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M. M. Abdallah 💿 ; E. V. Skopin 💿 ; F. Fillot 💿 ; D. Constantin 💿 ; M. Abusaa 💿 ; A. Bsiesy 🕿 💿

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M. M. Abdallah, 1.2 🐌 E. V. Skopin, 1 🗅 F. Fillot, 3 🕩 D. Constantin, 4 🕩 M. Abusaa, 2 🕩 and A. Bsiesy 1, a) 🕩

AFFILIATIONS

¹Univ. Grenoble Alpes, CNRS, CEA/LETI-Minatec, Grenoble INP, LTM, 38054 Grenoble, France

²Department of Physics, Arab American University, Jenin, Palestine

³Univ. Grenoble Alpes, CEA, Leti, F-38000 Grenoble, France

⁴Univ. Grenoble Alpes, Grenoble INP, CIME Nanotech, F-38000, Grenoble, France

^{a)}Author to whom correspondence should be addressed: ahmad.bsiesy@univ-grenoble-alpes.fr

ABSTRACT

The ferroelectric properties evidenced on undoped hafnium oxide, which are similar to those of doped HfO₂, are rather unexpected since it is believed that doping is a prerequisite for stabilizing HfO₂ ferroelectric behavior. Two different origins were invoked to account for this behavior. The first is related to the thermodynamic conditions of orthorhombic/ferroelectric HfO₂ phase formation, favored upon the monoclinic/non-ferroelectric one by its lower surface energy in very small crystallites, i.e., in very thin layers. The second one is related to the existence of mechanical stress within the HfO₂ layer, which allows stabilization of the non-centrosymmetric orthorhombic/ferroelectric phase. The mechanical stress is either due to doping or the top and bottom metal layers in the metal/HfO₂/metal stack. The origin of undoped HfO₂ ferroelectric behavior is still under debate. In this work, additional evidence of the role of mechanical stress in stabilizing the HfO₂ orthorhombic/tetragonal (o/t) phase is presented. The effect of top and bottom TiN electrodes on the crystallization of Gd-doped and undoped HfO₂ layers was studied as a function of HfO₂ layer thickness. The results show that the HfO₂ o/t phase of undoped HfO₂ disappears when the bottom TiN electrode is absent. In contrast, Gd-doped HfO₂ layers show the presence of a high o/t phase amount, even without the TiN bottom layer. The mechanical stress role is further evidenced by atomic plane interplanar distance measurements, which show large deformation between in-plane and out-of-plane x-ray diffraction geometries, only in the case of Gd-doped HfO₂.

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I. INTRODUCTION

The report by Böscke *et al.* on ferroelectric behavior of silicondoped hafnium oxide Si:HfO₂ has revitalized the potential use of ferroelectric non-volatile memories in complementary metal– oxide–semiconductor (CMOS) technology.^{1–9}

Although HfO_2 can crystallize in four different phases: cubic, monoclinic, tetragonal, and orthorhombic; the monoclinic crystallographic phase is the most stable one. The HfO_2 monoclinic phase is centrosymmetric, which prevents it from being ferroelectric. In contrast, the HfO_2 orthorhombic phase with a space group Pca2₁ (29) is non-centrosymmetric, and hence, it is ferroelectric, but its formation should be favored over the monoclinic phase.

Different approaches, leading to the formation of a stable noncentrosymmetric o-phase, have been adopted, among which, doping with different elements, such as Si,¹ Al,¹⁰ Sr,¹¹ Y,¹² Gd,^{13–18} Zr,^{19,20} La,²¹ and N,²² were the most effective ones. Thus, it was evidenced that doping leads to stabilization of the HfO₂ ferroelectric orthorhombic phase, although the physical origin of this stabilization remained under debate.²³

Indeed, earlier reports advanced the effect of doping in reducing the free energy difference between the monoclinic and orthorhombic phases as a possible origin of orthorhombic phase stabilization,²⁴ while other reports attributed such stabilization to the mechanical stress applied to the HfO₂ layer.^{22,25–29} Indeed, several reports evidenced orthorhombic phase stabilization on undoped HfO₂ where the free energy reduction cannot be invoked.^{30–35}

