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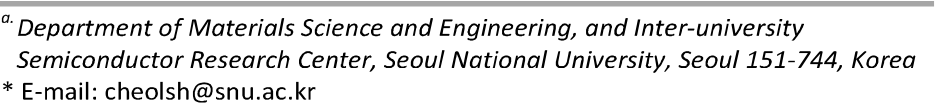
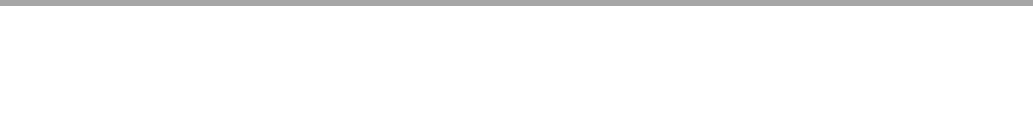
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| Published on 08 October 2015. Downloaded by University of Liverpool on 14/10/2015 03:25:32. | **ale Accepted Manuscript** |
| **Study on the wake-up effect of ferroelectric Hf0.5Zr0.5O2 films by** | | | | | |
| **pulse-switching measurement** | | | | | |
| Received 00th January 20xx, Accepted 00th January 20xx | | Han Joon Kim, Min Hyuk Park, Yu Jin Kim, Young Hwan Lee, Taehwan Moon, Keum Do Kim, Seung Dam Hyun, and Cheol Seong Hwang\* | | | |
| DOI: 10.1039/x0xx00000x | | | | | |
| The appearance of ferroelectric (FE) and anti-ferroelectric (AFE) properties in HfO2-based thin films is highly intriguing in | | | | | |
| **www.rsc.org/** | | terms of both scientific context and practical application in various electronic and energy-related devices. Interestingly, | | | |
| these materials showed a “wake-up effect”, which refers to the increase in remanent polarization with increasing electric | | | | | |
| field cycling number before the occurrence of fatigue effect. In this work, the wakeup effect from the Hf0.5Zr0.5O2 was | | | | | |
| carefully examined by the pulse-switching experiment. At the pristine state, the Hf0.5Zr0.5O2 film mostly showed the FE-like | | | | | |
| behavior with small contribution of AFE-like distortion, which could be ascribed to the involvement of AFE phase. The field | | | | | |
| cycling of only 100 cycles almost completely transformed the AFE phase into FE phase by depinning the pinned domains. | | | | | |
| The influence of field cycling on the interfacial layer was also examined through the pulse-switching experiments. | | | | | |
| respectively.12 The composition boundaries between these | | | | | |
| **Introduction** | | | | | different properties are not clear, which could be further |
| Since the first report on the emergence of (unexpected) ferroelectricity in a doped-HfO2 film in 2011,1 motivations for the deeper understanding of this phenomenon occurred2-6 and the active research in this field for its practical application to semiconductor and energy related devices has been triggered.7-9 It is now generally being accepted that the emergence of unexpected ferroelectricity in this material system is due to the formation of non-centrosymmetrical orthorhombic phase (o-phase) of which space group is Pca21. This phase is not thermodynamically stable at usual processing conditions (several hundred degree Celsius and near atmospheric pressure). The thin film fabrication processes, therefore, appear to induce various (asymmetric) stresses and grain size effects,10, 11 which stabilize the ferroelectric (FE) o-phase over the other phases, such as monoclinic (m-phase) or tetragonal (t-phase) phases.  HfO2–ZrO2 (HZO) solid solution system is one of the very promising FE materials due to its wide composition range (Hf:Zr ratio) and lower processing temperature (400 – 700 oC) for the emergence of these functional properties compared with other doped-HfO2, such as Si-doped HfO2, which requires precise control of Si concentration (~4%) and high processing temperature (~1000oC). Even more interesting aspect of HZO material is that it shows wide range of electrical properties (and crystal structure too) depending on Hf:Zr ratio; when it is ~0.9:0.1, ~0.5:0.5, and ~0.1:0.9, the film showed dielectric, | | | | | modified by detailed processing conditions.  Recovering the usual dielectric property with increasing Hf concentration in HZO film is understandable considering the well-known high-k dielectric property of HfO2. However, emergence of AFE property in Zr-rich composition and unclear composition boundary with the mostly FE-like 0.5:0.5 HZO impose a certain conceptual difficulty on the understanding of the origin of these unexpected FE-AFE behaviors in this material system. This difficulty is becoming even worse when identifying the fact that the microstructures of HZO films showing feasible FE or AFE properties are not single crystalline or even a single phase; they generally have small grain size |
|  | with random orientation and often contain non-FE or non-AFE |  |
|  | phases. These factors hinder the straightforward application of several theoretical works based on the first-principles calculation. The involvement of so called “wake-up” effect in many of these films add more difficulties since the FE and AFE properties vary with the number of FE or AFE switching cycles. It has been reported that the FE properties of many doped-HfO2 thin films, including Hf0.5Zr0.5O2 film, became more evident as the cycle number increases, before they eventually become frustrated due to the fatigue effect.13-16 This suggests that some of the FE domains are pinned by defects or traps within the film or at the electrodes interface, which are typically TiN, at a pristine state, and repeated electrical cycles make the domains unpinned.  In this work, the authors systematically examined the FE property change with electrical cycling (wake-up effect) using | **Nanosc** |
| ferroelectric, | and | anti-ferroelectric | (AFE) | properties, |

