidence X-ray diffraction (GIXRD) method using an X-ray diffractometer SmartLab (Rigaku, Tokyo, Japan) and the $\text{CuK}\alpha$ radiation with a wavelength of 0.15406 nm. Scanning transmission electron microscopy (STEM) and elemental mapping of the $\text{ZrO}_2\text{:Al}_2\text{O}_3$ films in cross-sectional orientation were performed in a Cs-corrected Titan Themis 200 microscope (FEI, Hillsboro, OR, USA) equipped with a Super-X energy dispersive X-ray spectrometry (EDX) system (FEI/Bruker) at 200 kV. EDX maps were acquired using Esprit software version 1.9 (Bruker, Billerica, MA, USA). Thin cross-sectional samples for STEM observations were prepared using the in situ lift-out technique using Helios Nanolab 600 scanning electron microscope/focused ion beam system (FEI, Hillsboro, OR, USA). In order to protect the surface from ion milling during the preparation of STEM samples, the area of interest was covered with a platinum protection layer.

For the electrical measurements, the samples were supplied with titanium top electrodes, electron-beam evaporated (EBE) to a thickness of 70 nm through a shadow mask at 230 °C. The titanium electrodes of 6 nm for periodical $\text{ZrO}_2\text{:Al}_2\text{O}_3$ film structures were additionally covered with 100 nm of gold in the same EBE process to ensure sufficiently low contact resistance between a measurement probe and the Ti layer remaining in a direct contact to ZrO_2 . The top electrodes used in the measurements had diameters of 50 and 250 μm , and areas of 0.002 and 0.052 mm^2 , respectively. Electrical measurements were carried out in a light-proof and electrically shielded box on Cascade Microtech MPS150 probe station (Beaverton, OR, USA), using Keithley 2636A source-meter (Keithley Instruments, Cleveland, OH, USA) and Agilent E4980A LCR analyzer (Agilent Technologies, Palo Alto, CA, USA).

3. Results and Discussion

3.1. Composition

The XRF analysis revealed that the contents of aluminum and zirconium were expectedly correlated to the $\text{ZrO}_2\text{:Al}_2\text{O}_3$ cycle ratios used for growing the films with cycle sequences providing homogeneous distribution of Al_2O_3 intermediate layers throughout the film thickness (Table 1). The zirconium content was naturally higher in the film grown using a higher relative amount of ZrO_2 deposition cycles. The contents of oxygen and metal atoms approximately corresponded to that in oxygen-deficient zirconium dioxide, influenced by the presence of Al_2O_3 . In addition, the presence of residual chlorine, originating from the ZrCl_4 precursor, was detected in the films. The content of chlorine that did not depend on the Zr to Al ratio (Table 1) was well comparable to the contents measured in the ZrO_2 films grown from ZrCl_4 and H_2O under similar conditions earlier [41].

The presence of rather low contents of aluminum was detected in the films deposited directly on the TiN electrode surface by applying successive ZrCl_4 , $\text{Al}(\text{CH}_3)_3$ and H_2O pulses, followed by the deposition of the main ZrO_2 layer, thus creating asymmetric solid media. The XRF results (Table 2) indicated that the relative amounts of aluminum, as measured, did not correlate with the amounts of ZrCl_4 , $\text{Al}(\text{CH}_3)_3$ and H_2O pulse sequences. This could be explained by the small thickness of the $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layer between TiN and ZrO_2 . The host ZrO_2 has somewhat variable thicknesses because of either experimental uncertainty or lateral thickness profile characteristic of chloride-based ALD of ZrO_2 or other chloride-based processes in research-scale flow-type reactors, which has been known over decades [42,43].

Expectedly the reference $\text{Zr}_x\text{Al}_y\text{O}_z$ film, grown by applying 80 ALD cycles, each consisting of successive ZrCl_4 , $\text{Al}(\text{CH}_3)_3$ and H_2O pulses, contained relatively small amounts of aluminum; 7.4 at.% of aluminum against 26.8 at.% of zirconium (Table 2). Analogous phenomenon has been studied earlier in an ALD process, where the Al deposition rate was inhibited in the case on consecutive $\text{TiCl}_4\text{-Al}(\text{CH}_3)_3\text{-H}_2\text{O}$ pulses, compared to that in the case of conventional $\text{TiCl}_4\text{-H}_2\text{O-Al}(\text{CH}_3)_3\text{-H}_2\text{O}$ cycle sequence [44]. This effect was due to the occupation and screening of adsorption sites for $\text{Al}(\text{CH}_3)_3$ by species formed during the preceding TiCl_4 pulse. The reason for why $\text{Al}(\text{CH}_3)_3$ can be adsorbed on the surface

saturated by a metal chloride is the saturation of chloride adsorption because of steric effects rather than due to the occupation of all possible adsorption sites. It appeared that steric effects, which were able to stop further adsorption of TiCl_4 , did not avoid adsorption of $\text{Al}(\text{CH}_3)_3$ [44].

It has been studied and recognized earlier that, in thermal ALD process of ZrO_2 from ZrCl_4 and H_2O , submonolayer growth per cycle is to be considered [45] and obtained because of steric effects limiting the adsorption of ZrCl_4 [46]. As ALD of Al_2O_3 from $\text{Al}(\text{CH}_3)_3$ and H_2O should be more feasible process on hydroxylated surfaces, compared to the growth of ZrO_2 from ZrCl_4 and H_2O [47], $\text{Al}(\text{CH}_3)_3$ can be adsorbed even on sites that are not able to adsorb ZrCl_4 due to the steric limitations. However, because of the occupation and screening of adsorption sites by the metal precursor first adsorbing in the sequence, the amount of precursor adsorbing after the first one is limited.

Within the accuracy limits of XPS analysis, the composition estimates derived from the XPS survey spectra (Figure 2a) revealed the stoichiometric zirconium to oxygen (Zr:O) atomic ratio of 1:2 within the 2–3 nm analysis depth from the reference zirconium oxide film surface. At the same time for the reference aluminum oxide, the Al:O atomic ratio estimated was approximately 2.0:4.5, instead of the nominal 2:3 for the stoichiometric Al_2O_3 , indicating the presence of excess oxygen. This can be accepted as somewhat expected result, because formation of aluminum hydroxides can be considered as a possible result of surface reactions between Al precursors and H_2O . This result is consistent, for instance, with that earlier obtained for Al_2O_3 films grown by chemical vapor deposition in the work of Rawat et al. [48] where the results of XPS analysis were interpreted assuming dominance of surface hydroxyls over the fully oxidized aluminum.

Similarly, from the O 1s spectrum measured in the present study (Figure 2b), one could recognize the presence of a strong hydroxyl signal. Even the Al 2p band (Figure 2c) could suggest the hydroxide being even more dominant, with a narrow single feature spectrum at ~ 0.6 eV higher than that detected in the mixed $\text{Zr}_x\text{Al}_y\text{O}_z$ reference film. The spectra from the latter film well converged with the values earlier reported for crystalline alumina [49,50] and also for ZrO_2 - Al_2O_3 composite oxides [51].

The Zr 3d binding energy spectra (Figure 2d) allowed one to consider full Zr^{4+} oxidation state in both ZrO_2 and $\text{Zr}_x\text{Al}_y\text{O}_z$ reference films. One could also note a visible, but numerically negligible, broadening of the Zr 3d lines without appearance of the second component (doublet) in the $\text{Zr}_x\text{Al}_y\text{O}_z$ spectrum, suggesting all the Zr being accommodated in equivalent sites.