Moreover, in a recently published paper,³⁶ we investigated the ferroelectric behavior of undoped HfO₂ and Gd-doped HfO₂ layers lying between TiN electrodes as a function of layer thickness. We

showed an identical remnant polarization (P_r) amplitude for ultrathin layers, up to \sim 7 nm, above which the polarization amplitude kept increasing in the doped layer, while it slowed down and started to decrease for the undoped layer thickness above 13nm. In parallel, this decrease was accompanied by the apparition of a progressively dominant monoclinic phase in the undoped HfO₂ case. It was assumed that the HfO2 non-centrosymmetric o-phase stabilization and its subsequent ferroelectric behavior are related to mechanical stress, applied by the TiN top and/or bottom electrodes, in the case of undoped materials, or by doping, in the case of Gd-doped materials.

In this work, we bring further evidence of the role of mechanical stress in stabilizing the HfO2 ferroelectric phase. This study was performed, by investigating the effect of the absence of a bottom TiN electrode, on the crystallization of doped and undoped HfO₂, while varying the HfO2 layer thickness. Both stacks were prepared under the same experimental conditions, which enables a straightforward analysis of the experimental results.

II. EXPERIMENT

Different samples, containing either thin HfO2 layers, TiN/ HfO₂, or TiN/Gd:HfO₂ stacks, were prepared using a plasma enhanced atomic layer deposition (PEALD) FlexAL chamber from Oxford Instruments. The deposition was performed on 100 nm-thick SiO₂, thermally grown on a Si substrate. The substrate temperature during HfO2, TiN, and Gd:HfO2 PEALDs was kept at 250 °C without exposure to air between different layer depositions within a given stack.

The TiN deposition PEALD involves a series of consecutive cycles. Each PEALD cycle consists of four distinct steps. The first step was the injection of a Ti precursor, tetrakis(dimethylamido) titanium(IV) or Ti[N(CH₃)₂]₄, hereinafter called TDMATi, from a bubbler, which was heated at 60 °C. The second step was the Ar flow reactor chamber purge, the third was the exposure to N2/H2/ Ar plasma, and the fourth was a reactor purge under Ar flow. The number of TiN PEALD cycles was fixed to deposit a 10 nm-thick layer used as a top electrode.

For HfO₂ PEALD, the number of PEALD cycles was varied to have the desired thickness. Each HfO2 PEALD cycle includes four distinct steps. The first step was a Hf-precursor injection-tetrakis (ethylmethylamido) hafnium(IV) or Hf[N(C₂H₅)(CH₃)]₄, hereinafter called TEMAHf. The second step was a reactor purge under Ar flow, the third step was exposure to O2 plasma, and the fourth step was a reactor purge with Ar gas flow.

The PEALD process of HfO2 doped with Gd (Gd:HfO2) involved a supercycle approach. Each Gd:HfO2 PEALD supercycle consisted of four HfO2 PEALD cycles, as described previously, followed by one PEALD cycle of Gd doping. The Gd-doping PEALD cycle within the supercycle included four steps similar to the HfO2 PEALD deposition cycle, i.e., Gd-precursor injection-tris(cyclopentadienyl) gadolinium(III) or Gd(Cp)3, a reactor purge by Ar, and O₂ plasma exposure.

Some of the samples, prepared by PEALD, were annealed using rapid thermal annealing (RTA) for 10 min at 650 °C by RTA-100 equipment from UniTemp GmbH. The increase temperature rate was 50 °C per second under a constant N2 flow of 2 l/min.

The thicknesses of TiN, undoped HfO₂, and Gd-doped HfO₂ grown layers were measured by x-ray reflectometry (XRR). The measurements were performed by Empyrean, Malvern Panalytical x-ray diffractometer in the $\alpha_i - \alpha_f$ angle range $[0-6]^\circ$, using CuK_{α} wavelength of 1.5406 Å. The XRR measurement yielded a reflectivity curve as a function of the incident angle. The reflectivity data were fitted using the PANalytical X'Pert Reflectivity software for the fitting process, where the parameters for thickness, surface roughness, and density were adjusted to match the experimental curve.