standard polarization-electric field (P-E) hysteresis curve

measurements and pulse-switching (PS) technique. The former

is useful to examine the evolution of FE – AFE properties with

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increasing cycling number while the latter can gives the detailed quantitative information on the evolution of HZO/TiN contact property, coercive field (Ec), and possibly involved interfacial capacitance (Ci).

In general, the involvement of Ci is more complicated to understand. The presence of Ci in FE thin films has been identified in many experiments,17-20 and is now quite well understood for standard FE materials with an epitaxial structure, such as SrRuO3/BaTiO3/SrRuO3, based on the

respectively. The cross-sectional images of HZO film were obtained by high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL). The focused ion beam (Helios 650, NanoLab) in the NCIRF of Seoul National University was used to prepare the sample for HRTEM analysis. The crystal structure of the HZO films was analyzed using an X-ray diffractometer (X’pert Pro, Panalytical) via grazing-angle incidence X-ray diffraction (GIXRD, incidence angle=0.5°). For electrical characterization, the polarization - electric field (P-E)

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| on 08 October 2015. Downloaded by University of Liverpool on 14/10/2015 03:25:32. | imperfect interfacial charge screening model using atomic | characteristics were measured using a ferroelectric tester (TF | **Accepted Manuscript** |
| scale simulations.21 However, it is quite evident that such | Analyzer 2000, Aixacct Systems) in virtual mode. Triangular |
| standard approach can hardly be applicable in polycrystalline | bipolar pulses with a 1 kHz frequency were applied to the TE |
| microstructure with relative random orientation of the FE | with the BE grounded. The dielectric constant-electric field (εr- |
| grains, which would be the case for TiN/HZO/TiN. It has to be | E) characteristics were measured using an impedance analyzer |
| noted that such small grain size with relatively random | (4194A, Hewlett-Packard, at the AC bias frequency of 10 kHz |
| orientations is the prerequisite for achieving FE and AFE | and amplitude of 50 mV). For the pulse switching |
| properties, otherwise they will regain the stable m-phase with | measurements, rectangular positive or negative pulses with a |
| well-known high-k property. The possible involvement of | pulse width of 10µs and rising/falling time of 2ns, were |
| physical interfacial layer by the oxidation of TiN, i. e. TiOx (x ~ | supplied by a pulse generator (81110A, Agilent) with an |
| 2), cannot be completely disregarded although its formation | internal resistance of 50 Ω. The switching current response |
| must be highly suppressed in well-performing HfO2-based FE | from the HZO film was monitored using an oscilloscope |
| (TDS684Dm Tektronix) with an internal resistance of 50 Ω. |
| films. In addition, the involvement of intrinsic low-k layer at |
| the interface due to the incomplete screening of FE bound | **Results and discussion** |
| charges by the free carriers in TiN must be considered to |
| correctly interpret the electrical properties. Nevertheless, the |
| comprehensive understanding in this field is still lacking, | Figure 1 (a) shows the cross-sectional TEM image of the |
| especially in conjunction with the wake-up effect. Therefore, in | Pt/TiN/Hf0.5Zr0.5O2/TiN capacitor on a SiO2/Si substrate. The |
| this work, pulse switching technique, which is useful to | deposition of uniform and flat HZO films with clean interfaces |
| examine the evolution of various physical parameters with the | could be confirmed. From the HRTEM image shown in figure 1 |
| switching cycles, in addition to the standard polarization – | (b), the polycrystalline nature of HZO films could be confirmed |
| electric field technique, was adopted. The evolutions of | from the lattice fringes with different directions in different |
