O-23

Electric field-induced phase transformations in ferroelectric polycrystalline $Hf_{0.5}Zr_{0.5}O_2$ thin films

A. Chouprik[1], S. Zakharchenko[1], M. Spiridonov[1], S. Zarubin[1], A. Chernikova[1], R. Kirtaev[1], P. Buragohain[2], A. Gruverman[2,1], A. Zenkevich[1], D. Negrov[1]

[1]*Moscow Institute of Physics and Technology, 9 Institutskiy lane, Dolgoprudny, 141700, Russia*
e-mail: chouprik@gmail.com

[2]*Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588, USA*

Because of their full compatibility with the modern Si based technology, the HfO_2-based ferroelectric (FE) films have recently emerged as viable candidates for application in nonvolatile memory devices [1]. Both theoretical [2] and experimental [3-5] studies ascribe the ferroelectricity in polycrystalline HfO_2-based thin films to the presence of a metastable non-centrosymmetric orthorhombic (o) HfO_2 phase (space group $Pbc2_1$), which crystallizes during the annealing of doped HfO_2 thin films. Although it is well established that in the HfO_2-based FE films ac electric cycling of the FE capacitor (training process, also called “wake-up” effect) leads to the increase in the remnant polarization value [6], the origin of such effect as well as the exact mechanism of the polarization switching in this material are still not fully understood. In this work, we correlate the information on the local piezoresponse (domain maps) of the pristine versus trained $Hf_{0.5}Zr_{0.5}O_2$ (HZO) film with the structural properties revealed by the transmission electron microscopy to explain the origin of the wake-up effect in $Hf_{0.5}Zr_{0.5}O_2$ (HZO) film.

TiN (18 nm)/HZO (10 nm)/TiN (18 nm) capacitors were fully grown by the atomic layer deposition technique. Pulsed switching measurements of FE TiN/HZO/TiN capacitors were performed using PUND (Positive Up Negative Down) technique with triangular voltage sweeps. To wake-up pristine FE capacitors, the voltage was cycled 10^4 times by applying rectangular pulses with ±3 V amplitude and 100 μs duration with the pulse generator. P_r-V curves for trained capacitors derived from PUND data are shown in Figure 1g. The obtained remnant polarization was $2P_r \sim 35$ μC/cm^2.

The structural properties of HZO films in FE capacitors were investigated by high-resolution transmission electron microscopy (HRTEM). The selected-area electron diffraction patterns of pristine vs. trained TiN/HZO/TiN stack cross-sections evidence that the nonpolar monoclinic (m) phase is fully converted into polar o- and/or nonpolar tetragonal (t) phase following the electrical cycling.

Piezoresponse mapping of pristine TiN/HZO/TiN capacitor was performed by the resonance-enhanced mode of PFM. The amplitude map of as prepared polycrystalline $Hf_{0.5}Zr_{0.5}O_2$ reveals the mixture of both the grains of polar o-phase with high vertical projection of polarization vector and regions with low PFM amplitude associated with nonpolar m- and t-phases and misaligned o-phase film (Fig. 1b,c), which is consistent with TEM results.

Domain structure of the trained HZO film and its evolution following the applied switching pulses were visualized by the resonance-enhanced band-excitation (BE) PFM. To eliminate the effect of the top polycrystalline TiN electrode surface morphology (Fig. 1a) on the visible domain structure, piezoresponse maps were normalized by mechanical contact response maps obtained simultaneously by the BE atomic force acoustic microscopy [7]. Normalized BE PFM maps in Figure 1e,f,h,i do not contain any regions without piezoresponse. Local decreases in the piezoresponse signal on the fully polarized HZO film (Fig. 1e,h) can be associated with o-phase seeds with opposite polarization vector direction, horizontally oriented domains, antiferroelectric t-phase grains and passive m-phase grains less than 100 nm in size. When comparing these data with those for pristine structures (Fig. 1b,c), it is evident that during the wake-up process the amount of the non-ferroelectric phase is decreasing dramatically. Taking into account the TEM data, we conclude that during the wake-up of TiN/HZO/TiN capacitors, both m- and t-phases undergo almost complete phase transition to the ferroelectric o-phase.