By using the same diffractometer, the crystallinity of HfO₂ deposited layers in HfO2/SiO2/Si, TiN/HfO2/SiO2/Si, and TiN/Gd: HfO₂/SiO₂/Si sample stacks was analyzed by grazing incidence x-ray diffraction (GIXRD). The incident angle was 1° . The 2θ angle was in the $[20-80]^{\circ}$ range.

XRD peak reference positions of the monoclinic, tetragonal, and non-centrosymmetric ferroelectric orthorhombic phases were taken from Ref. 23.

Crystalline interplanar distance d in HfO2 (in TiN/HfO2/ SiO₂/Si and TiN/Gd:HfO₂/SiO₂/Si stacks) was measured perpendicular and parallel to the sample surface by performing out-of-plane and in-plane XRD ($\theta/2\theta$ Bragg-Brentano geometry) analysis with 2θ in the $[27^{\circ}-34^{\circ}]$ range, using the 2D detector of an Empyrean, Malvern Panalytical x-ray diffractometer and a five circle diffractometer (Smartlab, Rigaku) equipped with a copper or molybdenum 9kW rotating anode generator (radiation wavelength, $\lambda_{Cu} = 1.5406$ Å), respectively.

For the purpose of electrical measurements, a TiN/Gd:HfO₂/ For the purpose of electrical measurements, a Tay density $330_2/Si$ metal-oxide-semiconductor (MOS) stack was obtained, 37 and TiN and Gd:HfO₂ layers were grown by PEALD on a 22 nm-thick SiO₂ layer grown on Si by thermal oxidation at 371050 $^{\circ}$ C under O₂ ambient. The number of Gd:HfO₂ PEALD supercycles was 20, to obtain a layer thickness of about 11 nm.

Afterward, this sample was patterned by depositing a 🔅 10nm-thick Ti layer first, and then a 30 nm-thick Pt layer on the sample surface (TiN/HfO2/SiO2/Si stack), using the metal evaporator MEB550 from Plassys. The growth rate was controlled in situ by a quartz crystal microbalance (QCM) and was around 0.25 nm/s for Ti and Pt layer growth.

Then, photoresist patterns were produced by the photolithography process using positive photoresist AZ5214 and MJB4 Mask Aligner from SUSS MicroTec Group.

Finally, the Pt/Ti/TiN metal stack was etched back down to the Gd:HfO2 layer using ion beam etching (IBE) from Plassys MU400 IBE 01. ICP Ar plasma was used as an ion beam source with an Ar flow of 3sccm and an RF power of 400 W. The substrate was rotating during the etching (10 rpm), and the angle between the substrate surface and the Ar flow direction was 55°. An integrated secondary ion mass spectrometry (SIMS) detector allowed an etch-stop at the HfO₂ layer surface. The sample was then placed in acetone in an ultrasonic bath to remove the photoresist, after to isopropanol, and dried by N₂.

Capacitance-voltage characteristics were performed on annealed and not-annealed TiN/Gd:HfO2/SiO2/Si MOS capacitors using a two-probe electrical setup connected to an Agilent E4980A 20 Hz-2 MHz precision LCR meter, which was able to deliver a combined AC signal and a DC bias. The AC signal frequency and amplitude were 1 MHz and 25 mV, respectively.

III. RESULTS

The XRR was used to measure the thicknesses of different types of sample stacks: $HfO_2/SiO_2/Si$, $TiN/HfO_2/SiO_2/Si$, and $TiN/Gd:HfO_2/SiO_2/Si$. Figure 1 shows a series of the XRR curves obtained on annealed samples (blue solid lines) and their fit lines (red solid lines).

For example, Fig. 1(a) shows the XRR curve for four $HfO_2/SiO_2(100 \text{ nm})/Si$ samples. As mentioned previously, the HfO_2 layer thickness was varied by applying different numbers of PEALD cycles. One can see that the distance between XRR oscillations decreases by increasing the number of HfO_2 PEALD cycles (hereinafter cy), i.e., upon an HfO_2 layer thickness increase. The extracted HfO_2 layer thickness were 5.4 nm, 10.7 nm, 16.1 nm, and 21.3 nm for 40, 80, 120, and 160 PEALD cycles, respectively.