Comparison of the O 1s spectra (Figure 2b) allowed one to recognize surface hydroxyls present in similar minor amounts in both $\text{Zr}_x\text{Al}_y\text{O}_z$ and ZrO_2 reference films, but in much lesser amounts than in the Al_2O_3 reference film. The binding energy of the hydroxyl groups, however, coincides with that attributed, in an earlier study, to oxygen vacancies at neighboring sites [51]. There with the possible presence or absence of such defects in different samples can be rationalized to a certain degree by looking at elemental abundancies. At first, the feature just below 532 eV binding energy (Figure 2b, an orange dashed component line) is strong in the O 1s spectrum of the Al_2O_3 sample, where the content of oxygen is above that required for Al_2O_3 stoichiometry, which therefore suggests the presence of OH groups rather than oxygen vacancies. In the $\text{Zr}_x\text{Al}_y\text{O}_z$, the oxygen content, which was estimated from the survey spectrum (Figure 2a), was lower than that in the corresponding stoichiometric oxide. The latter observation could indicate the likely presence of oxygen vacancies, considered to be also present in the alumina-stabilized zirconia studied in an earlier work [51].

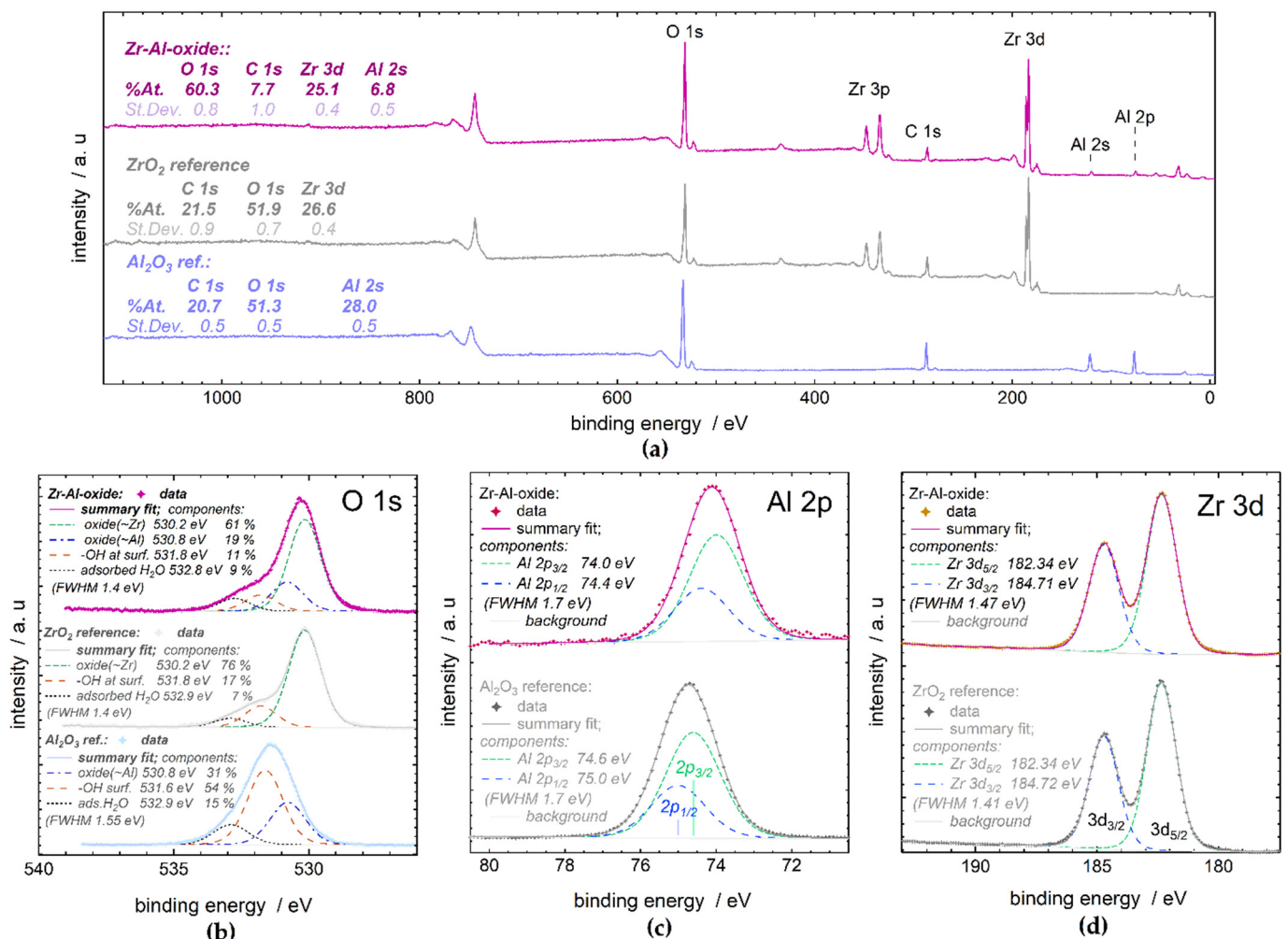


Figure 2. (a) Survey, (b) O1s, (c) Al 2p and (d) Zr 3d, X-ray photoelectron spectra of a $Zr_xAl_yO_z$ film grown using cycle sequence of $80 \times (ZrCl_4 + Al(CH_3)_3 + H_2O)$, and reference ZrO_2 and Al_2O_3 films.

3.2. Structure

Figure 3 depicts X-ray diffraction patterns of films deposited as multilayer $ZrO_2:Al_2O_3$ structures. One can see that the films were crystallized in their as-deposited state. The low intensity and large broadening of the XRD reflections indicated that the films could be regarded as nanocrystalline, as it was possible to expect, taking into account the doping effect and low thickness of the films. The patterns indicated the formation of metastable tetragonal or cubic polymorphs in ZrO_2 . It became also obvious that the application of decreasing amounts of successive ZrO_2 deposition cycles between single Al_2O_3 cycles, has led to the growth of more homogeneously mixed oxide layers, inhibiting the structural ordering down to the complete disordering, that is, inducing growth of amorphous matter, as observed in the cases of $ZrO_2:Al_2O_3$ films grown using a cycle ratio of 4:1 (Figure 3).

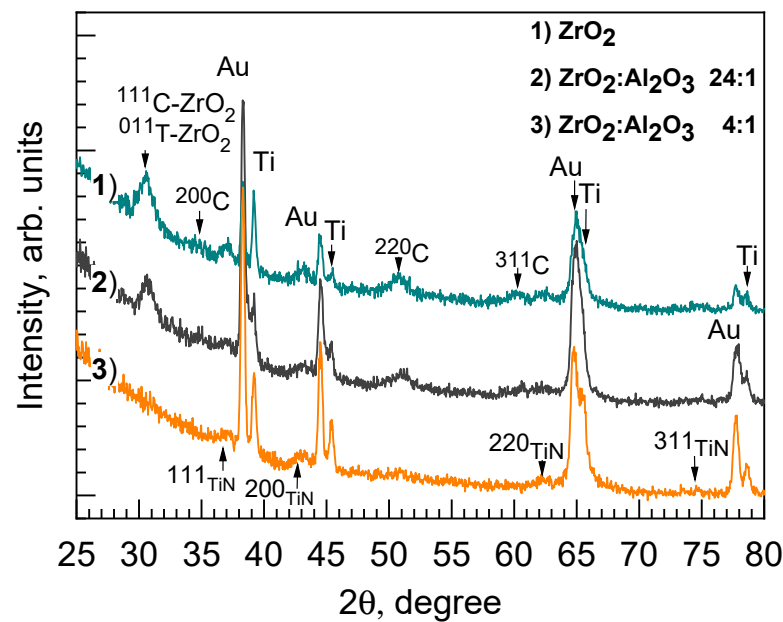


Figure 3. GIXRD patterns from (1) pure ZrO_2 and (2,3) periodically layered $\text{ZrO}_2:\text{Al}_2\text{O}_3$ films deposited by applying single Al_2O_3 deposition cycles between successive ZrO_2 cycles in ratios of (2) 24:1 and (3) 4:1. Patterns were measured from the films supplied with top Au/Ti electrodes. Miller indexes are assigned to the cubic phase of ZrO_2 , in addition to the reflections attributed to top metal and bottom TiN electrode films.