| physical interface properties are discussed in detail in | areas. The crystal structure of the HZO films might be o-phase, |
| conjunction with the depinning of the pinned domains and the | which were examined via fast Fourier transformation of the |
| possible field-induced phase transition between the FE and | lattice fringes. However, it was challenging to clearly |
|  |
| hed | AFE phases. | distinguish the o-phase from t-phase (d-spacing value of o- |  |
| Publis | **Experimental** | phase (111) plane and t-phase (101) plane are 2.94 and 2.97 Å, | **Nanoscale** |
| respectively) due to their structural similarity. Figure 1 (c) |
| shows the GIXRD spectra in 2θ range of 25°-50° for the |
| The 9nm-thick HZO films were deposited on a 50-nm-thick TiN | Hf0.5Zr0.5O2 film. The diffraction peaks from the (111), and |
| bottom electrode (BE) formed on a SiO2/Si substrate via | (200) planes of the o-phase (or t-phase) HZO could be clearly |
| thermal ALD at a substrate temperature of 280 oC using | observed in the diffraction patterns. According to the Joint |
| Hf[N(C2H5)CH3]4 (TEMAH), Zr[N(C2H5)CH3]4 (TEMAZ), and ozone | Committee on Powder Diffraction Standards, 2θ of the (111) |
| (170 g/cm3) as the precursor of Hf, Zr, and oxygen source, | plane of the o-phase and (101) plane of the t-phase are 30.35° |
| respectively. The TiN BE was deposited via DC reactive | and 30.09°, respectively, indicating the challenge for making |
| sputtering. The growth per cycle of HfO2 and ZrO2 was almost | clear identification of GIXRD peaks. Similar difficulty is |
| identical (~0.12 nm/cycle), so the HZO films with a 0.5:0.5 | encountered when identifying the peak near 2θ value of ~36°. |
| Hf:Zr ratio could be deposited using a 1:1 HfO2:ZrO2 ALD cycle | Therefore, the diffraction peaks near 2θ values of ~31° and 36° |
| ratio. | are assigned to be the mixture of o-phase (111) and t-phase |

For electrical characterization, a Pt(30nm-thickness)/TiN(5nm-thickness) top electrode (TE) was deposited via DC sputtering through a shadow mask with a 400 µm hole diameter (TiN

(101), and o-phase (200) and t-phase (110), respectively. In fact, the coexistence of these two phases has important implication for the electrical characteristics of the films as

contacted the HZO film). After the TE deposition, post- discussed below.

metallization-annealing was performed for 30 seconds at 500 oC in a N2 atmosphere using rapid thermal annealing for the film crystallization. The composition and the film thickness of the HZO films were examined via X-ray fluorescence (Quant’X, Thermo SCIENTIFIC) and ellipsometry (L-116d, Gaertner),

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Figures 2 (a) shows the change in the P-E hysteresis loops with an increase in the number of electrical switching cycles of the Hf0.5Zr0.5O2. For these experiments, the film samples were field-cycled using the pulse generator with a field strength of ±3.8 MV/cm and 10µs duration, and the P-E hysteresis loops

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were obtained by an FE tester after the intended number of cycling was performed. When the Hf0.5Zr0.5O2 film is in the pristine state, shape of the P-E hysteresis loop was slanted including bumps especially in the left portion of the curve, which might be induced by the inclusion of charged defects, non-FE phase, and AFE-like phase. However, after the cycling by only 102 times, the film showed an almost complete FE-like P-E curves, and further increase in the cycle number makes the

increases during the wake-up process. In addition, the peaks of dielectric constant near Ec decrease with increasing number of switching cycles. Although the low-frequency dielectric constants of the FE-phase HZO along the parallel and perpendicular direction to the Pr direction have not been solidified yet, experimental and theoretical results for the conventional FE material, such as BaTiO3 and Pb(Zr,Ti)O3 (PZT), reasonably illustrate that the dielectric constant is lower along