Figures 1(b) and 1(c) show the XRR curves for $TiN/HfO_2/SiO_2/Si$ and $TiN/Gd:HfO_2/SiO_2/Si$ samples, and the corresponding extracted HfO_2 and $Gd:HfO_2$ layer thicknesses.

The TiN layer thickness was also extracted by fit. The average thickness of the top TiN electrode extracted from XRR measurements was found to be 10 nm.

To study the effect of the TiN top electrode on the postannealing crystalline phase of undoped HfO₂, x-ray diffraction was performed on two different stacks: HfO₂/SiO₂/Si (HfO₂ without the top TiN electrode, i.e., uncapped HfO₂ layer) and TiN/HfO₂/ SiO₂/Si (HfO₂ with the top TiN electrode, i.e., capped HfO₂ layer).



FIG. 1. XRR curves (blue solid lines) and their fits (red solid lines) measured after annealing with different numbers of HfO₂ and Gd:HfO₂ PEALD cycles and supercycles for different types of sample stacks: (a) HfO₂/SiO₂/Si, (b) TiN/HfO₂/SiO₂/Si, and (c) TiN/Gd:HfO₂/SiO₂/Si.

The thickness of the HfO_2 layer in both stacks was varied up to about 22nm.

Figure 2 shows the GIXRD curves for $HfO_2/SiO_2/Si$ (a) and (b) and $TiN/HfO_2/SiO_2/Si$ (c) and (d) stacks.

GIXRD curves were measured in the $[20-80]^{\circ} 2\theta$ range [Figs. 2(a) and 2(c)] and also with higher diffraction angle scan resolution in the $[27-34]^{\circ} 2\theta$ range [Figs. 2(b) and 2(d)].

In the case of uncapped HfO₂/SiO₂/Si [Figs. 2(a) and 2(b)], there are no clear diffraction peaks associated with the orthorhombic or tetragonal phase. In contrast, two diffraction peaks were observed in the 2θ range between ~28.5° and ~31.5°. Based on the reference peaks from Fig. 2, these diffraction peaks can be attributed to the HfO₂ monoclinic phase. In addition, the intensity of these peaks increases with the HfO₂ layer thickness.

In the case of TiN-capped HfO₂ [Figs. 2(c) and 2(d)], a weak diffraction peak appears at 2θ between 30.0° and 30.5° that can be attributed to the orthorhombic or tetragonal phase. However, besides being weak, this diffraction peak is observed only at a very thin HfO₂ layer thickness (4.9 nm) and tends to decrease drastically



FIG. 2. GIXRD curves of HfO₂/SiO₂/Si (a) and (b) and TiN/HfO₂/SiO₂/Si (c) and (d) samples with different HfO₂ layer thicknesses (after RTA): (a)–(c)—in the 2 θ angle range 20°-80° and (b)–(d)—in the 2 θ angle range 27°–34° with higher angular resolution. The upper part represents the GIXRD pattern of the reference HfO₂ structure, corresponding to the monoclinic, tetragonal, and orthorhombic phases.²³



FIG. 3. Evolution of the integrated area of the o/t phase peak as a function of HfO_2 layer thickness for $HfO_2/SiO_2/Si$, $TiN/HfO_2/SiO_2/Si$, and $TiN/Gd:HfO_2/SiO_2/Si$ stacks.

and vanishes above 7.6 nm layer thickness, whereas the monoclinic phase peak intensity steadily increases with thickness. Figure 4(d) shows the GIXRD curves obtained on Gd-doped HfO₂ capped with TiN, i.e., the TiN/Gd:HfO₂/SiO₂/Si stack. The diffraction peak related to the orthorhombic/tetragonal (o/t) HfO₂ phase is observed at $2\theta \sim 30.5^{\circ}$. The intensity of this peak increases upon the HfO₂ layer thickness.