Figure 4 demonstrates cross-sectional bright-field (BF) STEM images from a representative $\text{ZrO}_2:\text{Al}_2\text{O}_3$ film grown on TiN bottom electrode and supplied with Au/Ti top electrodes. Crystal growth in the $\text{ZrO}_2:\text{Al}_2\text{O}_3$ film has become obvious according to the STEM images, supporting the XRD results. The interface between $\text{ZrO}_2:\text{Al}_2\text{O}_3$ film and TiN electrode appeared somewhat diffuse due to certain roughness of the TiN layer, but the whole medium was clearly crystallized throughout all layers.

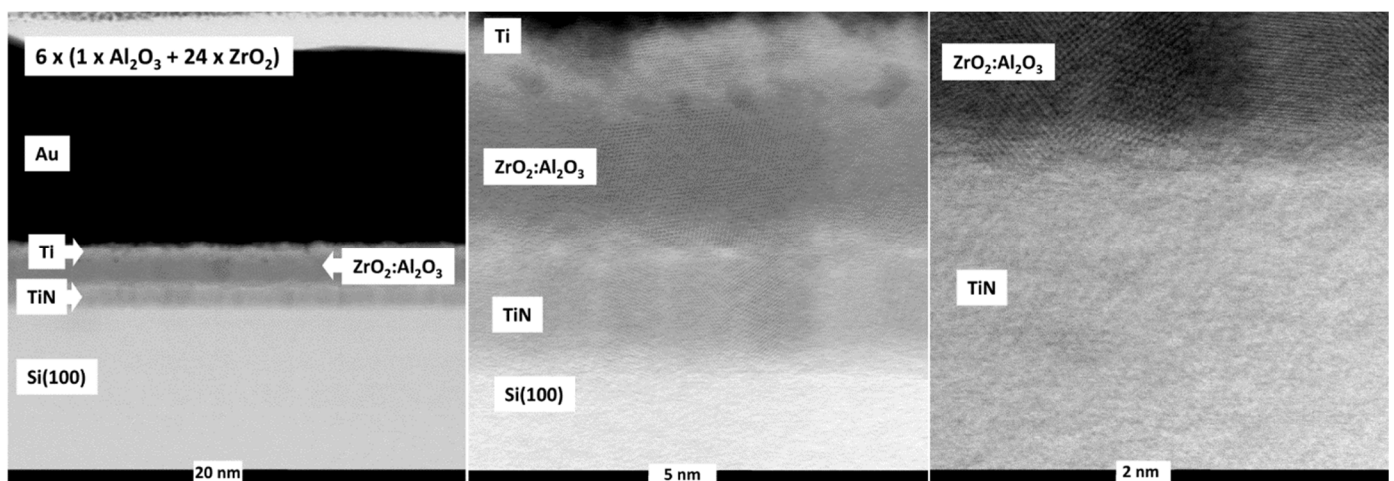


Figure 4. BF STEM images of the $\text{ZrO}_2:\text{Al}_2\text{O}_3$ film deposited using the ALD cycle sequence of $6 \times (1 \times \text{Al}_2\text{O}_3 + 24 \times \text{ZrO}_2)$. The images were taken under different magnifications implied by the scale bars. The locations of substrates, electrodes and $\text{ZrO}_2:\text{Al}_2\text{O}_3$ medium are indicated by corresponding labels.

Figure 5 presents the results of STEM-EDX elemental composition mapping carried out on a representative $\text{ZrO}_2\text{:Al}_2\text{O}_3$ film grown on TiN bottom electrode and supplied with Au/Ti top electrodes. One can clearly see that the constituent films have formed with defined interfaces between the switching medium and mounting electrodes. Quite expectedly, no separate continuous Al_2O_3 layers have been formed during single Al_2O_3 deposition cycles, applied periodically between multiple ZrO_2 layers, rather a diffuse, mixed-oxide film containing both Zr and Al oxides has been formed.

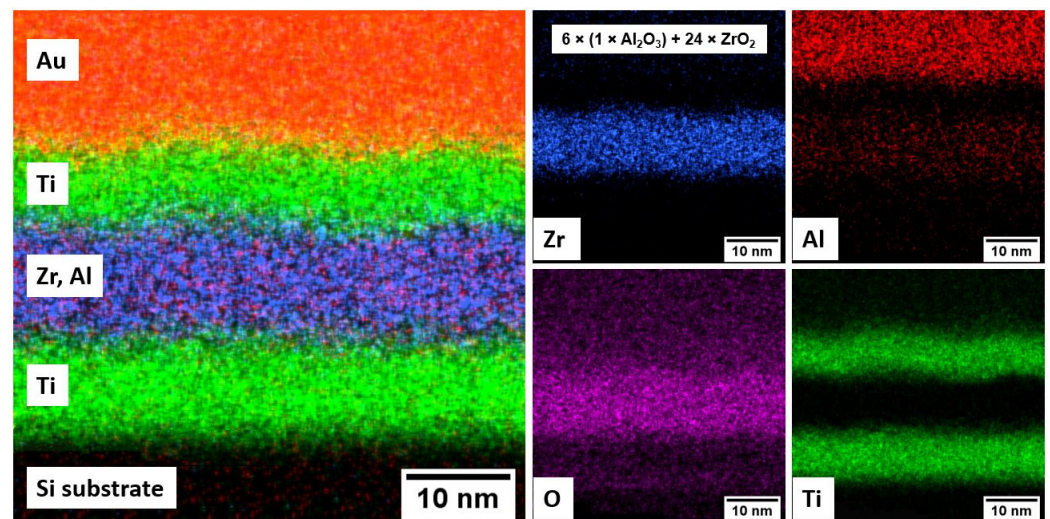


Figure 5. Elemental composition mapping of an Au/Ti/ $\text{ZrO}_2\text{:Al}_2\text{O}_3$ /TiN stack containing $\text{ZrO}_2\text{:Al}_2\text{O}_3$ film deposited using the ALD cycle sequence of $6 \times (1 \times \text{Al}_2\text{O}_3 + 24 \times \text{ZrO}_2)$. The chemical elements (Au [orange], Ti [green], Zr [blue], Al [red] and O [magenta]) as detected and mapped are indicated by the corresponding labels. Note that the high intensity of the Al signal in the Au contact region is due to the X-ray continuum. The intensity of the X-ray continuum is higher in regions with high atomic numbers. Although the X-ray continuum contributes to all maps, the effect is especially pronounced in the Al map due to low concentration of Al and, as a result, low signal/background ratio.

Figure 6 represents X-ray diffraction patterns of the double-layer $\text{Zr}_x\text{Al}_y\text{O}_z\text{-ZrO}_2$ structures. Quite expectedly, these films showed higher crystallinity in comparison to those deposited as multilayer $\text{ZrO}_2\text{:Al}_2\text{O}_3$ structures. The 10–15 nm thick ZrO_2 layers obtained in the $\text{Zr}_x\text{Al}_y\text{O}_z\text{-ZrO}_2$ structures after applying 80 ALD cycles were ordered in the form of metastable cubic and/or tetragonal polymorphs. Similarity of diffraction patterns of these polymorphs did not enable distinction between tetragonal and cubic phases unambiguously. Nevertheless, domination of the tetragonal phase in the films seems to be more likely considering the results presented in Figure 6. A possible effect of the nominal thickness of interfacial $\text{Zr}_x\text{Al}_y\text{O}_z$ layer between TiN electrode and ZrO_2 was not clarified in terms of its correlation to the structural ordering. The interfacial layer itself must have grown as amorphous, as was concluded on the basis of XRD results obtained for the reference film grown using 80 ALD cycles (the bottom pattern in Figure 6).