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| oaded by University of Liverpool on 14/10/2015 03:25:32. | P-E curve more square-like, i. e. FE-property improved. Inset | the Pr-direction.25, 26 Therefore, the εr-E characteristics of the | | **d Manuscript** |
| figure shows the increase in the 2Pr value with increasing the | film with increasing cycle number correspond to the εr-E | |
| cycle number. It can be understood that the 2Pr of the | characteristics of typical FE materials with field cycling, | |
| Hf0.5Zr0.5O2 film increased from 30.2 µC/cm2 at the pristine | meaning that the obtained Hf0.5Zr0.5O2 film was mostly FE, and | |
| state to 43.4 µC/cm2 after the 105 cycles. 2Pr of > ~40 µC/cm2 | it becomes more uniformly “poled” along the field direction | |
| has not been reported for the HZO film yet, and is a highly | during the cycling. | |
| promising value for FE memory application. Such increase in | The change in FE domain switching kinetics with cycling is | |
| 2Pr and general disappearance of the AFE-like distortions in | further examined by adopting the PS experiments as shown in | |
| the P-E curves with increasing the cycle number indicate the | Figs. 3. For this experiment, the films were pre-poled to the | |
| followings could have occurred. The pristine film appears to | opposite direction to the switching pulse direction and domain | |
| have pinned domains, indicated by the smaller 2Pr value, some | switching current (Isw) was estimated as a function of time with | |
| of which are anti-parallel with each other, thereby induces the | different magnitude of applied field, for the differently cycled | |
| AFE-like distortions of the P-E loop. These domain pinning | films. | |
| could be induced by the presence of charged point defects | Figure 3 (a) shows the schematic diagram for pulse application | |
| such as oxygen vacancies, or even non-FE phases such as t- | with time. For these experiments, 10µs pulses were adopted, | |
| phase Hf0.5Zr0.5O2.22 Therefore, the field cycling is believed to | which is long enough to induce sufficient FE switching even at | |
| induce the depinning the pinned domains, combined with the | the lowest field (2.2MV/cm). The switching charges for both | |
| local phase transition from non-FE phase to FE phase. It has | negative to positive switching (up → down) and positive to | |
| negative (down → up) switching were estimated for different | |
| wnl | been identified from the careful fitting of the GIXRD patterns |  |
| Published on 08 October 2015. Do | that field cycled Hf0.5Zr0.5O2 which apparently is FE-like still | electrical cycling numbers. Figures 3 (b) - (d) show the | | **Nanoscale Accepte** |
| switching current transient for the pristine, after cycling for | |
| contains non-negligible t-phase. Confirming the possible |
| transition of some of the non-FE phase, t-phase, into FE o- | 102 and 105 times, respectively. According to the polarization | |
| phase during the field cycling by an in-situ type experiment, | reversal theory in FE film mediated by the reverse domain | |
| such as focused X-ray analysis using synchrotron source on | nucleation and growth, of which detailed functional form can | |
| field cycling device would be an interesting topic for future | be varied depending on the specific circumstance (Komogolov- | |
| research. This work provides an indirect proof for the change | Avrami-Ishibashi kinetic model or nucleation limited switching | |
| of the non-FE phases into FE phase by the field cycling using | model), the Isw can be described by Eq. (1) at a given electric | |
| the pulse switching technique as shown later. |
| field. | |
| Figure 2 (b) shows the εr-E characteristics with different | ������ = ���� � | ����� ���� ��� ≤ � ≤ ���� (1) |
| number of electrical switching cycles within the same film. It |
| shows the butterfly-like feature, a typical characteristic of FE |
| materials, at the pristine state. The εr value of the film over the | , where t0, tsw, RL, and Ci are the time when ferroelectric film | |
| ~2 MV/cm electrical field where the FE switching effect is |
| excluded, was ~33.0 when the film was at the pristine state, |
| starts switching, the time when the switching process is | |
| and it gradually decreased with electrical switching cycles. | completed, the total resistance of measurement circuit and | |
| Finally, the εr value reached to ~30.5 at the 105 cycles. From |
| sample, and the interfacial capacitance, respectively. The RL is | |
| the changes in P-E and εr-E characteristics during electrical |
| the summation of the internal resistance of pulse/pattern | |
| switching cycles, it could be conjectured that the phase | generator (RW) and digital oscilloscope (RO), parasitic | |
| transition from t- to o-phase had occurred. Lomenzo et al. and | resistance (RP), and contact resistance (RC). The summation of | |
| Park et al. also suggested the phase transformation from t- to | RW, RO and RP is estimated to be ~104 Ω in this experiment. | |
| o-phase based on the simultaneous increase in Pr and decrease |
| This representation basically assumes that the FE capacitor has | |
| in εr during field cycling in Si-doped HfO2 thin film23 and HZO |
| a non-FE interfacial capacitance (Ci) which is invariant during | |
| thin film.24 Also, the intersection points of the butterfly curve |
| the field application time, so capacitive charging current flows | |
| are shifted toward the positive bias with increasing switching | with a time constant, RLCi, while a constant switching current | |
| cycles, which implies that the internal field of the HZO film |
| flows into the FE layer during the switching time period. This | |
| increases simultaneously. It has been reported that the | means that the FE layer itself behaves like a resistor during the | |
| distribution of oxygen vacancies within the HZO film could be | FE switching.27 Therefore, if there is no interfacial capacitance | |
| affected by the pulsed wake-up cycling.16 As the internal field |
| involved (Ci ~ ∞) a constant Isw must be achieved during | |
| is significantly related with charged defects, the internal field |
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| switching, which is generally not the case. The observed Isw vs. | which is connected on circuit in parallel, for the future |
| time curves at different field in Figs. 3 (b) - (d) show an abrupt | calculations. |