To analyze the evolution of diffraction peaks related to the HfO_2 orthorhombic/tetragonal phase, the GIXRD curves of Figs. 2(b) and 2(d) were deconvoluted using Gaussian functions, with the peak's position, width, and area as the fitting parameters. In particular, the same width was applied for all peaks. Figures 2(b) and 2(d) show in red the (-111) and (111) monoclinic phase peaks and in blue the (111) orthorhombic or (101) tetragonal phase peaks. The integrated o/t peak area was then calculated as a function of HfO_2 layer thickness and plotted in Fig. 3.

For $HfO_2/SiO_2/Si$, i.e., uncapped HfO_2 , the integrated peak area (intensity) is close to zero in the HfO_2 thickness range [5.4– 21.3] nm. For the TiN/ $HfO_2/SiO_2/Si$ stack, i.e., TiN-capped HfO_2 , one can see a very small o/t peak area that increases as a function of HfO_2 thickness and reaches the maximum at 4.9 nm, and then vanishes above 7.6 nm, whereas in the TiN/Gd: $HfO_2/SiO_2/Si$ stack case, i.e., capped and Gd-doped HfO_2 , the o/t integrated peak area is higher for thin layers and it continues to increase as a function of Gd-doped HfO_2 layer thickness. This means that in the latter case, the HfO_2 o or/and t crystalline phases are dominant.

The GIXRD results, outlined in Fig. 3, evidence the role of Gd-doping in stabilizing the orthorhombic HfO_2 phase, which is at the origin of ferroelectric behavior in this material.

By studying the crystallization of doped and undoped HfO_2 layers grown on TiN, we recently suggested the role of mechanical stress in stabilizing the HfO_2 o-phase.³⁶ Indeed, o-phase presence and ferroelectric behavior observed in TiN/HfO₂/TiN/SiO₂ and TiN/Gd:HfO₂/TiN/SiO₂ stacks were attributed to the lattice deformation due to mechanical stress applied by the bottom TiN layer or by Gd-doping, respectively. Our present results (Fig. 3) bring



FIG. 4. In-plane (a) and out-of-plane (b) XRD curves measured for the TiN/Gd: HfO₂/SiO₂/Si sample stacks as a function of Gd:HfO₂ thickness. Crystalline phase position reference values are taken from Ref. 23.

additional evidence to this assumption, as the absence of the pottom TiN layer (TiN/HfO₂/SiO₂/Si) shows that the ratio of the o/t phase is drastically reduced, despite a very weak o/t diffraction peak, likely due to the TiN capping layer. Direct evidence of this mechanical stress effect can be brought by investigating the HfO₂ o-phase lattice parameters by performing the XRD curves in in-plane and out-of-plane, in Bragg–Brentano $\theta - 2\theta$ geometry.

Figures 4(a) and 4(b) show, respectively, the in-plane and out-of-plane XRD curves measured for the $TiN/Gd-HfO_2/SiO_2$ samples.

The o/t peak position shows opposite shifts for the cases of in-plane and out-of-plane XRD. In the case of in-plane XRD [Fig. 4(a)], the o/t peak position is shifted to smaller 2θ values, and in the case of out-of-plane XRD [Fig. 4(b)], it is shifted to higher 2θ values.

Based on the XRD curves of Fig. 4, the interplanar distance d was calculated using Bragg's law. Calculated d corresponds to the (111) ferroelectric orthorhombic phase or (101) tetragonal phase XRD planes.

Figures 5(a) and 5(b) show calculated $d_{o(111)}/d_{t(101)}$ for undoped and Gd-doped HfO₂ layers as a function of thickness, respectively.

Blue squares in the figures show d calculated using the in-plane XRD data (diffraction planes are perpendicular to the sample surface). Red circles on the figures show d calculated using the out-of-plane XRD data (diffraction planes are parallel to the sample surface).

In the case of undoped HfO_2 in the HfO_2 thickness range [4.9–7.6] nm [Fig. 5(a)], d is the same as the reference d value for the planes perpendicular to the sample surface and d is slightly smaller for the planes, which are parallel to the sample surface.