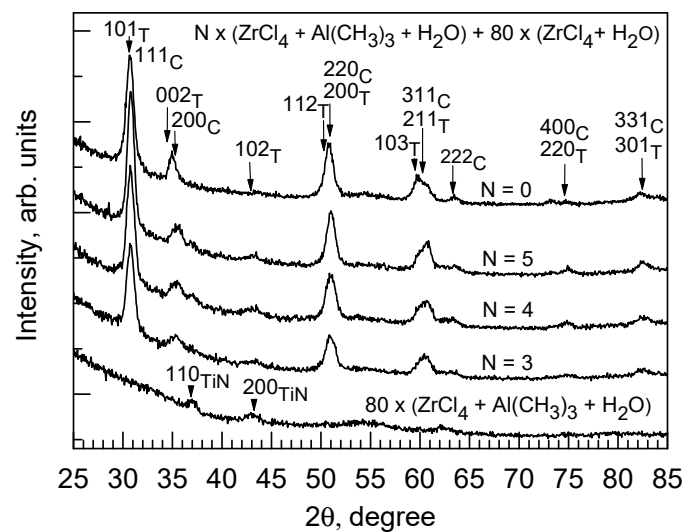


Figure 6. Grazing incidence X-ray diffraction patterns from asymmetrically deposited $\text{Zr}_x\text{Al}_y\text{O}_z\text{-ZrO}_2$ films, comprising successive pulses of ZrCl_4 , $\text{Al}(\text{CH}_3)_3$ and H_2O , applied N times (N indicated by labels) directly on TiN bottom electrode surface and followed by 80 ZrO_2 deposition cycles. Labels also indicate the Miller indexes attributable to either cubic or tetragonal phases of ZrO_2 , as well as those of the cubic TiN substrate layer. The bottom pattern, enclosed for comparison, represents that from X-ray amorphous reference film grown with 80 ALD cycles including successive pulses of ZrCl_4 , $\text{Al}(\text{CH}_3)_3$ and H_2O .

Figure 7 demonstrates a cross-section image from the $\text{Zr}_x\text{Al}_y\text{O}_z\text{-ZrO}_2$ stack deposited on a TiN bottom electrode. One can see, that both the main ZrO_2 film and the TiN electrode layer contain crystallites with hardly distinguishable boundaries between crystallites with different orientations and between crystallites and amorphous regions. The $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layer has, quite expectedly, also remained too thin for the unambiguous detection by energy-dispersive X-ray elemental analysis (not shown), as accumulation of aluminum could not be recognized.

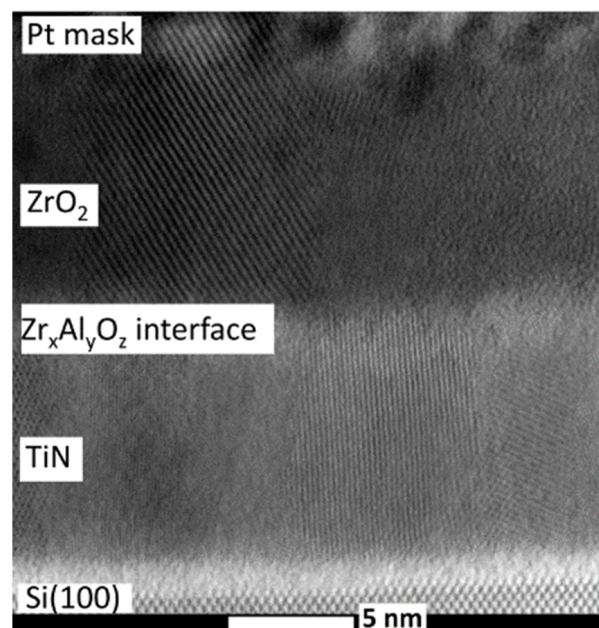


Figure 7. BF STEM image of $\text{Zr}_x\text{Al}_y\text{O}_z\text{-ZrO}_2$ film deposited using the cycle sequence of $5 \times (\text{ZrCl}_4 + \text{Al}(\text{CH}_3)_3 + \text{H}_2\text{O}) + 80 \times \text{ZrO}_2$. Substrate, bottom electrode and component layers are denoted by labels.

3.3. Dielectric Properties

Figure 8 depicts results of the capacitance dispersion measurements, transferred to the permittivity-frequency dependences. Since the TiN and Ti electrodes of the stacks could unlikely cause formation of interface layers, which would have been insulating and of lower permittivity compared to the main medium, simple parallel-plate capacitor formula based on a single dielectric material could be used for the estimation of the relative permittivity (k) in a good approximation. Herewith the k versus frequency curves (Figure 8) were averaged over at least ten measurement points on different dot electrodes arbitrarily selected over the electrode matrix.

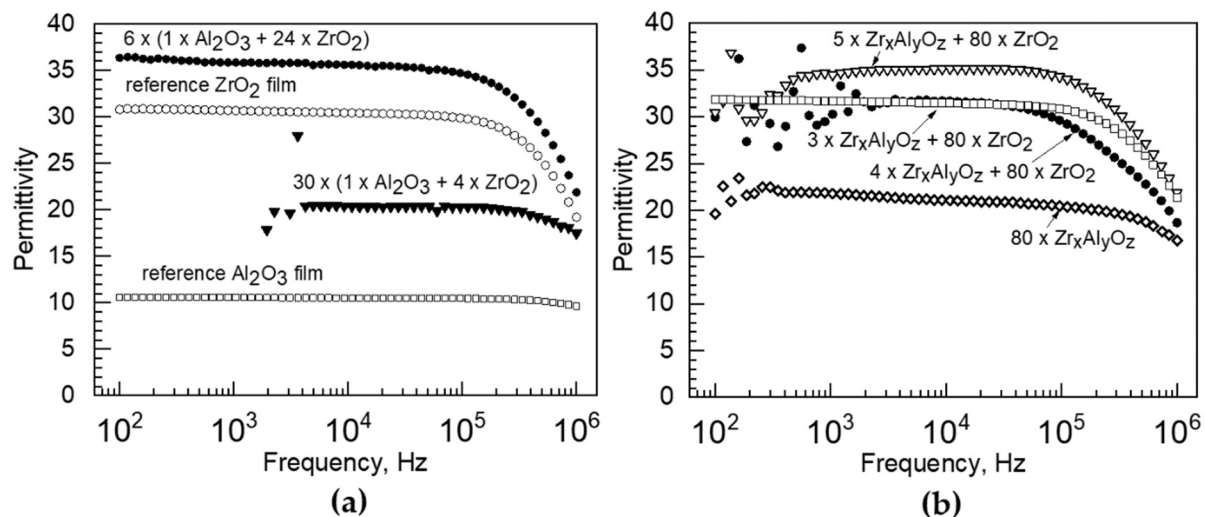


Figure 8. Relative dielectric permittivity versus measurement frequency curves for (a) periodically layered ZrO₂:Al₂O₃ stacks compared to those of reference ZrO₂ and Al₂O₃ films and (b) stacks deposited by applying 3, 4 or 5 ALD cycles of interfacial Zr_xAl_yO_z followed by 80 ALD cycles of ZrO₂. The growth cycle sequences are indicated by the labels pointing via arrows to the corresponding dispersion curves. For the thicknesses and composition data, see Tables 1 and 2.

The k values of dielectric layers with different compositions expectedly appeared as clearly distinguishable. The amorphous Al₂O₃ film possessed the lowest k value in the sample set, not exceeding 11 (Figure 8a). The nanocrystalline ZrO₂ film, possibly containing also some amount of amorphous phase in addition to metastable cubic/tetragonal phases, exhibited k slightly above 30. Remarkably, in the ZrO₂:Al₂O₃ film grown using one Al₂O₃ ALD cycle alternately with 24 ZrO₂ cycles, k values exceeding 35 were measured. In the latter film, the medium was also crystallized dominantly in the form of cubic or tetragonal polymorph (Figure 3). Higher content of tetragonal phase in these films compared to that in the undoped ZrO₂ films is a possible reason for the increase of permittivity with this kind of doping with Al₂O₃.