increase in current at the beginning of pulse application, which corresponds to the capacitive charging of overall capacitor structure, followed by a rapid decrease in Isw with time as the charging completes. At t = t0, indicated by the black arrow within the figures, which is the time when the film starts switching, Isw(t) aligns with Eq. (1) and follows the linear behavior of the semi-log plot (dotted lines). According to Eq.

Figures 5 (a) and (b) show the summary of the estimated variation of Ci, Ec and Rc for positive-to-negative and negative-to-positive PS, respectively, as a function of cycle number. Rc does not show any notable variations suggesting that the electrical contact between the TiN electrode and HZO film does not vary with field cycling. However, Ec shows clear increase from ~0.8 MV/cm at pristine state to ~0.95 MV/cm

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| 5 03:25:32. | (1), the I0 sw, which is the current at the moment when FE | | | | after 105 cycles with increasing cycle number. These values are |  |
| generally smaller than the value estimated from the P-E |
| switching starts, is given as Eq. (2). | | | |
| ���� | = | ��������� | (2) | hysteresis curves in Fig. 2 (a), where the +Ec and –Ec are ~1.2 |
| MV/cm and ~0.9 MV/cm. This is because the voltage drop |
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| across the series components (RL and Ci) is involved when |
| , where Ea is an applied field and tf is a thickness of the film. | | | | obtaining the Ec from the P-E curves. |
| The increase in Ec with cycle number indicates that the |
| following critical change has occurred in the FE property of the |
| This means that at the moment of the FE film switching, Ec, a | | | |
| film. If the field cycling merely induces the depinning of the |
| portion of Ea, is applied to the FE layer while the rest portion of | | | |
| pinned domains while the amount of the FE domains |
| the Ea is applied over RL. Therefore, for different cycling | | | |
| exhibiting FE performance remains invariant, Ec should have |
| conditions, RL and Ec can be calculated from the slope and the | | | |
| been decreased. Therefore, the increase in Ec suggests that the |
| intercept of abscissa by taking I0 sw at each Ea and plotting the | | | |
| amount of actively contributing FE domains with slightly higher |
| value as a function of Ea (Figs. 3 (e) - (g)). Since RL value is | | | |
| local Ec values actually increases with cycle number. This is |
| achieved from Eq. (2), Ci can also be calculated from the slopes | | | |
| consistent with the increase in the 2Pr values with the cycle |
| of the fitting graphs of Isw at each Ea (dashed lines in Figs. 3 (e) | | | |
| number, and also consistent with the idea that some of the |
| - (g)), which showed a common value at different Ea’s for the | | | |
| originally non-FE phases in the pristine film could be changed |
| given cycle number. It has to be noted that the calculated Ec | | | |
| into the FE phase by the sufficiently high field cycling. The Ec of |
| value corresponds to the genuine coercive field value of the FE | | | |
| such transformed FE phase could be slightly higher than that of |
| layer without involving any additional term that could be | | | |
| induced from the series resistance and Ci, which is not how Ec | | | | the originally FE phase. |
| Change in Ci is also consistent with the idea of changing the |
| is obtained from the P-E hysteresis loops. | | | |
| non-FE phase into the FE phase with cycling. While the |
| From the integration of Isw with time, the 2Pr value can be | | | |
| accurate nature of the Ci, generally estimated from such PS |
| estimated as a function of time, where the charges due to the | | | |
| reversible capacitive charging are excluded by including the | | | | measurements, is not very well understood yet, it might be |
| closely related with the presence of an interfacial dielectric |
| discharging peak at the moment of pulse termination into the | | | |
| layer and/or an intrinsic dead-layer. Although it is an indirect |
