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**Grain size engineering for ferroelectric Hf0.5Zr0.5O2 films by an insertion of Al2O3**

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[Grain size engineering for ferroelectric Hf0.5Zr0.5O2 films by an insertion of Al2O3 interlayer](http://dx.doi.org/10.1063/1.4902072)

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The degradation of ferroelectric (FE) properties of atomic layer deposited Hf0.5Zr0.5O2 films with increasing thickness was mitigated by inserting 1 nm-thick Al2O3 interlayer at middle position of the thickness of the FE film. The large Pr of 10 lC/cm2, which is 11 times larger than that of single layer Hf0.5Zr0.5O2 film with equivalent thickness, was achieved from the films as thick as 40 nm. The Al2O3 interlayer could interrupt the continual growth of Hf0.5Zr0.5O2 films, and the resulting decrease of grain size prevented the formation of non-ferroelectric monoclinic phase. The Al2O3 interlayer also largely decreased the leakage current of the Hf0.5Zr0.5O2 films. V 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4902072>]

Recently, it was reported that HfO2 can show ferroelec-tric (FE) properties when doped with various dopants such as Zr, Si, Y, Al, Gd, La, and Sr.1–7Compared to the conven-tional ferroelectrics based on perovskite or layered perov-skite structure, such as Pb(Zr,Ti)O3 and SrBi2Ta2O9, the FE HfO2-based films showed quite distinctive physical and elec-trical properties. The HfO2-based films can be extremely thin (film thickness, tf < 10 nm) with feasible ferroelectricity (remanent polarization, Pr � 10–40 lC/cm2), whereas the much thicker thicknesses (tf > 100 nm) are required for the stable FE properties of conventional ferroelectrics thin films, especially with the metal-ferroelectric-metal (MFM) config-uration.8–10Due to their small thickness, the HfO2-based films are considered promising for the three-dimensional ca-pacitor structure which is highly required for the future ferro-electric random-access-memory (FeRAM) device according to International Technology Roadmap for Semiconductors.11 This results from the relatively large bandgap (Eg � 5.5 eV),12,13high compatibility with Si, and matured atomic layer deposition (ALD) technique of HfO2-based films. In fact, due to their high Si-compatibility, the non-FE HfO2 thin film has been used as the buffer layer in ferroelec-tric field-effect-transistor (FeFET) to solve the interfacial problems of conventional ferroelectrics and Si substrate.14 Furthermore, the authors recently reported that the feasible FE performance of Hf0.5Zr0.5O2 (HZO) films could be main-tained after the hydrogen annealing at temperatures as high as 600�C due to the absence of weak metal-oxygen bonding such as Pb-O.15   
 It is generally accepted that the ferroelectricity within

the general growth mechanism for the most of dielectric film growth on metal substrate, as in this work. In addition, suffi-ciently small grain size is required to prevent the formation of the stable monoclinic phase (m-phase, space group: P21/c). The small grain size is accompanied with the high surface to volume ratio, and the smaller surface energy of the tetrago-nal phase (t-phase, space group: P42/nmc) induced the for-mation of t-phase when the nuclei size is smaller than the critical value (�26 nm for Hf0.5Zr0.5O2). During the initial stage of film growth, nuclei of t-phase were formed on the bottom electrode layer and they transformed into the o-phase at the moment of zipping occurs, which is accompanied with the asymmetric strain that was necessary to induce the un-usual phase transition.16   
 The feasible ferroelectricity (Pr > 20 lC/cm2) with extremely small tf (<10 nm) is considered highly promising for various applications. In contrast, such a small tf can be a critical barrier for exploring the physics behind the unex-pected FE phenomenon, including domain dynamics and structural analysis. However, it was already reported that the ferroelectricity of HZO thin films is significantly degraded when the thickness of the thin films increases over 20 nm,18 which was also observed in Si-doped HfO2 films.19The rea-son for the degradation is that the FE o-phase transforms into non-FE m-phase with the increasing film thickness which must be accompanied with the grain growth (increase in grain size) for polycrystalline HfO2-based FE thin films.20,21 Thus, it is highly required to suppress the formation of the m-phase by independently controlling the grain size of HZO films to achieve the feasible ferroelectricity in films thicker

these materials originates from the formation of non- than 20 nm.