Expectedly, the amorphous ZrO₂:Al₂O₃ film grown using one Al₂O₃ cycle alternately with four ZrO₂ ALD cycles (Figure 3) exhibited k values close to 20, that is, values which are between those of Al₂O₃ and ZrO₂ (Figure 8a). At the same time, the capacitance values could not be measured reliably at relatively low measurement frequencies, i.e., below 5 kHz, for the same sample. This might be indicative of an increasing role for the space charge polarization or, at least, a tendency towards conductivity enhancing stepwise when closer steady state potentials. The polarization stability influenced by the internal distribution of Al and Zr in the solid medium evidently affected the electrical characteristics even further. Notably, the ZrO₂-Al₂O₃ films behaved differently under direct current measurements in resistive switching regime. The films grown using ZrO₂:Al₂O₃ cycle ratio of 24:1 enabled defined bipolar wide-window resistive switching, whereas the films grown using ZrO₂:Al₂O₃ cycle ratio of 4:1 allowed one to observe certain destabilization of the window with the concurrent appearance of multilevel switching, as will be described below.

The experimental k values measured for different materials in the present study are approximately consistent with those reported in the literature. In the case of crystalline ZrO_2 , calculations have allowed one to expect orientation-dependent k values up to 10–17, 32, and over 40 for the monoclinic, cubic and tetragonal ZrO_2 polymorphs, respectively [52]. High permittivity values have also been forecasted for amorphous ZrO_2 . According to the first principles calculations of Vanderbilt et al. [53], the electronic density distribution indicated that there are no defect states in the band gap of ZrO_2 , despite the amorphous nature of the material and accompanying fairly broad distribution of coordination numbers of the atoms. The atomic- and coordination-number-dependent Born effective charges in amorphous material, naturally smaller than those in the crystal lattice, would yield somewhat lower dielectric activities for the phonon modes, and an orientation-averaged lattice k may not exceed 17.6. Nonetheless, it has been concluded earlier that the average k of disordered ZrO_2 as high as 22.2 can be considered [53]. Such permittivity values for crystalline and disordered ZrO_2 have been supported by a number of experimental studies and may be regarded as reference values for ZrO_2 films synthesized by various methods [54].

The k values of single-crystal Al_2O_3 , as reported, should not rise over a value of 9.5 [55] while those ranging from 6 to 7 have been measured for 12 nm thick amorphous Al_2O_3 films grown by ALD from $\text{Al}(\text{CH}_3)_3$ and H_2O in the temperature range of 125–425 °C, without clear dependence on the growth temperature [56]. Higher k values up to 8.9 may have been achieved and reported for ALD-grown 3–5 nm thick Al_2O_3 films after specific substrate electrode surface treatments [57].

For comparison, studies on composites, or sandwiched and multilayered stack structures consisting of ZrO_2 and Al_2O_3 , have reported permittivity values correlated to the relative content of constituents. For instance, in ZrO_2 -strengthened Al_2O_3 powders containing 15 wt.% ZrO_2 , divided to 9 wt.% of tetragonal and 6 wt.% of monoclinic ZrO_2 phases, k reached 14 at room temperature [58]. A k value of 20.1 was measured in electron beam evaporated ZrO_2 – Al_2O_3 composite films, annealed and partially crystallized as tetragonal ZrO_2 [59]. In sol-gel processed crystallized ZrO_2 – Al_2O_3 nanolaminates, consisting of 7–40 nm thick ZrO_2 and Al_2O_3 constituent layers sandwiched to total thicknesses of 70 nm, k correlated to the relative content of ZrO_2 , with edge values of 6.9 and 20.3, characteristic of reference Al_2O_3 and ZrO_2 , respectively [60]. Similar behavior in sol-gel deposited ZrO_2 – Al_2O_3 nanolaminates was observed and described in another, more recent, paper, as well [61]. Although the alternately layered sandwich structures of Al_2O_3 and ZrO_2 are not necessarily to be regarded as homogeneous mixtures, the effective permittivity values should at least partially follow certain mixing rules relevant to composites of distinct compounds [62,63].

Waggoner et al. [64] have measured a k value of 15 for ZrO_2 : Al_2O_3 nanolaminates, which were grown by ALD from Zr alkylamide and $\text{Al}(\text{CH}_3)_3$, consisted of 1.25–15 nm thick Al_2O_3 layered alternately with ZrO_2 to total thicknesses of 40–200 nm, and contained 75% of ZrO_2 , whereas in the reference Al_2O_3 and ZrO_2 films, the k values were 7 and 25, respectively. In another study, triple layers consisting of 2 nm-thick Al_2O_3 , 20-nm-thick ZrO_2 and 2 nm-thick Al_2O_3 , sequentially grown by ALD from $\text{Al}(\text{CH}_3)_3$ and $\text{Zr}[(\text{CH}_3)_2\text{N}]_4$, possessed k up to 41.9 after microwave annealing [65]. Yet in even earlier study, k values up to 38 were reported as characteristic of industrially relevant memory dielectric stacks consisting of sandwiched 0.3–5.5 nm-thick tetragonal ZrO_2 and amorphous Al_2O_3 layers grown from $\text{Zr}[\text{N}(\text{CH}_3)\text{C}_2\text{H}_5]_4$, $\text{Al}(\text{CH}_3)_3$, and O_3 at 300 °C by ALD [2].

The averaged k values measured for the ZrO_2 , ZrO_2 : Al_2O_3 , and $\text{Zr}_x\text{Al}_y\text{O}_z$ – ZrO_2 films in the present study were, in a good approximation, consistent with the values either predicted or measured earlier for the amorphous, metastable, or appreciably crystallized media composed of the same elements. It is reasonable to assume that higher permittivity values accompany better-defined phase composition with higher concentration of tetragonal phase in the films. Furthermore, defined phase composition could ensure a clearer distinction between different conductivity states, provided that the capacitance (permit-

tivity) dispersion behavior remains stable, without fluctuations in insulating properties at low frequencies.

3.4. Resistive Switching Performance

Resistive switching was observed and recorded in the films, which contained ZrO_2 constituent layers, but could not be initiated in reference Al_2O_3 as well as in reference $\text{Zr}_x\text{Al}_y\text{O}_z$, whereby the latter was deposited via successive adsorption steps and reactions between ZrCl_4 , $\text{Al}(\text{CH}_3)_3$ and H_2O .

In the 14.6-nm-thick multilayered film grown using the deposition cycle sequence of $6 \times (1 \times \text{Al}_2\text{O}_3 + 24 \times \text{ZrO}_2)$, clear bipolar switching behavior was achieved (Figure 9a). The SET and RESET voltages were around -1.6 and 2.2 V, respectively. Remarkably, the $I_{\text{LRS}}/I_{\text{HRS}}$ ratios reached values up to 10^5 . However, despite an initially markedly uniform and wide switching window, the endurance of such devices did not reach acceptable ranges, as the switching collapsed after 25 switching cycles (Figure 9b). For comparison, somewhat analogous switching current–voltage curves have earlier been recorded for $\text{Au}/\text{HfO}_2/\text{TiN}$ devices [2,66], whereby the endurance tests allowed monitoring of stable switching during about 10^2 cycles with an $I_{\text{LRS}}/I_{\text{HRS}}$ ratio of 10^4 [66]. Clarification of the reasons behind high, but unstable, current ratios would require further detailed studies, including evaluation after structural modifications. In general, higher switching stability could be a result of higher chemical stability and structural uniformity of the medium in terms of the phase composition. Speculatively, one could expect higher switching stability in the HfO_2 -based medium, due to its tendency to preferably grow in the stable monoclinic phase, differently from ZrO_2 that can more easily occur as a multiphase material comprising stable and metastable phases.

