Structure and Electrical Behavior of Hafnium-Praseodymium Oxide Thin Films Grown by Atomic Layer Deposition

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Abstract: Crystal structure and electrical properties of hafnium-praseodymium oxide thin films grown by atomic layer deposition on ruthenium substrate electrodes were characterized and compared with those of undoped HfO2 films. The HfO2 reference films crystallized in the stable monoclinic phase of HfO2. Mixing HfO2 and PrO, resulted in the growth of nanocrystalline metastable tetragonal HfO2. The highest relative permittivities reaching 37–40 were measured for the films with tetragonal structures that were grown using HfO2:PrOx cycle ratio of 5:1 and possessed Pr/(Pr + Hf) atomic ratios of 0.09–0.10. All the HfO2:PrOx films exhibited resistive switching behavior. Lower commutation voltages and current values, promising in terms of reduced power consumption, were achieved for the films grown with HfO2:PrOx cycle ratios of 3:1 and 2:1 and showing Pr/(Pr + Hf) atomic ratios of 0.16–0.23. Differently from the undoped HfO2 films, the Pr-doped films showed low variability of resistance state currents and stable endurance behavior, extending over 10⁶ switching cycles.

Keywords: hafnium oxide; praseodymium oxide; atomic layer deposition; crystal structure; dielectric properties; resistive switching

1. Introduction

HfO2, as a high-permittivity metal oxide, has attracted marked attention as a functional component of different nanoelectronic devices. HfO2 films have been studied and exploited as gate dielectric layers in both planar [1] and three-dimensional (3D) Fin-type [2] field-effect transistors. In order to modify the phase composition and enhance the functionality of the films, HfO2 has been doped with foreign metals or metal oxides. For example, Al-doped phase-stabilized HfO2 has been investigated as a dielectric for volatile dynamic random access memories [3]. In addition, stabilization of orthorhombic phase of HfO2 by doping with aluminum [4,5] or praseodymium [6] has been reported to cause the appearance of ferroelectric behavior, opening up routes to HfO2-based nonvolatile memories.

Regarding other potential applications of HfO2, resistive switching (RS) memory devices [7–17] are of significant importance. RS media based on metal oxides have been of interest for materials scientists and engineers over several decades, dating back to the beginning of 1960-ies [7]. The diversity in the choice of the materials suited to this application is still large, as one can decide on the basis of several recent reviews [7–10]. Amongst the metal oxide thin films under investigation, different compounds, such as TiO2, Al2O3, Ta2O5, ZrO2, or HfO2, can be considered.

HfO2 thin films have been examined as RS media in several studies [12–17]. At the same time, to improve the RS performance, the effect of doping has also been investigated.
For instance, aluminum has been used as a dopant in RS HfO₂ films [18,19]. In a long list of other dopants used in oxide films, praseodymium (Pr) is the one that has been applied to improve RS properties of CeO₂ [20] and ZnO [21]. Moreover, Pr has found application as a component of a rather complex compound, Pr₀.₂Ca₀.₃MnO₃, examined as RS media in a number of studies [22–27]. In the case of HfO₂, Pr has mainly attracted attention as a dopant allowing stabilization of metastable phases with ferroelectric properties and high permittivity values [6]. These results led us to a conclusion that the further investigation of Pr-doped HfO₂ as an electronic material could be of significant interest, especially because the Pr impurities might also influence the RS performance of HfO₂.

Among the methods that can be used for the deposition of HfO₂ thin films, atomic layer deposition (ALD) is the one that allows conformal coating of substrates with complex shapes [3]. For this reason, the method is of particular importance in the production of electronic devices with 3D integration [2,3]. The HfO₂ thin films have been grown by ALD from different hafnium precursors [4,5,13–15,18,19,28] of which HfCl₄ [46,47] is a carbon-free metal precursor allowing self-limited ALD-type growth in an extremely wide temperature range extending from 225 to 940 °C [28]. H₂O has been the most common oxygen precursor applied in ALD of HfO₂. However, ozone (O₃) as a hydrogen-free oxygen precursor has also been exploited for ALD together with HfCl₄ [29–32]. As HfCl₄ and O₃ had advantages in the deposition of films with low contamination levels, the ALD process based on these precursors was also employed in the present work.

Praseodymium oxide (PrOₓ) thin films have been grown using chemical vapor deposition [33] as well as ALD [34] routes based on Pr(thd)₃ (thd = 2,2,6,6-tetramethyl-3,5-heptanedione). The paper by Hansen et al. [34] implies that H₂O does not serve as an appropriate co-reactant together with Pr(thd)₃ because this precursor combination does not yield films with well-developed crystallinity and sufficient thickness uniformity. Another study on crystallization in lanthanide oxides [35] has indicated that PrOₓ films can be grown at 300 °C from Pr(thd)₃ and O₃. However, the films tend to be of multiphase composition, containing Pr₆O₁₁ and cubic PrO₂ phases due to the ability of this lanthanide to form Pr³⁺ and Pr⁴⁺ oxides and the latter’s mixed phases.