centrosymmetric Pca21 (Pbc21 in some references) ortho-rhombic phase (o-phase), which is not a stable phase under the usual temperature and pressure conditions. The authors suggested that this unusual FE phase can be formed due to the huge tensile stress ascribed to the island coalescence pro-cess of Volmer-Webber-type thin film growth,16,17which is

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In ZrO2/Al2O3/ZrO2 stack system, which has been widely used as high-k dielectric layer in capacitors for

dynamic random access memory, the Al2O3 interlayer can reduce the grain size of the adjacent ZrO2 layers by interrupt-ing continuous grain growth of the ZrO2 layer.22When the physical and chemical similarities of ZrO2 and HZO are con-sidered, the Al2O3 interlayer is also expected to effectively control the grain size and produce polymorphism with the

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layered structure of HZO/Al2O3/HZO (HZAHZ). In this study, therefore, the stacked HZAHZ film with various HZO layer thicknesses was prepared, and the physical and FE properties of HZAHZ system were compared to those of sin-gle layer HZO films. It was observed that the transformation into the m-phase resulting from grain growth could be effec-tively suppressed by inserting a 1 nm-thick Al2O3 layer between HZO layers. Moreover, it could be confirmed that the HZO layers on and under the Al2O3 interlayer had differ-ent crystallographic orientations via high resolution trans-mission electron microscopy (HRTEM). As a result, the ferroelectricity (Pr � 11.4 lC/cm2) of HZAHZ film was not degraded with increasing total thickness up to �40 nm. The HZO films were deposited on a 50 nm-thick TiN bottom electrode (BE) formed on SiO2/Si substrate via ther-mal ALD at a 280�C substrate temperature using Hf[N(C2H5)CH3]4 (TEMAH), Zr[N(C2H5)CH3]4 (TEMAZ), Al2[CH3]6 (TMA), and ozone (170 g/cm3) as the precursor of Hf, Zr, Al, and oxygen source, respectively. The TiN BE was deposited via DC reactive sputtering. The growth per cycle of HfO2 and ZrO2 were almost identical (�0.12 nm/ cycle), so the HZO films with a 0.5:0.5 Hf:Zr ratio could be deposited using a 1:1 HfO2:ZrO2 ALD cycle ratio. 1 nm-thick Al2O3 layers were inserted between adjacent HZO layers having various tf. Totally, 20, 30, and 40 nm-thick HZAHZ films with the Al2O3 interlayer were prepared, where the 1 nm-thick Al2O3 layer located at the center posi-tion of the film thickness. For comparison, the HZO films without the Al2O3 interlayer were also deposited under the identical conditions.

For electrical characterization, a Pt(30 nm)/TiN(5 nm) top electrode (TE) was deposited via DC sputtering through a shadow mask with a 300 lm hole diameter (TiN contacted the HZO film). After the TE deposition, post-metallization-annealing was performed for 30 s at 500�C in a N2 atmosphere using rapid thermal annealing, for the films’crystallization. The composition and tf of the HZO films were examined via X-ray fluorescence (Quant’X, Thermo SCIENTIFIC) and ellipsometry (L-116d, Gaetner), respec-tively. The cross-sectional images of HZO film were obtained by HRTEM (JEM-3000F, JEOL) and 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 ¼ 0.5�). The grain size of HZO films was calculated from in-plane image of scanning electron microscope (SEM, S-4800, Hitachi). For electrical characterization, the polarization-electric field (P-E) charac-teristics were measured using a ferroelectric tester (TF Analyzer 2000, Aixacct Systems) at a 1 kHz frequency and current density-electric field (J-E) characteristics were meas-ured using pA meter/DC voltage source (HP 4140D, Hewlett Packard). An endurance test was performed using a ferro-electric tester (TF Analyzer 2000, Aixacct Systems) with 2.5 MV/cm electric field and 100 kHz electrical cycling fre-quency. For the transient switching current analysis, the pulse/pattern generator (81110A, Agilent) and digital oscil-loscope (TDS684c, Tektronix) were used.