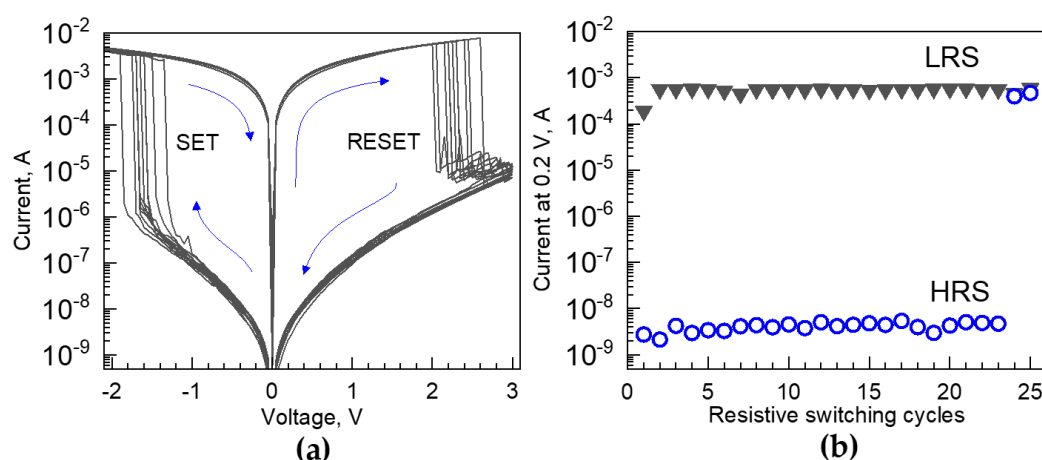


Figure 9. (a) Current–voltage and (b) endurance characteristics measured in resistive switching regime on an $\text{Au}/\text{Ti}/\text{ZrO}_2:\text{Al}_2\text{O}_3/\text{TiN}$ structure containing $\text{ZrO}_2:\text{Al}_2\text{O}_3$ films grown to a thickness of 14.3 nm using the deposition cycle sequence of $6 \times (1 \times \text{Al}_2\text{O}_3 + 24 \times \text{ZrO}_2)$.

In a film grown using the deposition cycle sequence of $30 \times (1 \times \text{Al}_2\text{O}_3 + 4 \times \text{ZrO}_2)$, the maximum $I_{\text{LRS}}/I_{\text{HRS}}$ ratios also reached values close to 10^5 (Figure 10). In the case of this sample, differently from the previously described one, clear indications of multi-state switching were observed, as implied by two appreciably distinct RESET voltages established nearby 1 V and above 2 V (denoted as RESET I and RESET II in Figure 10a). The sequential SET and RESET I events, followed by SET and RESET II operations carried out, can be better followed in Figure 10b, where rather minor, but still distinct differences can be noticed between LRS from different sequences denoted as LRS1 and LRS2 although in general the difference is not sufficient for practical application. The difference between LRS1 and LRS2 is probably caused because of the lower resistance in HRS1 and quicker current rise during the SET operation hence longer duration of higher current being applied. The implications of multilevel performance were, thus, observed in the sample

deposited by layering Al_2O_3 into ZrO_2 with markedly shorter period, that is, in the sample containing more Al_2O_3 . Thus, the multilevel RS might be related to the lower electrical stability of highly disordered, X-ray amorphous medium, although high $I_{\text{LRS}}/I_{\text{HRS}}$ ratios were initially observed.

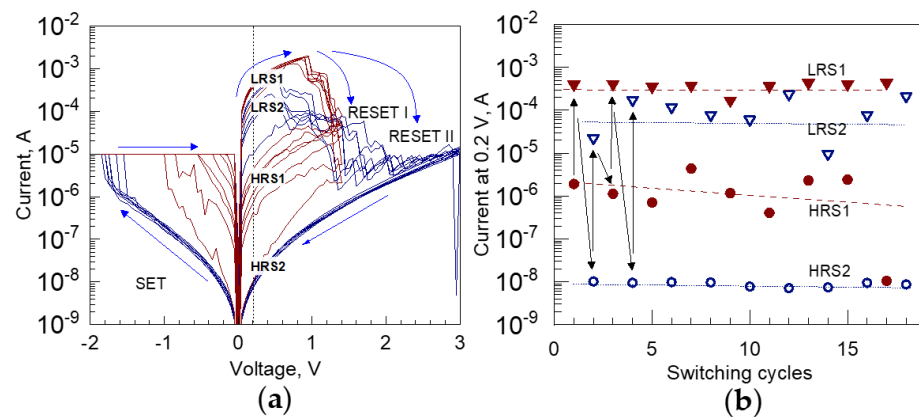


Figure 10. (a) Current–voltage characteristics and (b) endurance characteristic of resistive switching sequences measured in Au/Ti/ZrO₂:Al₂O₃/TiN structure containing 14.3 nm thick ZrO₂:Al₂O₃ film grown using the deposition cycle sequence of $30 \times (1 \times \text{Al}_2\text{O}_3 + 4 \times \text{ZrO}_2)$. Numbered LRS and HRS assign low and high resistivity levels, respectively, recorded at 0.2 V during two-level switching cycles before RESET events depicted in panel (a). Arrows in panel (b) are guides to eye, following the order of recording currents at different resistivity levels.

Multilevel RS has, probably intentionally, been initiated and recorded in ZrO₂-based devices earlier, whereby the appearance of multistate behavior was explained by the effects of dopant atoms or layers of variable composition embedded by the host material. For instance, multilevel switching was observed in Ti/ZrO₂/n⁺-Si cells where Cu atoms from a Cu layer deposited between top Ti electrode and the host ZrO₂ medium were thermally diffused as dopants into a sputtered ZrO₂ layer [67]. In the latter study, the rise of multilevel switching was attributed to the filamentary conduction while the formation and destruction of otherwise parallel filaments were affected by the distribution of dopants, occurring at different current levels and voltages. Further, multilevel switching was initiated also in sputtered ZrO₂ films mounted between TiN electrodes, with nonstoichiometric ZrO_{2-x} layer embedded in the host ZrO₂ [68]. In the latter study, the multistate performance was supposedly due to the transformation of interface type switching mechanism to the filamentary conduction, affected by the embedded layer with modified defective stoichiometry.

Regardless of the instabilities and implications of multistate conductivity levels, the switching voltage amplitudes of the structures in the present study exceeded 1–2 V. Yildirim and Pachter [69] have proposed after using an ab initio simulation, that dopants favoring interstitial doping, such as aluminum in ZrO₂, could facilitate an electrochemical metallization mechanism in RS cells, whereby the switching becomes manifested by conductive bridge formation due to dissolution of cations of the active electrode. This means that metallic filament is formed by the cations of an active electrode, instead of vacancy driven channel formation. This might, partially, explain the necessity for rather high switching voltages required for such media. Regarding the samples devised in the present study, the unambiguous distinction between dominant switching mechanisms, either metallic or oxygen vacancy driven filamentary or interfacial, may not be solved at this stage. However, most studies carried out earlier on switching oxide media seem to presume and trust in filamentary conduction pathways. Domination of interfacial conduction requires detailed specific studies on the interdependences between electrode materials, areas, and switching directions. Herewith it is worth mentioning, that in very few cases, direct proofs of the

physical existence of filaments have been reported, realized using an in situ TEM approach, e.g., in HfO_2 [70], TiO_2 [71], SiO_2 [72], or WO_x [73].

Current–voltage curves measured from a 12.2 nm thick reference ZrO_2 films grown without aluminum additives revealed appreciably low switching voltage amplitudes remaining between 0.5 and 1.0 V under both voltage polarities (Figure 11a). Analogously, all the devices built on asymmetric $\text{Zr}_x\text{Al}_y\text{O}_z$ - ZrO_2 films with $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layers grown between the bottom TiN electrodes and ZrO_2 films (Figure 1b) demonstrated RS behavior (Figure 11c,e). Notably, in all these samples the switching voltages were below 1 V, that is, lower than those needed for $\text{ZrO}_2:\text{Al}_2\text{O}_3$ media (Figure 1a) described above.