Mixed PrOₓ and hafnium oxide films have been grown by ALD using Pr(thd)₃, HfCl₄, and O₃ as the precursors [36]. In these experiments, the effects of deposition process parameters on the growth rate, crystal structure, phase composition, and optical properties (refractive index, optical bandgap, and photoluminescence efficiency) of the films were characterized [36]. The results revealed that the main phases observed in the praseodymium oxide films were PrO₂ formed at 225–250 °C, Pr₆O₁₁ formed at 275 °C, and Pr₇O₁₂ and Pr₁₀O₁₇ formed at 300–325 °C. The studies on ALD of HfO₂ from HfCl₄ and O₃ [32] have revealed that the monoclinic phase is predominantly obtained in the thicker (>40 nm) films at the substrate temperatures ranging from 225 to 600 °C. However, in the thinner films, the metastable cubic, tetragonal, or orthorhombic phase has also been observed [32]. Pr-doping stimulated the growth of the metastable phases while at sufficiently high Pr concentrations; only the tetragonal t′-form has been obtained in the films [36].

In nanoelectronics, ruthenium (Ru), as a noble metal with a high work function, has been of interest and studied as an electrode material of dynamic random access memory capacitors [37–40] with high permittivity dielectrics and very high capacitance density values [37]. Ru has also been applied as an electrode material of RS stacks [41–43]. Ru electrodes of RRAM devices have been directly contacted to Nb₂O₅ [44], tantalum oxide [43,45], or HfO₂ films [41]. Depending on the processes investigated, the Ru electrodes [43] and/or switching metal oxide layers [42,46] may have been grown by ALD.

Although RS can be based on several underlying mechanisms, the switching phenomena in the metal–insulator–metal stacks with metal oxide dielectrics and electrochemically inactive metal electrodes are usually governed by the valence change mechanism (VCM) [46,47]. In this type of RS media, conductive filaments are formed by oxygen vacancies and grow in the dielectric until they connect metal electrodes. To create these filaments for the first time, it is usually necessary to perform an electroforming process applying
voltage values that are higher than those needed later for RS [48,49]. Thereafter, using voltage with inverted polarity, the filament can be partially disrupted (RESET event). To form the conductive filament again (SET event), a voltage with the same polarity as in the electroforming process, but with a much lower value, can be applied [50]. VCM has been suggested to be the main RS mechanism in the structures with HfO$_2$ dielectric and with inert metal electrodes [51,52]. Recently, the conductive filamentary model has been described in an RS medium consisting of alloyed HfTiO$_x$ films in silicon-based contact hole structures where the oxide was grown by ALD from tetrakisethylmethyl(amino) hafnium, titanium tetraisopropoxide, and water [53]. The VCM of RS has also been observed in the case of other oxides. For instance, there is experimental evidence of this filamentary conduction in Ta$_2$O$_5$-based films [54]. Therefore, the same RS mechanism was expected to appear in Pr-doped HfO$_2$ as well.

The present work was performed to investigate the effect of Pr-doping on the electrical properties of HfO$_2$, in particular, on the permittivity and RS performance. High permittivity together with high bandgap values is important in applications where HfO$_2$ is used as a high-permittivity gate or capacitor dielectric. Earlier studies have revealed that Pr doping of HfO$_2$ causes an increase in the bandgap values and stabilization of a metastable tetragonal phase [36] that was expected to lead to the permittivity increase. A goal of this work was to obtain experimental data on the permittivity of Pr-stabilized metastable HfO$_2$. Another goal of this work was to investigate if the stabilization of the metastable phase and increase in the bandgap energy influence the RS performance, particularly the low to high resistance state ratio during RS and the stability of that ratio in terms of the endurance of such samples on ruthenium electrodes.

2. Materials and Methods

The Pr-doped HfO$_2$ films studied in this work were deposited in an in-house built hot-wall flow-type ALD reactor [55] at 325 °C using HfCl$_4$ (99.9 %, Aldrich Chemicals Co. St. Louis, MO, USA) and O$_3$ as the precursors for deposition of HfO$_2$ [32], and Pr(thd)$_3$ (Volatec Oy, Porvoo, Finland) and O$_3$ for adding PrO$_x$ to the film material [36]. Nitrogen (99.999%, AS Linde Gas, Tallinn, Estonia) was the carrier as well as purging gas in these experiments. The deposition process parameters were similar to those used earlier [36].