Figure 1(a) shows the cross-sectional TEM image of the Pt/TiN/HZO/Al2O3/HZO/TiN structure, confirming the uni-form and flat HZO films with clean interfaces. The 1 nm-thick Al2O3 interlayer was well deposited between adjacent top and bottom 15 nm-thick HZO layers, clearly separating them. The HZO films consist of many separate grains, which are well crystallized, of which average vertical and lateral grain sizes are �15 and �30 nm, respectively. It is believed that the vertical grain growth of the bottom HZO film was in-terrupted by the Al2O3 interlayer, and the grain size of HZO films would have been increased with the increasing tf if there was no Al2O3 interlayer.23As mentioned in the intro-ductory part, the polymorphism of HZO films are strongly influenced by their microstructure, so the structural proper-ties of HZO and HZAHZ films were examined via GIXRD. Figures 1(b) and 1(c) show the GIXRD spectra in the 2h range of 25�–65�for the HZO and HZAHZ films having var-ious thicknesses, respectively. The diffraction peaks from the (111), (200), and (220) planes of the o-phase HZO could be clearly observed in the diffraction patterns. In fact, it is very challenging to unambiguously assign those peaks to only o-phase because of its structural similarity to t-phase.

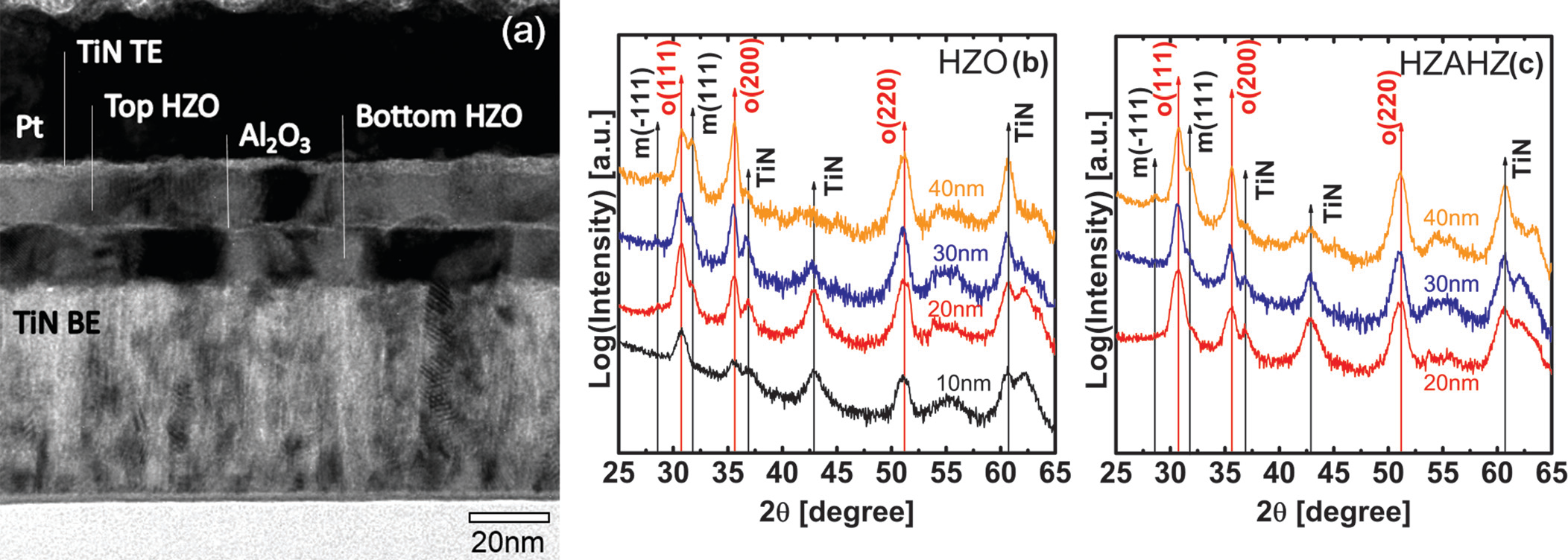


FIG. 1. (a) Cross-sectional transmission electron microscope image of the Pt/TiN/Hf0.5Zr0.5O2/Al2O3/Hf0.5Zr0.5O2/TiN structure. Grazing incidence X-ray dif-fraction pattern of (b) the Hf0.5Zr0.5O2 films and (c) the Hf0.5Zr0.5O2/Al2O3/Hf0.5Zr0.5O2 films with various thicknesses.