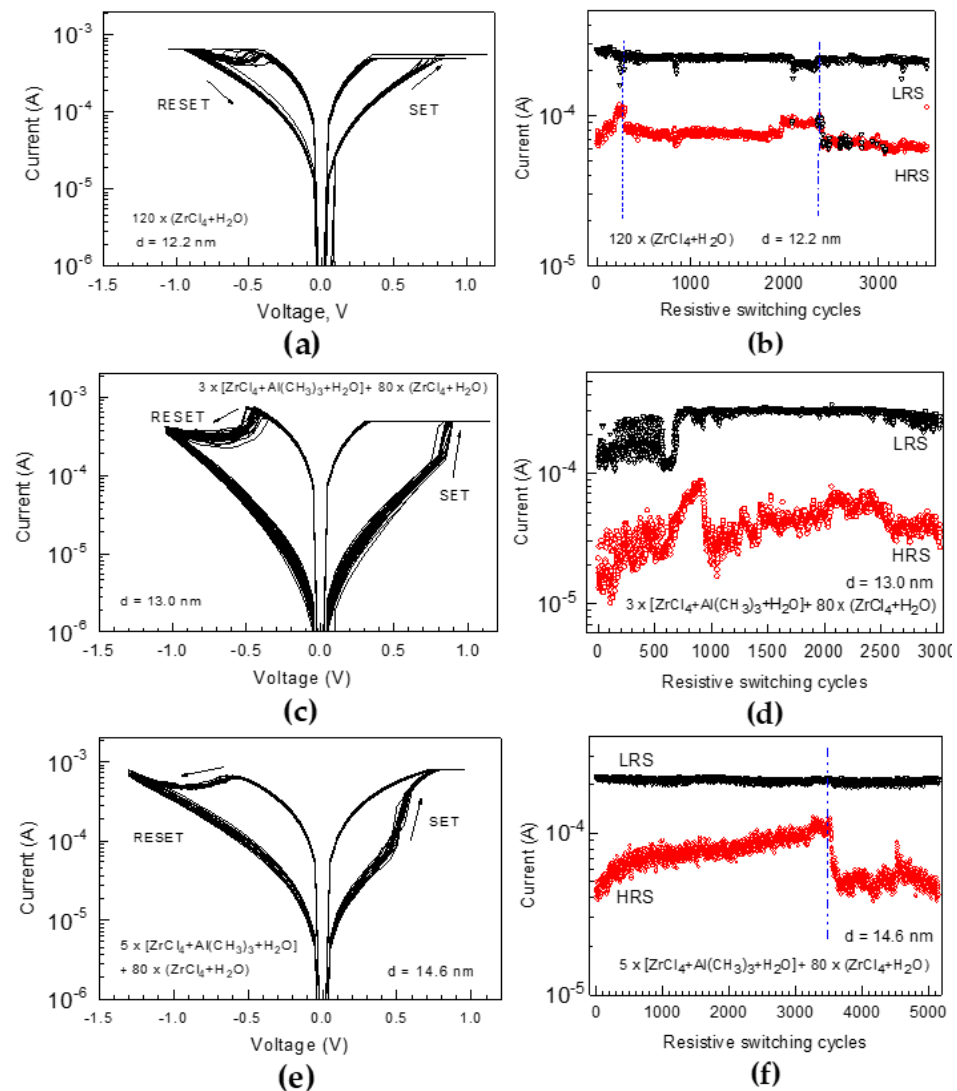


Figure 11. (a) Current–voltage switching and (b) endurance characteristics of a ZrO_2 reference film, compared to (c) current–voltage and (d) endurance behavior of a $\text{Zr}_x\text{Al}_y\text{O}_z$ - ZrO_2 stack deposited using 3 $\text{Zr}_x\text{Al}_y\text{O}_z$ and 80 ZrO_2 ALD cycles, and (e) current–voltage and (f) endurance test results for a $\text{Zr}_x\text{Al}_y\text{O}_z$ - ZrO_2 stack deposited using 3 $\text{Zr}_x\text{Al}_y\text{O}_z$ and 80 ZrO_2 ALD cycles. The deposition cycle sequences are indicated by labels.

The endurance tests on the 12.2 nm thick reference ZrO_2 films revealed marked instability, expressed by a decrease in the $I_{\text{LRS}}/I_{\text{HRS}}$ values during the first 300 switching cycles (Figure 11b), mainly due to an increase in the conduction currents in the high resistance state during consecutive measurement cycles. However, it was possible to recover the high resistance state value and improve the RS stability during the following 1700 switching cycles (Figure 11b) changing the programming RESET voltage from the

starting value of -0.65 V to -0.85 V. After reaching 2000 switching cycles, an abrupt change in the properties of the switching media occurred, as implied by moderate, but clear decrease in the I_{LRS}/I_{HRS} ratio. The decrease could, however, be compensated and the switching ratio restored setting the programming voltage at the RESET event to -1.0 V. The necessity for intentional drift in programming voltage toward higher values was noticed earlier, and the procedure may be regarded as work in process while seeking optimized parameters for stable switching performance. Somewhat speculatively, it may give a hint about that more conductive pathways or filaments can start to form after multiple switching cycles. Alternatively, and possibly, just one relatively large filament might also form, which in any case would require higher electric field strengths for disruption during RESET events. Specific kinetics analysis would require in depth investigations by high speed and precisely time controlled short pulses that would allow one to estimate and model the process [74].

Regardless of the obviously tunable endurance, the I_{LRS}/I_{HRS} values of the un-doped ZrO_2 films remained rather low, not exceeding 5. This observation referred to the necessity for combining ZrO_2 with another, a higher-band gap oxide such as Al_2O_3 , in order to reduce the conduction currents, in particular, in the high resistivity states. Since the $ZrO_2:Al_2O_3$ structures with periodical distribution of Al_2O_3 throughout the RS medium (Figure 1a) enabled switching between dramatically differing resistivity states (Figures 9a and 10) but without acceptable endurance (Figure 9b) and contact yield, the further measurements were conducted on stacks where just the interface between TiN and ZrO_2 was modified by deposition of defective $Zr_xAl_yO_z$ buffer layers, presumably able to ensure higher stability of switching.

The samples based on $Zr_xAl_yO_z$ - ZrO_2 stacks that contained the interfacial layers grown by applying 3 $Zr_xAl_yO_z$ cycles exhibited more stable counterclockwise switching (Figure 11c) with I_{LRS}/I_{HRS} ratios extending to values of 30–40. Such a difference in the switching direction compared to that obtained in multilayer $ZrO_2:Al_2O_3$ structures might indicate that the deposition of the $Zr_xAl_yO_z$ layer caused an increase in defect (vacancy) density at the interface between TiN and ZrO_2 , whereby the Al-rich interface served as a source of oxygen vacancies and conduction electrons. Relatively uniform switching could, after initial device stabilization over about a thousand cycles, easily become extended over 3000 cycles (Figure 11d), similarly to that observed in the reference ZrO_2 (Figure 11b). The latter is indicative of the necessity for the application of work-in cycle sequences after formation pulses, before the reliable switching process can be induced. It is, thus, worth underlining, that counterclockwise switching direction dominated in all $Zr_xAl_yO_z$ - ZrO_2 stacks as well as in reference ZrO_2 film (Figure 11), whereas in the case of periodically layered $ZrO_2:Al_2O_3$ films the clockwise switching was established (Figures 9 and 10). Reasons for the changes in the switching direction may not yet be unambiguously determined and explained at this stage of studies. Nevertheless, one might suppose that, in the case of $Zr_xAl_yO_z$ - ZrO_2 stacks, the $Zr_xAl_yO_z$ buffer layers have indeed served as reservoirs for defects, promoting channeling electronic currents under positive bias first, whereas in the case of periodically layered $ZrO_2:Al_2O_3$ media, the surface of the deposited film below the top metal electrode contact might have remained and regarded as the most defective junction of the whole structure.