FIG. 5. Interplanar distances d as a function of HfO₂ layer thickness corresponding to the diffraction peak at $2\theta \sim 30.5^\circ$ extracted from in-plane and out-of-plane XRD of Fig. 4 for (a) TiN/HfO₂/SiO₂/Si and (b) TiN/Gd:HfO₂/SiO₂/Si stacks (from not shown figures). The represented d reference value corresponds to the interplanar distance for the ferroelectric orthorhombic HfO₂ phase.

This corresponds to lightly compressed crystalline planes that are parallel to the sample surface.

In the case of Gd-doped HfO_2 in the HfO_2 thickness range [5.3–22.6] nm [Fig. 5(b)], d is higher than the reference d for the planes perpendicular to the sample surface and d increases as a function of HfO_2 thickness. The value of d for the planes parallel to the sample surface is smaller than the reference d, and d decreases as a function of HfO_2 thickness.

Thus, the Gd-doped HfO_2 layer undergoes significant d parameter deformation due to mechanical stress compared to the undoped HfO_2 layer that shows a small d parameter change.

The ferroelectric behavior of Gd-doped HfO₂ in the TiN/Gd: $HfO_2/SiO_2/Si$ MOS stack was investigated by capacitance-voltage (C-V) characteristics analysis. Figure 6 shows the C-V curves for annealed and as deposited, i.e., not annealed, TiN/Gd:HfO₂ (11 nm)/SiO₂(22 nm)/Si(p) MOS capacitors.

The positive to negative voltage scan between 1 and -4 V showed well-behaved inversion \rightarrow depletion \rightarrow accumulation typical of a MOS stack on a p-type substrate.

The theoretical equivalent accumulation capacitance (C_{eq}) value was calculated to be 189.3 pF using the following equation: $1/C_{eq} = 1/C_{HfO_2} + 1/C_{SiO_2}$, where C is the capacitance measured in Farad (F): $C = \varepsilon \varepsilon_0 A/t$, where ε_0 is the permittivity of free space (8.85×10^{-14} F/cm) and ε is the relative permittivity of HfO₂ ($\varepsilon_{HfO_2} = 25$)¹¹ or SiO₂ ($\varepsilon_{SiO_2} = 3.9$).³⁷ A is the area of the capacitor device (1.3×10^{-3} cm²) and t is the layer thickness, 11 and 22 nm for HfO₂ and SiO₂, respectively.

The measured accumulation capacitance value for both annealed and not-annealed Gd:HfO₂ capacitors is between 163 and 170 pF, which is consistent with the theoretical value (189.3 pF). In addition, the annealed sample C–V characteristic shows a voltage shift ΔV toward negative voltages, by approximately 1 V. This means



FIG. 6. Capacitance–voltage (C–V) curves for annealed and as-deposited TiN/ Gd:HfO₂/dry SiO₂ MOS capacitors on a p-Si substrate.

that the flatband voltage is different in both samples, which can be explained by the presence of remnant dielectric polarization (which causes the ferroelectric behavior of the annealed $Gd:HfO_2$ film³⁸).

Indeed, x-ray analysis showed that annealing at 650 $^\circ$ C leads to the crystallization of the otherwise amorphous as-deposited Gd-doped HfO₂ layer.

By attributing the observed voltage shift to a ferroelectric behavior, a remnant dielectric polarization 2 μ C/cm² was calculated, using the following equation: $P_r = \Delta Q/A$, where $\Delta Q = C_{HfO_2} \times \Delta V$ and *A* is the area of the capacitor device. This confirms the ferroelectricity of the annealed 11-nm thick Gd:HfO₂ layer.

IV. DISCUSSION

The results shown in Figs. 2–6 suggest that exposing the HfO_2 are layer to mechanical stress leads to its stabilization in the orthorhombic (ferroelectric) crystalline phase. In the case of the undoped HfO_2 layer, the analysis of these results shows that mechanical stress is mainly due to the bottom TiN electrode. Indeed, in the case of the TiN/HfO₂/SiO₂/Si(p) stack, Figs. 2 and 5(a) show, respectively, the absence of a significant amount of the HfO_2 o/t crystalline phase, and the absence of interplanar distance deformation between in-plane and out-of-plane diffraction geometries, i.e., the absence of mechanical stress.