During the deposition, the net gas pressure in the reactor was kept at 200–220 Pa. O$_3$ was produced from O$_2$ (99.999% purity, AS Linde Gas, Tallinn, Estonia) using a BMT 802N ozone generator (BMT Messtechnik, Stahnsdorf, Germany). The O$_3$ concentration, measured by a BMT 964 ozone analyzer (BMT Messtechnik, Stahnsdorf, Germany) in the O$_3$/O$_2$ mixture at the outlet of the O$_3$ generator, was 240–260 g/m$^3$. The partial pressure of the O$_3$/O$_2$ mixture was set at 22 Pa in the reaction chamber during the oxygen precursor pulses. The Ru bottom electrodes were deposited on Si(100) substrates at room temperature by DC-magnetron sputtering in Ar (99.999%) environment using a Ru (99.95%) planar target of 25 mm in diameter. The pressure during the sputtering process was $3 \times 10^{-3}$ mbar, the DC-power was 2 W and the distance between target and substrate was 60 mm.

For the deposition of Pr-doped HfO$_2$, supercycles—including one cycle of Pr(thd)$_3$-O$_3$ per 2–5 cycles of HfCl$_4$-O$_3$—were repeated 25–50 times to obtain 19–50-nanometer thick Pr-doped films studied in this work. Each ALD cycle used for deposition of HfO$_2$ included a HfCl$_4$ pulse, purge, O$_3$ pulse, and another purge with durations of 5, 2, 5, and 5 s, respectively, while those used for deposition of PrO$_x$ included a Pr(thd)$_3$ pulse, purge, O$_3$ pulse, and purge with durations of 5, 2, 5, and 5 s, respectively. No post-deposition annealing was applied for samples studied in this work.

The crystalline phases formed in the films were determined by the grazing incidence XRD (GIXRD) method using an X-ray diffractometer SmartLab (Rigaku, Tokyo, Japan) and Cu K$\alpha$ radiation. The incidence angle chosen for the GIXRD measurements was 0.42°, corresponding to the scattering depth of 20 nm in cubic PrO$_2$ and 11 nm in monoclinic HfO$_2$ [36]. The diffractometer was also employed for X-ray reflection (XRR) measurements to determine the film thickness and surface roughness values. Additionally, the film thick-
nesses were measured with a GESSE spectroscopic ellipsometer (Semilab Sopra, Budapest, Hungary). Combining these two methods, the thicknesses of thinner (19–28 nm) films were determined with an accuracy better than ±2 nm while those of thicker (50–65 nm) films were obtained with an accuracy of ±3 nm. The mass thicknesses and elemental compositions of the films were determined with X-ray fluorescence (XRF) analyzer ZSX400 (Rigaku, Tokyo, Japan). Scanning electron microscope (SEM) Helios NanoLab 600 (FEI Company, Hillsboro, OR, USA) was used in a high-resolution mode (at an acceleration voltage of 10 kV and electron beam current of 86 pA) to characterize the surface microstructure.

For the electrical measurements, titanium top electrodes with circular geometry and thicknesses of 50 nm were electron-beam evaporated on the dielectric through a shadow mask at 230 °C. The Ti electrodes used in the measurements had areas of 0.002 and 0.052 mm². Electrical measurements were carried out in a probe station using a Keithley 4200-SCS semiconductor analyzer (Keysight Technologies, Cleveland, OH, USA). In the DC measurements, the bias voltage was applied to the top electrode while the bottom electrode remained grounded. To initiate RS, every sample required an electroforming procedure that was carried out as a voltage sweep with positive bias using a current compliance set at 1 μA to avoid irreversible breakdown of devices. In general, the electroforming took place between 7 and 13 V. The current–voltage (I-V) curves were obtained by applying positive and negative voltage sweeps to switch between the resistance states (bipolar RS), while the memory maps [56,57] were measured by reading the current value at 0.1 V after applying every increasing (or decreasing) voltage value used in the I-V envelope curves. To carry out the endurance measurements, a high number of relatively fast RS cycles were recorded. Each cycle was defined by a voltage pulse sequence of V_set, 0.1 V, −V_reset, and 0.1 V with switching pulse time durations of 0.1 s for V_set as well as for V_reset. Capacitance frequency measurements were carried out by applying a 30-millivolt signal without a DC bias in the 10 kHz–1 MHz frequency range.

3. Results and Discussion

3.1. Composition and Structure

The Pr/(Hf + Pr) atomic ratio in the HfO_2:PrO_x films was appreciably correlated with the ratio of HfO_2 and Pr_2O_3 deposition cycles (Figure 1) and equaled to 0.23, 0.16, and 0.10 in the 28-, 23-, and 19-nanometer thick films, grown using the HfO_2:PrO_x cycle ratios of 2:1, 3:1, and 5:1, respectively. In the 50-nanometer thick film grown using the HfO_2:PrO_x cycle ratio of 5:1, the Pr/(Hf + Pr) atomic ratio was 0.09.