Studies of devices containing 12–15 nm thick $Zr_xAl_yO_z$ - ZrO_2 dielectrics, based on interfacial $Zr_xAl_yO_z$ layers deposited using 5 $ZrCl_4$ - $Al(CH_3)_3$ - H_2O cycles on TiN followed by 80 ALD cycles of ZrO_2 , revealed increased initial stability of the switching voltages (Figure 11e). The I_{LRS}/I_{HRS} values reaching 7–10 were recorded for these devices during the first tens of the switching cycles. Along with the further endurance tests, the I_{LRS}/I_{HRS} ratio fluently decreased down to two because of increase in the high-resistive state current during the following 3500 switching cycles (Figure 11f). After changing the programming voltage of the RESET event from -1.0 to -1.2 V, the initial I_{LRS}/I_{HRS} ratio was restored and even stabilized for further switching cycles, analogously to the performance of I_{LRS}/I_{HRS} observed in the ZrO_2 -based reference device (Figure 11b).

In regard with the literature reporting the capacitive parameters of ZrO_2 -based thin films, a reader could attend a recent review paper by Xie et al. [54] and references therein. The results reported to date allow one to conclude that the permittivity of capacitive ZrO_2 -based cells can vary between 7 and 37, depending on the processing parameters, thickness, structural order, and dopant metal in ZrO_2 , together with the electrode materials selected to complete the cell structure. Regarding the parameters characteristic of ZrO_2 -based RRAM cells, including doped media, Panda and Tseng [8] have listed a considerable number of case studies, although without aluminum as an alternative dopant metal. Effects of different ionic dopants in ZrO_2 based RS media have been studied theoretically [75,76], without consideration of Al. Recently, the influence of aluminum dopant in ZrO_2 has also been investigated [77] in accord with density functional theory, revealing that the defect formation energy in ZrO_2 should decrease due to the doping effect. Studies on RS behavior in aluminum (oxide)-doped ZrO_2 media have so far evidently been rather scarce. In Table 3, nevertheless, some basic RS parameters are represented, concerning switching cell structures built on ZrO_2 films supported by Al_2O_3 layers, together with selected devices containing un-doped ZrO_2 .

Table 3. Comparison of RS stacks containing ZrO_2 or different combinations of ZrO_2 with Al_2O_3 as RS media. Given are also the film growth techniques, thicknesses, and maximum switching voltage range from negative to positive polarity in relation to bottom electrode. For low and high resistivity state ratios as well as amounts of endurance cycles, order of magnitudes implied in the reference studies are indicated. Data not revealed in the reference papers, and thus not available, are denoted by “NA”.

Switching Cell Structure	Deposition Technique	Film Thickness, nm	Switching Voltage Range, V	LRS:HRS Current Ratio	Endurance, Number of Cycles	Reference
Al/Ti/ ZrO_2 - Al_2O_3 /TiN/Si/Al	ALD	276	−1.5–1.5	2	NA	[23]
Al/Ti/ ZrO_2 - Al_2O_3 /TiN/Si/Al	ALD	41	−1.5–1.2	7.3	NA	[24]
TiN/ ZrO_2 - Al_2O_3 /Pt/Ti	Sputtering	50	−1.5–1.5	10	10^4	[76]
Al/ ZrO_2 /Cu/ ZrO_2 /Al	EBE	43	−2–1.5	10^3	10^2	[16]
TiN/ ZrO_2 / ZrO_{2-x} / ZrO_2 /TiN	Sputtering	45	−6–5	10^2	10^2	[68]
ITO/ ZrO_2 /AlON/ITO	ALD/Sputtering	10	−4–2	10	10^4	[26]
Al/ Al_2O_3 / ZrO_2 /Al	Sputtering	NA	−4.5–2.5	10^2	10^2	[25]
Au/Ti/ ZrO_2 : Al_2O_3 /TiN	ALD	14.6	−2–3	10^5	20	This study
Ti/ ZrO_2 / $\text{Zr}_x\text{Al}_y\text{O}_z$ /TiN	ALD	14.6	−1.5–1	10	3×10^3	This study

The results have implied that the low- to high-resistivity state ratio in ZrO_2 -based dielectrics along with the decrease in the thickness of the thin solid films, could be increased dramatically after alternate deposition of ZrO_2 and Al_2O_3 constituent layers. At the same time, the repeatability of the switching, expressed by the endurance cycle number, may inversely relate to the switching reliability between highly insulating and highly conducting states of the solid medium. Therefore, trade-off between endurance and feasibly achievable composition of the structured medium should further be targeted.

Notably, the results obtained from the ZrO_2 films grown on interfacial $\text{Zr}_x\text{Al}_y\text{O}_z$ layers between bottom TiN electrodes and the host media, implied possibilities to improve the switching behavior in terms of lowering the conductivity in the high-resistive states, compared to that in the ZrO_2 films deposited directly on TiN, and providing stabilized switching, compared to both periodically layered ZrO_2 : Al_2O_3 structures and reference ZrO_2 films. Notably, the $I_{\text{LRS}}/I_{\text{HRS}}$ instability and decrease during the endurance test could be suppressed by modifications of the programming voltage in real time.

4. Conclusions

In the present study, zirconium–aluminum oxide thin films were grown by ALD and mounted between bottom TiN and top Ti electrode layers. Multilayered $\text{ZrO}_2\text{:Al}_2\text{O}_3$ films, containing aluminum oxide up to 2 at.%, were ordered as nanocrystalline metastable tetragonal or cubic polymorph of ZrO_2 , in their as-deposited states. In double-layered $\text{Zr}_x\text{Al}_y\text{O}_z\text{-ZrO}_2$ stacks, where the $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layers were grown by applying 3–5 ALD cycles comprising successive ZrCl_4 and $\text{Al}(\text{CH}_3)_3$ pulses followed by an H_2O pulse, the 10–15 nm thick ZrO_2 layers deposited on top of $\text{Zr}_x\text{Al}_y\text{O}_z$ were all crystallized in the tetragonal or cubic phase. Notably, the crystallinity of ZrO_2 implied a tendency to enhance with increasing number of ALD cycles used for the deposition of the $\text{Zr}_x\text{Al}_y\text{O}_z$ buffer layer. The relative permittivity increased up to 36 and its instability at low measurement frequencies due to the dispersion effects decreased with increasing crystallinity in both multilayer $\text{ZrO}_2\text{:Al}_2\text{O}_3$ and double-layer $\text{Zr}_x\text{Al}_y\text{O}_z\text{-ZrO}_2$ stacks.

Resistive switching behavior was awoken in both $\text{Ti/ZrO}_2\text{:Al}_2\text{O}_3\text{/TiN}$ and $\text{Ti/ZrO}_2\text{-Zr}_x\text{Al}_y\text{O}_z\text{/TiN}$ devices. In the periodically layered $\text{ZrO}_2\text{:Al}_2\text{O}_3$, the conduction currents in the initial high resistance state could remain at the nanoampere level, resulting in remarkably high $I_{\text{LRS}}/I_{\text{HRS}}$ ratios reaching 100,000. Although the endurance of such a device reached few tens of cycles, the stability of the switching was appreciably uniform before collapsing. Significantly, upon engineering the structure of the medium by shortening the period of alternating metal oxides, thus increasing the number of Al_2O_3 dopant layers and aluminum content together with structural disorder in the RS medium, multilevel switching could be caused. In the double-layered $\text{Zr}_x\text{Al}_y\text{O}_z\text{-ZrO}_2$ films with $I_{\text{LRS}}/I_{\text{HRS}}$ ratios in the range of 10–40, the endurance characteristics were markedly improved, extending over 5000 cycles. Interestingly, in the case of the $I_{\text{LRS}}/I_{\text{HRS}}$ ratios either fluctuating or fluently decreasing during the endurance tests, one could restore and stabilize the low to high-resistivity state ratio by increasing the programming voltage amplitude in real time. An important result of this work was the demonstration that the RS direction depends on the Al distribution in the dielectric. Further studies could be devoted to the optimization of dopant concentration and related endurance limits, also after application of post-deposition heat treatments with optimum duration at selected temperatures.

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