| current integration. Figure 4 (a) summarizes the results for | | | |
| method to characterize the Ci parameters of the non-FE parts |
| negative to positive switching (open symbols) and positive to | | | |
| negative switching (closed symbols). While the former shows a | | | | from the whole measurement circuit which includes FE parts, |
| this method can be feasibly used for identifying the nanoscale |
| generally slightly higher switching charge, possibly due to the | | | |
| changes within the FE thin films. It has been reported that the |
| involvement of a small imprint effect, both data show a | | | |
| common trend with increasing cycle number. At the pristine | | | | critical nuclei size of a few nm level could be examined during |
| the initial stage of polarization switching using similar PS |
| state, the film shows a quite gradual switching, i. e. 2Pr varies | | | |
| technique, signifying the usefulness of this technique to |
| over a wide field region, with the smallest saturation 2Pr value. | | | |
| evaluate the nanoscale structural change.27 Since the dielectric |
| With increasing cycle number, the switching became more and | | | |
| more abrupt with higher saturation 2Pr value, which is in | | | | constants of the FE HZO and the non-FE HZO phases are not |
| very much different (~30 for o-phase and ~35-40 for t-phase), |
| accordance with the results in figure 2 (a). | | | |
| compared with the cases involving the conventional FE |
| To confirm the reliability of the PS technique, change in the Ci | | | |
| material, such as PZT, the large increase in Ci value during the |
| as a function of a cell area at the pristine film is plotted in Fig. | | | |
| cycling (from ~19 µF/cm2 at pristine state to ~62 µF/cm2 after |
| 4 (b). As the data points, although not sufficiently many, are | | | |
| 105 cycles) may correspond to the decrease in the thickness of |
| fitted well with a straight line, it is believed that the PS | | | |
| the interfacial non-FE phase. Since there are two interfaces |
| technique gives reliable results. The intercept at the y-axis of | | | |
| the fitted line corresponds to the parasitic capacitance of the | | | | that contribute to the estimated Ci, the actual capacitance of |
| one interface must be twice the estimated values (38 – 124 |
| PS measurement system, which was ~ 2.2 nF. The parasitic | | | |
| µF/cm2). It must be reasonable to assume that these non-FE |
| capacitance is induced by the probe station, pulse generator | | | |
| and oscilloscope in the experimental set-up. Hence, Ci is | | | | phases are present mostly at the interface region with the |
| electrodes. At this region, after the nucleation stage when the |
| subtracted by the value (~ 2.2 nF) of the parasitic capacitance, | | | |
| film grows, the phase transition from t-phase (non-FE phase) |

to the o-phase is restricted due to surface energy effect. It can

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be concluded that the field cycling changes the interfacial non-FE phases into FE phase. This is consistent with the idea of increasing the FE domain volume with slightly higher Ec

approximate the change in Cnon-FE when the Cint,top and Cint,btm are assumed to be identical and not affected by the wake-up effect, which is a reasonable assumption. When the dielectric

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| mentioned | above. | As | can | be | understood | from | the | constant of the non-FE layer was taken as 40 (t-phase), an |

continuously increasing 2Pr value with increasing cycle number up to 105 in Figure 4 (a), there could be further increase in the FE performance at even higher cycle number. However, further increase in cycle number induced the fatigue effect and was excluded from the data. Hence, it is believed that there is

approximate thickness decrease of 1.1 nm was calculated for two interfaces by the 105 electrical switching cycles. This can be a negligible value in conventional FE capacitor, where the FE thickness is usually higher than ~100nm. However, in this HZO case, the total film thickness is only 9 nm, which means