![Figure 1. Pr/(Hf + Pr) atomic ratio as a function of PrO_x/(HfO_2 + PrO_x) cycle ratio, used for ALD of HfO_2:PrO_x films.](image)

As expected, the Pr content influenced the crystal structure of the HfO_2:PrO_x films. As can be seen in Figure 2, the 65-nanometer thick HfO_2 reference film, i.e., the one which did not contain PrO_x, was unambiguously crystallized in the form of the stable monoclinic polymorph. Furthermore, the expected and also obvious effect of the doping
was the stabilization of a metastable polymorph. It should be mentioned, however, that the distinction between metastable cubic, tetragonal, and even orthorhombic phases of HfO$_2$ was quite complicated, considering the small crystallite sizes accompanied by peak broadening and possible effects of doping and substrate structure, causing shifts in the peak positions. The corresponding reflections, peaking at 30.3, 35.5, 50.3, 60.5, and 63.0 degrees (Figure 2), were attributable to the 101, 110, 112, 211, and 202 reflections of tetragonal HfO$_2$ (PDF card 01-078-5756). At the same time, the reflections might also be assigned as 111, 002, 022, 113, and 222 reflections of the cubic HfO$_2$ (PDF card 96-900-9017), or as 111, 020, 022, 113, and 311 reflections of the orthorhombic HfO$_2$ (PDF card 00-021-0904). However, it is worth mentioning that the refinement of similar diffraction patterns of Pr-doped HfO$_2$ thin films grown by ALD on silicon substrates to thicknesses of 140–328 nm revealed the formation of tetragonal $t'$ form rather than other phases of HfO$_2$ in the films with Pr/(Pr + Hf) atomic ratios $\geq 0.095$ [36]. The tetragonal $t'$ form is characterized by the relatively small tetragonality of its lattice (with lattice parameter ratios $c/a$ ranging from 1.004 to 1.012 for the pseudo-fluorite unit cell), and therefore is an intermediate structure form between the cubic and tetragonal HfO$_2$. Nevertheless, it is also possible that the structure of the relatively thin films deposited on Ru in the present work had not been fully formed and, for this reason, was of a multiphase nature. In particular, low GIIXRD reflection intensities of the thinner films grown with a HfO$_2$:PrO$_x$ cycle ratio of 5:1 indicated the presence of amorphous and/or nanocrystalline phases with poorly developed structure in the films.

![Figure 2. Grazing incidence diffraction patterns from HfO$_2$:PrO$_x$ films deposited on Ru. The growth cycle sequences for HfO$_2$ and PrO$_x$, and Miller indexes attributed to either tetragonal (T) or monoclinic (M) phases of HfO$_2$ are shown at the diffraction patterns. Reflections from substrate Ru layers are denoted by corresponding labels. The film thicknesses (d) and compositions (Pr/(Hf + Pr) atomic ratios) are also indicated by labels.](image-url)

Although no direct correlation between the resistance state values and dielectric thickness had been observed in the VCM type RS media, based on HfO$_2$ [59] and other media [60], the dependence of the permittivity and RS performance on the structure development related to the dielectric thickness (Figure 2) could not be neglected. However, the results of electrical measurements presented below were dominantly influenced by the chemical and phase composition rather than by the thickness of the dielectric. For this reason, the further downscaling of the thickness was not studied in the present work.

The fitting of XRR data, measured for a 19.5-nanometer-thick Ru film used as a bottom electrode (Figure 3a), yielded a surface roughness value as low as 0.4 ± 0.2 nm. Thereby, the density of Ru was found to be 12.5 g/cm$^3$, that is, close to the bulk value. The SEM
studies confirmed the almost featureless and artifact-free nature of Ru electrode films (Figure 3b), allowing one to rely on smooth contact interfaces between the electrode and the RS medium. This was an important result because the SET events of the RS processes took place at positive voltages applied to the top electrodes. In such a case, the smoothness of the bottom electrode was assumed to reduce the parasitic leakage currents related to the electronic conduction and allowed us to expect reliable and reproducible electrical performance, uniform and stable over the electrode matrix formed on a sample used for electrical studies.

Figure 3. (a) XRR pattern on bare Ru bottom electrode, and (b–f) SEM images of (b) bare Ru bottom electrode, and (c–f) surfaces of HfO$_2$:PrO$_x$ films deposited using cycle sequences indicated by labels.