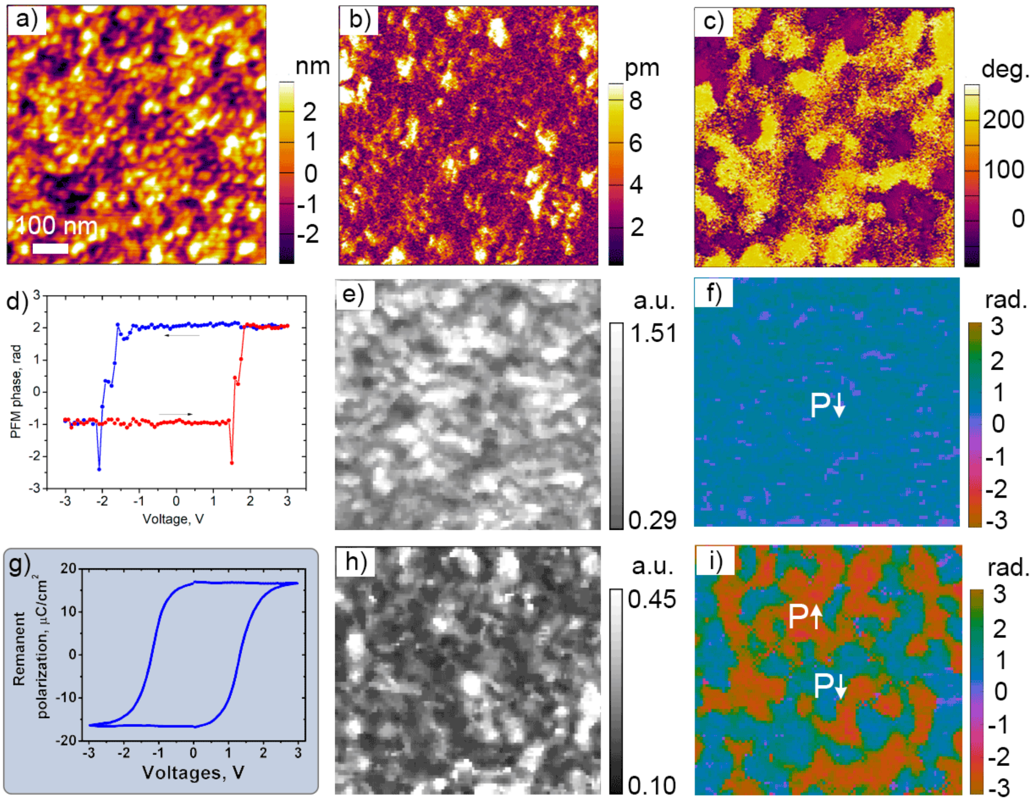

Figure 1. Static domain structure for pristine and trained HZO capacitors: (a) TiN surface morphology; PFM for pristine film (b) amplitude map, (c) phase map; (d) BE PFM phase hysteresis loop; BE PFM for trained film at the fully polarized state (-3 V) (e) amplitude map, (f) phase map; (g) P-V hysteresis curves derived from PUND measurements; BE PFM for trained film at the intermediate state (1.4 V) (h) amplitude map, (i) phase map.

Piezoresponse hysteresis loops measured by BE technique within the area subjected to the cycling confirm FE properties of the TiN/HZO/TiN structures (Fig. 1d).

Recently, using DFT calculations, Barabash et al. [8] have shown that the o →t→o phase transition in the HZO films can occur during each switching cycle. We do not see any regions without a relatively strong piezoresponse signal on the BE PFM/AFAM maps of the intermediate domain structures (Fig. 1e,f). Therefore, we consider that the switching process proceeds in a conventional way, i.e. like in other ferroelectrics the polarization reversal in the o-phase grains is due to the nucleation and growth of seeds with the opposite polarization. The o→t→o phase transition in the HZO films during each switching cycle is possible but cannot be detected if the intermediate t-phase is unstable in PFM excitation field.

In conclusion, the PFM results along with TEM analysis for the pristine vs. trained TiN/HZO/TiN FE capacitors indicate the electrically stimulated m→o phase transition during the wake-up process.

1. T.S. Boscke et al., *Appl. Phys. Lett.* **99**, 102903 (2011).
2. S. Clima et al., *Appl. Phys. Lett.* **104**, 092906 (2014).
3. D. Zhou et al., *Appl. Phys. Lett.* **103**, 192904 (2013).
4. M. Pešic et al., *Adv. Funct. Mater.* **26**, 4601 (2016).
5. D. Martin et al., *Adv. Mater.* **26**, 8198 (2014).
6. T. Schenk et al., *ACS Appl. Mater. Interfaces* **6**, 19744 (2014).
7. Chouprik et al. *ACS Appl. Mater. Interfaces* ***10***, 8818 (2018).
8. S.V. Barabash et al., *ECS Meeting Proceedings*, (2016).