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| Published on 08 October 2015. Downloaded by University of Liverpool on 14/10/2015 03:25:32. | not much room left for further improvement from the | | | | | | | | | | that ~ 12% of the whole thickness was non-FE phase at the | **Nanoscale Accepted Manuscript** |
| maximum value of Ci at 105 cycles. It can be understood that | | | | | | | | | | pristine state. Considering that the 2Pr value increased from |
| the low Ci value at low cycle number is due to the involvement | | | | | | | | | | ~30µC/cm2 to ~43 µC/cm2 after 105 cycles (in P-E |
| of both physical non-FE phase at the interface and intrinsic | | | | | | | | | | characteristics), which corresponds to ~43% increase from the |
| dead-layer effect. While the capacitance of intrinsic dead-layer | | | | | | | | | | initial value, the ~12% transition from the t-phase into the o- |
| in TiN/HZO interface has not been estimated yet, values for | | | | | | | | | | phase during the cycling cannot solely explain the 2Pr |
| the idealized perovskite/metal interfaces, such as PbTiO3/Pt | | | | | | | | | | enhancement. Therefore, it is believed that there was |
| and PbTiO3/SrRuO3, can be referenced to qualitatively | | | | | | | | | | significant contribution from the depinning of the pinned FE |
| estimate Ci values. They were calculated to be ~79 µF/cm2 and | | | | | | | | | | domains during the wake-up cycling. It might be possible that |
| ~58 µF/cm2, respectively, for one interface from the first | | | | | | | | | | the domain pinning of the original FE phase (o-phase) has been |
| principles | calculation.21 | | The | | relatively | | low | | electrical | caused by the presence of the non-FE phase (t-phase). The |
| conductivity (lower carrier concentration) of an oxide | | | | | | | | | | field cycling may induce the transition from the t-phase to o- |
| electrode (SrRuO3) compared with pure metal (Pt) generally | | | | | | | | | | phase and eliminate the pinning effect, which enable the FE |
| induced less efficient screening of the polarization charge of | | | | | | | | | | domains to switch more efficiently. |
| the ferroelectric or dielectrics layer in contact, and thus, the Ci | | | | | | | | | | **Conclusions** |
| value is lower. Because TiN has a resistivity (~220 µΩcm) | | | | | | | | | |
| closer to that of SrRuO3 (~100 – 200 µΩcm) than Pt (~10 | | | | | | | | | |
| µΩcm), electrode polarization must be rather significant, | | | | | | | | | | In conclusion, the wake-up behaviors of Hf0.5Zr0.5O2 with |
| which would render the smaller Ci. Therefore, the estimated | | | | | | | | | | increasing electric field cycling number were examined by the |
| 124 µF/cm2 (per one HZO/TiN interface) after the 105 cycling | | | | | | | | | | P-E hysteresis loop, εr-E curves, and pulse switching tests. |
| appears quite unusual, because this value must have come | | | | | | | | | | Hf0.5Zr0.5O2 film shows mostly the FE-like behavior from the |
| from two contributions, if any, from both electrode | | | | | | | | | | pristine state, where the slight AFE-like distortion could be |
| polarization and interfacial dielectric layer. Nevertheless, a | | | | | | | | | | ascribed to the anti-parallel distribution of some of the FE |
| specific form of BaTiO3/Pt interface (Ba – Pt bond formation) is | | | | | | | | | | domains and the AFE phase. The field cycling of only 100 cycles |
| reported to have an interfacial capacitance density as high as | | | | | | | | | |
| almost completely removed such anti-parallel pinned domains. |
| ~2,700 µF/cm2 implying the validity of having a Ci value > | | | | | | | | | |
| Further increase in the field cycling number more effectively |
| 100µF/cm2.21 In fact, Kim et al. and Jiang et al. also performed | | | | | | | | | | poled the domains making the Pr largely increase. The field |
| similar PS measurement on the Pt/PZT/Pt capacitor28 and | | | | | | | | | |
| cycling also transformed the non-FE phases, mostly at the |
| Pt/Al2O3/PZT/Ir capacitor.29 They acquired similar 2Ci value of | | | | | | | | | |
| electrode interface, to FE-phase, which could be inferred from |
| ~160 µF/cm2 | and | ~130 µF/cm2, | | | | respectively. | | | Further |
| the increase in the interfacial capacitance. These results |
| theoretical work is necessary in this field. | | | | | | | | | | indicate that the physical state of the FE-phases in the HZO |
| According to the above mentioned model, the Ci | | | | | | | | -1, which is the | |
| film is quite different from the conventional FE thin films, such |
| inverse interfacial capacitance, is given as Eq. (3). | | | | | | | | | |
| as PZT, in a sense that it is the outcome of variously oriented |
| � ��= | | � ����,���+ | | � �������+ | | � ����,���(3) | | | | domains, possibly including anti-parallel orientation. The field |
| cycling plays a role as the poling in conventional FE materials, |
| but the high field-induced non-FE t-phase to FE o-phase |
| transition could also contribute to the effective poling |