The thicker dielectric film grown using HfO$_2$:PrO$_x$ cycle ratio of 5:1 evidently consisted of densely packed grains (Figure 3c). A surface roughness of 1.9 nm, obtained from XRR measurements of this film, was notably higher than that of the Ru surface. For comparison, the surface roughness of a HfO$_2$ film of similar thickness was 1.7 nm. Smaller but distinctive grain-like features were observed by SEM on the surfaces of 2–3 times thinner oxide films (Figure 3d–f). The surface roughness values of these films grown using the HfO$_2$:PrO$_x$ cycle ratios of 5:1, 3:1, and 2:1 were 0.6, 1.4, and 1.2 nm, respectively. It is worth noting that the SEM images as well as surface roughness values were consistent with the degrees of crystallization characterized by GIXRD (Figure 2).

3.2. Dielectric Properties

Figure 4 depicts the results of capacitance frequency measurements carried out on HfO$_2$:PrO$_x$ films deposited on common Ru bottom electrodes and supplied with top electrodes arranged in a matrix. The capacitance did not show marked dispersion in a frequency range of 10–1000 kHz (Figure 4). This result could be considered as a plausible indication of the insignificant role of the relatively free space charge. Expectedly and most clearly, the capacitance correlated to the film thickness. However, the relative permittivity that depended on the phase composition of the HfO$_2$:PrO$_x$ films (Figure 2) also influenced the capacitance values.
The 23 and 28 nm thick films that were grown using HfO$_2$ could herewith be reasoned by the reduced polymorphic composition of the films under discussion (Figure 2). The permittivity values obtained for ALD films in our work (Figure 4), one can conclude that the formation of tetragonal phases, respectively. In this connection, the value of the relative permittivity, although lower than that predicted by the first-principles calculations, could herewith be reasoned by the reduced tetragonality of the $t'$ form or possible co-existence of tetragonal, cubic, and amorphous phases in the corresponding films. In contrast, the relative permittivity value as high as 32.1 were obtained at Pr concentrations of 5, 10, and 15 mol%, respectively, while the corresponding value for an undoped HfO$_2$ film was determined to be 18.3 [6]. The crystalline phases observed were the monoclinic one in the undoped films, the orthorhombic phase in the films with 5 mol% Pr, and the cubic phase in the films with 10 and 15 mol% Pr [6]. Comparing these results with those of theoretical calculations [61] and with the permittivity values obtained for ALD films in our work (Figure 4), one can conclude that the formation of the tetragonal structure was the main reason for the high permittivity values of our films deposited using a HfO$_2$:PrO$_x$ cycle ratio of 5:1.
The decrease in the permittivity observed with the decrease of the HfO$_2$:PrO$_x$ cycle ratio to 2:1 and increase of the Pr/(Pr + Hf) atomic ratio from 0.10 to 0.23 was probably caused by a decreasing amount of tetragonal phase in the films and/or decrease in the tetragonality of the $t'$ form of HfO$_2$ with increasing concentration of Pr. The decrease in the tetragonality of the $t'$ form with increasing concentrations of rare-earth dopant in HfO$_2$, has been observed, for instance, in the case of yttria-doped HfO$_2$ [60]. Unfortunately, because of relatively wide reflections in the GIXRD patterns of our films (Figure 2), revealing this kind of change in the crystal structure was not possible in the present work.

Another effect that might have contributed to the permittivity decrease observed with the increase of the Pr/(Pr + Hf) atomic ratio from 0.10 to 0.23 was the doping anisotropy that was most significant in the films grown with a HfO$_2$:PrO$_x$ cycle ratio of 5:1. In the growth direction of these films, the Pr concentration varied with a period of 0.8–1.0 nm, approximately. This value was evidently larger than the in-plane distance between Pr$^{3+}$ or Pr$^{4+}$ ions, provided that the solid-phase diffusion did not lead to uniform distribution of Pr in the films. For comparison, the Pr concentration was expected to vary with a period of 0.5–0.6 nm in the growth direction of the films deposited using a HfO$_2$:PrO$_x$ cycle ratio of 2:1. In this case, the period of dopant concentration variation was closer to the in-plane distances between Pr$^{3+}$ or Pr$^{4+}$ ions and, for this reason, the Pr distribution was more uniform than that in the films deposited with a HfO$_2$:PrO$_x$ cycle ratio of 5:1.

Finally, the lower permittivity of PrO$_x$ compared to that of tetragonal HfO$_2$ could be a reason for the permittivity decrease observed for Pr-doped HfO$_2$ with the decrease of the HfO$_2$:PrO$_x$ cycle ratio from 5:1 to 2:1. According to the literature data, the relative permittivity values of polycrystalline PrO$_x$ films have ranged from 8 to 26 [62,63] being higher for Pr$_2$O$_3$ and lower for PrO$_2$-rich films [62]. Therefore, to obtain the highest permittivity values, the Pr concentration in the Pr-doped HfO$_2$ films should not exceed significantly the value corresponding to the transition from the monoclinic to the tetragonal phase.