In contrast, in the case of Gd-doped HfO_2 , the TiN/Gd:HfO₂/ SiO₂/Si(p) stack shows a strong o/t diffraction (Fig. 4) peak correlated to significant interplanar distance deformation between in-plane and out-of-plane diffraction geometries resulting from internal mechanical stress due to Gd-doping. In addition, the existence of the orthorhombic ferroelectric phase in Gd-doped HfO_2 is further evidenced by C–V characteristics analysis.

Our conclusion on the role of electrode-applied mechanical stress in stabilizing the HfO_2 orthorhombic ferroelectric phase is supported by several reports. For example, Nishimura *et al.*²² reported that the TiN interface serves as the nucleation site of the ferroelectric phase in HfO_2 . They found that as the grain size of HfO_2 increases with the thickness of the HfO_2 film, the non-ferroelectric monoclinic phase becomes more stable than the ferroelectric phase. This finding is consistent with our work, where the absence of a bottom TiN interface leads only to a very small

portion of the HfO₂ o/t GIXRD diffraction peak that vanishes for HfO₂ film thickness exceeding 7.6 nm. Additionally, Kim *et al.*³⁹ have emphasized that the undoped HfO₂ thin films could be crystallized in both o- and t-phases when they are sufficiently thin with small grain size, where the mechanical stress is more pronounced in thinner films. It diminishes as the film thickness increases.

Moreover, similar arguments regarding the influence of mechanical stress from the bottom layer have been made for epitaxially grown HZO^{40,41} and La:HfO2⁴² layers on single crystal substrates. Finally, using simulations, Fan *et al.*^{25,26} reported that HfO2 exhibits antiferroelectric properties under compressive strain conditions. However, when subjected to in-plane tensile strain, nonferroelectric HfO2 can undergo a transition into an out-of-plane polarized orthorhombic ferroelectric phase after being poled by a small out-of-plane electric field. Moreover, under a biaxial tensile strain, the ferroelectric orthorhombic phase becomes further stabilized under a compressive strain exceeding 3%.

V. CONCLUSION

This work brings experimental evidence of the role of mechanical stress in stabilizing HfO₂ ferroelectric behavior. The results showed that when the undoped HfO₂ layer is deposited on the SiO₂ substrate, i.e., without a bottom TiN electrode, the o/t crystalline phase is very weak and can be observed only for ultrathin [4.9-7.6] nm HfO₂ layers. In addition, upon increasing the thickness, a strong increase of the monoclinic phase is observed alongside a vanishing o/t weak x-ray diffraction peak. In contrast, Gd-doped HfO₂ deposited on the SiO₂ substrate show a strong o/t x-ray diffraction peak that increases linearly with thickness. These results are well supported by the analysis of atomic plane interplanar distance measurements that show a large deformation between in-plane and out-of-plane x-ray diffraction geometries, only in the case of Gd-doped HfO2. The expected ferroelectric properties of Gd:HfO2 layers due to the presence of an intense o/t x-ray diffraction peak were evidenced by capacitance-voltage characteristics for the annealed and not-annealed TiN/Gd:HfO2/SiO2/Si(p) MOS capacitors. The result shows that annealing leads to the MOS capacitor flatband voltage shift toward negative voltages by approximately 1 Volt, which can be attributed to remnant electric polarization of approximately $2 \mu C/cm^2$.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

M. M. Abdallah: Data curation (equal); Formal analysis (lead); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). E. V. Skopin: Data curation (equal); Formal analysis (equal); Methodology (equal); Supervision (equal); Writing – original draft (supporting); Writing – review & editing (equal). F. Fillot: Data curation (equal); Formal analysis (equal); Methodology (equal). D. Constantin: Methodology (equal).
M. Abusaa: Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (lead); Validation (equal); Writing – original draft (equal); Writing – review & editing (lead). A. Bsiesy: Data curation (lead); Formal analysis (lead); Funding acquisition (lead); Investigation (lead); Methodology (lead); Project administration (lead); Resources (lead); Supervision (lead); Validation (lead); Writing – original draft (equal); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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