, where Cint,top and Cint,btm are intrinsic dead-layer capacitance at the top and bottom interface, respectively, and Cnon-FE is a

(depinning of pinned FE domains).

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| physical non-FE phase capacitance. It should be noted that the Cint,top and the Cint,btm are intrinsic values of the electrode, | **Acknowledgements** |

which must be remained invariant during the field cycling. The contribution from charged defects at the interfaces is linked with the Cnon-FE. Because Cint,top and Cint,btm are not known for TiN, Cnon-FE cannot be calculated from the estimated Ci values at pristine state and after 105 cycles. Nevertheless, the difference between the two estimated values can be used to

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| **Figure 1.** (a) Cross-sectional low magnitude transmission |
| electron microscope image and (b) Cross-sectional high |
| resolution transmission electron microscopy image of the | **Figure 2.** (a) Polarization - electrical field hysteresis and (b) |
| Pt/TiN/Hf0.5Zr0.5O2/TiN structure. (c) Grazing incidence X-ray | Dielectric constant - electrical field characteristics of the 9nm- |
| diffraction pattern of the Hf0.5Zr0.5O2 films. | thick Hf0.5Zr0.5O2 film with an increase in the number of electrical |
| switching cycles, respectively. |
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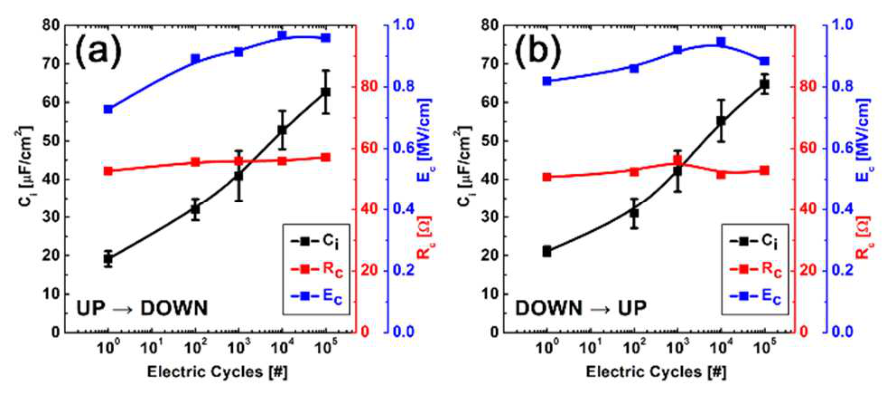
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|  | **Figure 4.** (a) Double remanent polarization - electric field curves measured by pulse-switching technique. (b) The change in the interfacial capacitance as function of cell area at the pristine state of the Hf0.5Zr0.5O2 film. |
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| **Figure 3.** (a) The schematic diagram for pulse application with | |
| time. The domain switching current transient - time curves of | |
| the Hf0.5Zr0.5O2 film with various applied electrical fields, (b) at  the pristine state, (c) after the 102 electrical switching cycles and  (d) after the 105 electrical switching cycles, respectively. The | |
| initial domain switching current as a function of the electric field | |
| and extracted genuine coercive field and resistance of the same  film, (e) at the pristine state, (f) after the 102 electrical switching  cycles and (g) after the 105 electrical switching cycles, | |
| respectively. | |
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| Published on 08 October 2015. Downloaded by University of Liverpool on 14/10/2015 03:25:32. | **Figure 5.** Summary of the estimated variation of interfacial | *Nanoscale*, 2013, **00**, 1-3 | **9** | **Nanoscale Accepted Manuscript** |
| capacitance, coercive field, and contact resistance for (a) |
| positive-to-negative and (b) negative-to-positive pulse-switching |
| measurement, respectively. |
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