The conductivity of metal oxide dielectrics is directly related to their bandgap widths. On the other hand, doping with foreign elements—otherwise beneficial in terms of the stabilization of high-permittivity phases—might introduce parasitic states in the bandgap which could, presumably, increase the conduction currents. For instance, in the case of doping HfO$_2$ with praseodymium (oxide), Pr$^{3+}$ ions have energy levels in the bandgap of HfO$_2$ [64]. At the same time, however, the optical bandgap increased from 5.55–5.65 eV, determined for undoped HfO$_2$, to 5.72–5.78 eV in the doped films, where Pr/(Pr + Hf) = 0.15–0.20 and a tetragonal phase was formed [36]. Notably, also the theoretical calculations have predicted a wider bandgap for the metastable tetragonal/cubic HfO$_2$, compared to that of stable monoclinic HfO$_2$ [65]. Therefore the bandgap widening compensates, at least to some extent, for the contribution of the additional states generated in the bandgap by doping, thereby enabling the formation of HfO$_2$:PrO$_x$ films appreciably insulating in the capacitor structures and in the low resistance state of RS devices.

### 3.3. Resistive Switching

The HfO$_2$ and HfO$_2$:PrO$_x$ films, which were deposited in this work on Ru electrodes and supplied with Ti top electrodes, demonstrated RS behavior, expressed by clear current-voltage envelope curves characteristic of RRAM devices (Figure 5). The electroforming voltages did not vary systematically with the HfO$_2$:PrO$_x$ ratio. All the samples demonstrated, however, an abrupt forming transitions at 11–13 V to a current value of 1 µA set as a compliance limit in order to prevent irreversible breakdown.
The nature of the switching process (Figure 5) was bipolar, meaning that in the SET process, the conductive filaments were formed applying positive voltage in relation to the Ru electrode, while in the RESET process, the conductive paths were disrupted by applying voltage of the opposite polarity. The smallest electrodes with the average area of 0.002 mm² provided the most reliable results, that is, the initial electroforming process did not typically cause the dielectric breakdown, which otherwise would indicate issues with lateral homogeneity in the switching media.

The results depicted in Figures 5 and 6 demonstrate that the Pr concentration in the RS layer influenced the commutation voltages, current values in the low-resistive state ($I_{LR}$) and high-resistive state ($I_{HR}$) as well as the $I_{LR}/I_{HR}$ ratio. The increase in the Pr/(Pr + Hf) atomic ratio from 0 to 0.10 caused a decrease in $I_{LR}$ (Figures 5a–c and 6) and a minor increase in the set voltages (Figure 5a–c). At the same time, no considerable changes in $I_{HR}$ appeared (Figure 6). As a result, the $I_{LR}/I_{HR}$ ratios of the films that were grown using a HfO$_2$:PrO$_x$ cycle ratio of 5:1 were lower than that of un-doped HfO$_2$.

**Figure 5.** Current voltage envelope curves describing resistive switching of HfO$_2$:PrO$_x$ films as-deposited on Ru electrode substrates. HfO$_2$:PrO$_x$ deposition cycle ratios, Pr/(Pr + Hf) atomic ratios, and film thicknesses are indicated by labels in panels (a–e), where multiple (6–20) current–voltage curves are presented for the same film and device, measured consecutively and presented in different colors to enable better distinction. In panel (f), the averaged current–voltage curves are depicted comparatively.

**Figure 6.** Current values recorded in low resistance state (LRS) and high resistance state (HRS) at a voltage value of 0.1 V (see Figure 5). The HfO$_2$:PrO$_x$ ALD cycle ratios are indicated by labels at corresponding data points.
Comparison of the data for films with similar Pr/(Pr + Hf) atomic ratios (0.09 and 0.10) and very different thicknesses (50 and 19 nm, respectively) revealed minor differences in I_{LR} (Figure 5b,c and Figure 6). However, as can be seen in Figure 6, these differences were comparable to the experimental uncertainty related mainly to the deviation of results in successive measurements of the current-voltage (I-V) curves.

With the increase of the Pr/(Pr + Hf) atomic ratio to 0.16, obtained at a HfO$_2$:PrO$_x$ cycle ratio of 3:1, the set and reset voltages and I_{HR} decreased while I_{LR}/I_{HR} increased to a level exceeding that of undoped HfO$_2$ (Figures 5d and 6). The further increase of the Pr/(Pr + Hf) atomic ratio to 0.23, observed in the films grown with a HfO$_2$:PrO$_x$ cycle ratio of 2:1, did not influence the commutation voltages and I_{LR}/I_{HR} significantly (Figure 5d–f). However, I_{LR} and I_{HR} somewhat increased when compared to the corresponding values of the film grown using a HfO$_2$:PrO$_x$ cycle ratio of 3:1 (Figure 6).

Besides the envelope I-V curves describing current values measured at the variable bias voltage values (Figure 5), memory maps were recorded at a constant reading voltage as well (Figure 7). In the latter case, the conduction currents were read at a voltage of 0.1 V in between the sequential programming voltage pulses. Two clearly defined plateaus were reached between sequential SET and RESET events (Figure 7). I-V loops, which can be termed as memory maps, were thus formed with prominently expressed memory windows between the high and low current states during multiple voltage loops (Figure 7).

![Figure 7](image-url)  
**Figure 7.** Current recorded at 0.1 V as a function of programming voltage used for biasing of the (a) HfO$_2$ and (b–d) HfO$_2$:PrO$_x$ media before the current measurement. The HfO$_2$:PrO$_x$ cycle ratios used for growing the films and film thicknesses are indicated by labels. Different colors correspond to different memory maps recorded for the same film and device. The Pr/(Pr + Hf) atomic ratios were (b) 0.09, (c) 0.10, and (d) 0.23.

The memory maps supported the results depicted in Figures 5 and 6, showing that narrower windows between the low and high resistivity states, that is lower I_{LR}/I_{HR} ratios, were obtained for the reference HfO$_2$ films (I_{LR}/I_{HR} ≈ 30, Figure 7a) and especially for
the films deposited using HfO$_2$:PrO$_x$ cycle ratio of 5:1 ($I_{LR}/I_{HR} \approx 10$, Figure 7b,c). The window between the low and high resistivity states was much wider in the case of samples containing oxide media grown with HfO$_2$:PrO$_x$ cycle ratios of 3:1 (not shown) and 2:1 ($I_{LR}/I_{HR} \approx 60$, Figure 7d). Hence, rather than being a monotonic function of the Pr-content, the $I_{LR}/I_{HR}$ ratio possessed a minimum value at Pr/(Pr + Hf) atomic ratios of 0.09–0.10, that is, at the HfO$_2$:PrO$_x$ cycle ratio of 5:1. Earlier a significant dependence of RS performance on the doping level has been reported for Pr-doped ZnO films where the best functional ratio between resistance states appeared in the case of a certain stoichiometry [66]. The argument of an optimal composition has also been supported by the first-principles calculations made on HfO$_x$-based films [67]. Furthermore, thicknesses may also become more optimized at certain film stoichiometries [68], and would, consequently, require further more detailed parametrization.

Comparing the results depicted in Figures 5–7 with the GIXRD patterns (Figure 2), one can see that the $I_{LR}$ decrease, caused by the increase of Pr/(Pr + Hf) to 0.09–0.10, was evidently related to the formation of the metastable phase in the films. The wider bandgap of this phase [36] and possible compensation of oxygen vacancies because of Pr-doping are the plausible reasons for this $I_{LR}$ decrease. A probable reason for why the $I_{HR}$ value did not decrease and, correspondingly, the $I_{LR}/I_{HR}$ value decreased was the presence of some inclusions of monoclinic phase in the films deposited using a HfO$_2$:PrO$_x$ cycle ratio of 5:1. An evidence of the monoclinic phase is a tail on the right side of the 30.3° reflection in the diffraction pattern of the 50-nm thick films grown with this cycle ratio (Figure 2). This tail was evidently related to the contribution of the 111 reflection of the monoclinic phase. Although the small amounts of the monoclinic phase were not able to have a marked effect on the low-resistive state, the contribution of those to the much lower $I_{HR}$ values was still an expected result. Correspondingly, the absence of the monoclinic phase in the films grown with HfO$_2$:PrO$_x$ cycle ratios of 3:1 and 2:1 and the formation of a more homogeneous crystalline phase in these films were reasons for lower $I_{HR}$ and higher $I_{LR}/I_{HR}$ values obtained. The latter films also possessed somewhat lower commutation voltages (Figures 5f and 7) than the rest of the samples did. This observation implies that the media which contain higher amounts of praseodymium and only metastable nanocrystalline phases might become better suited to low-power applications. Higher mobility of oxygen ions in these films might be one possible reason for lower commutation voltages observed.

Endurance measurements were carried out for samples with different doping levels to determine their reliability and resistance state variability during fast writing, erasing, and reading operations. In these measurements, a current compliance of 5 mA was set in order to prevent the irreversibly breaking of dielectrics when applying the commutation voltages in a short period of time. The use of compliance has been shown to improve the endurance characteristics in HfO$_x$-based RRAM [69]. However, the same functional windows between the high and low resistance states were not expected when comparing the results of endurance studies with the current-voltage envelope curves or memory maps.

First of all, the endurance characteristics presented in Figure 8 revealed higher stability of Pr-doped HfO$_2$ media compared to that of undoped HfO$_2$. In the case of samples with undoped HfO$_2$, the first instabilities in $I_{LR}$ as well as $I_{HR}$ appeared after applying a few hundred cycles, while a marked increase in $I_{HR}$ was observed after 3000 cycles. In contrast, the RS layer grown using a HfO$_2$:PrO$_x$ cycle ratio of 2:1 showed very stable $I_{LR}$ as well as $I_{HR}$ values up to the end of the endurance measurements (Figure 8). Therefore, the Pr-doping of HfO$_2$ and/or formation of metastable (tetragonal) phase in the RS medium play a significant in producing memory cells with superior RS performance.
Figure 8. Endurance characteristics of HfO$_2$:PrO$_x$ switching media measured in the small-signal regime. The HfO$_2$:PrO$_x$ cycle ratios used for ALD of dielectrics and the dielectric layer thicknesses are indicated by labels at corresponding curves. $I_{LR}$ and $I_{HR}$ values for every tenth measurement cycle are depicted in the figure.

An even more interesting performance was observed in the case of samples with Pr-doped HfO$_2$ deposited using a HfO$_2$:PrO$_x$ cycle ratio of 5:1 that yielded films with Pr/(Pr + Hf) atomic ratios of 0.09–0.10. Figure 8 demonstrates that with an increasing number of switching cycles, the $I_{HR}$ value of a 50-nanometer thick film considerably decreased while the $I_{LR}$ value increased resulting in a marked increase in the $I_{LR}/I_{HR}$ ratio. It is noteworthy that a similar performance was observed for a 19-nanometer thick films with a Pr/(Pr + Hf) atomic ratio of 0.10. In both cases, the changes in $I_{HR}$, $I_{LR}$, and $I_{LR}/I_{HR}$ were relatively smooth without significant random fluctuations of the current values. Therefore, it seems that the conductive filaments were additionally electroformed (stabilized) in this kind of RS medium during the endurance studies. Phase transitions leading to the formation of a more uniform crystal structure and/or more uniform distribution of Pr$^{3+}$/Pr$^{4+}$ ions in the vicinity of switching filaments can be considered as the main mechanisms causing this kind of modification of the RS medium.

Comparison of our results with literature data confirmed the excellent performance of Pr-doped HfO$_2$ studied in this work compared to that of many other HfO$_2$-based undoped and doped RS media. Typical $I_{LR}/I_{HR}$ values reported [16,70–75] have ranged from one to two orders of magnitude being well comparable to the corresponding values obtained in our work. However, $I_{LR}/I_{HR}$ values as high as three orders of magnitude have also been reported for samples with optimized electrode structure [76]. In most cases, the endurance tests, if performed, have been limited to 1000 switching cycles [70,71,73,75] but reports about endurance tests up to $10^5$ [72,74] and $10^8$ [16] switching cycles have also been published. Comparing the results described in the latter papers with those obtained in our experiments one can still conclude that after optimization of the device processing procedures, Pr-doped HfO$_2$ can also become a promising candidate for application in resistive switching random access memories.

4. Conclusions

Our studies of Pr-doped HfO$_2$ thin films grown by ALD on ruthenium electrodes revealed superior properties of these films for different electronic applications. The films grown using HfO$_2$:PrO$_x$ ALD cycle ratios, ranging from 5:1 to 2:1, crystallized in the tetragonal phase while the Pr/(Pr + Hf) atomic ratio ranged from 0.09 to 0.23 in these films. The relative permittivity values as high as 37–40 were measured for the films with Pr/(Pr + Hf) atomic ratios of 0.09–0.10. No considerable dependence of the permittivity on the measurement frequency was observed in a frequency range of 0.01–1 MHz. As the
films with this composition have also high bandgap values (5.72–5.78 eV), as revealed in our earlier work, they could successfully be applied as capacitor and gate dielectrics.

Additionally, stable-resistive switching performance was obtained in metal–dielectric–metal structures with HfO$_2$:PrO$_x$ dielectrics, ruthenium bottom electrodes, and titanium top electrodes. In the structures with as-grown dielectrics, the $I_{HR}/I_{LR}$ ratios ranged from 10 in the case of dielectrics with Pr/(Pr + Hf) atomic ratios of 0.09–0.10 to 60 in the case of dielectrics with Pr/(Pr + Hf) atomic ratios of 0.16–0.23. The resistive switching layers with Pr/(Pr + Hf) atomic ratios of 0.16–0.23 showed also lower $I_{HR}$, $I_{LR}$, and commutation voltage values compared to corresponding parameters recorded for devices with undoped HfO$_2$ dielectric. The endurance measurements demonstrated excellent stability of resistive switching in Pr-doped HfO$_2$ during $10^8$ switching cycles. Thus, Pr-doped HfO$_2$ could be considered as a promising material for application in resistive switching memory devices as well.

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