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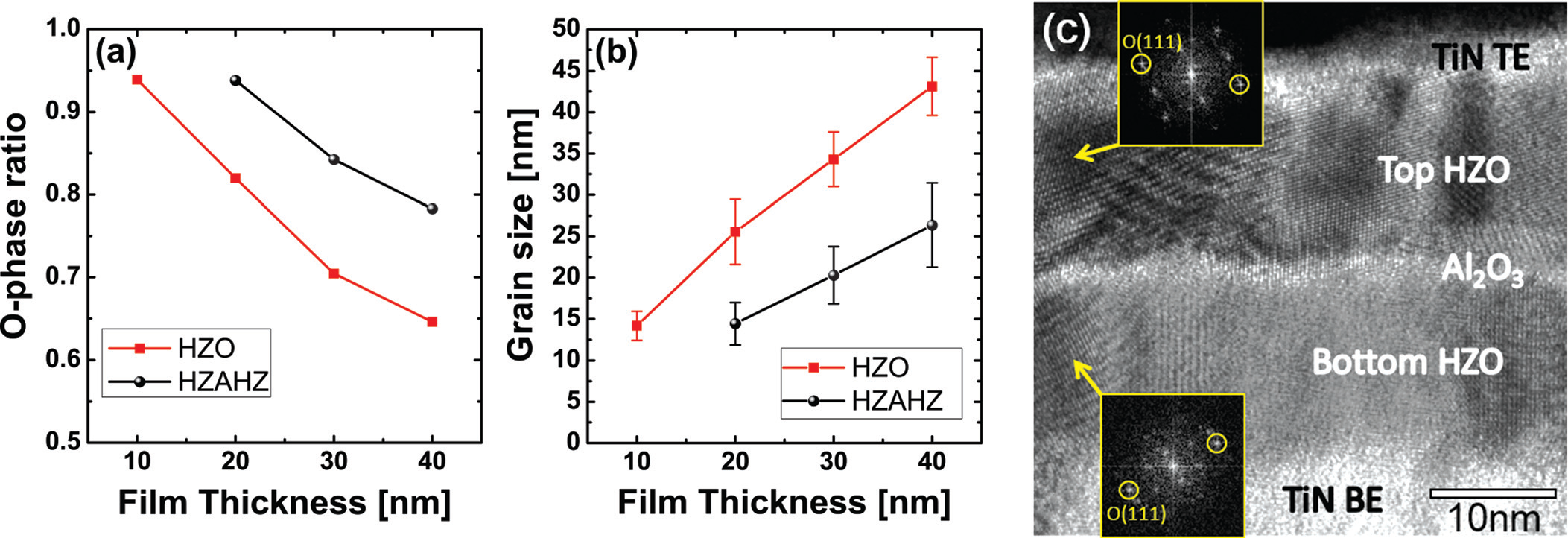


FIG. 2. (a) Variations in the relative ratio of the o(111)/{o(111) þ m(111)}, and (b) those in the average grain size (with error bars whose magnitudes refer to

the standard deviation of the average grain sizes from measurements) of Hf0.5Zr0.5O2 films and Hf0.5Zr0.5O2/Al2O3/Hf0.5Zr0.5O2 films. (c) Cross-sectional high

resolution transmission electron microscopy image of the 30 nm-thick Hf0.5Zr0.5O2/Al2O3/Hf0.5Zr0.5O2 film. Two in-set figures are fast Fourier transformation

image at the Hf0.5Zr0.5O2 layers on and under the Al2O3 interlayer.

The peaks assigned to (111), (200), and (220) planes of o-phase could be actually a signature of mixed o- and t-phases ((101), (110), and (200) planes of t-phase). Therefore, this must be taken as the indication that m-phase formation was suppressed. The more notable difference in the GIXRD pat-terns of the HZO and HZAHZ films could be identified from the enhanced and suppressed, respectively, increase in the It could be readily understood that the increase in the inten-(111) peak (m(111) peak) intensity of m-phase (2h ¼ 31.7�). sity of this peak with the increasing tf is quite largely sup-pressed for the case of HZAHZ compared with the HZO.

This could be more quantitatively understood in Fig. 2(a).

Figure 2(a) shows the variations in the relative ratio of the area of o(111)/{o(111) þ m(111)}, which were estimated from the 2h range of 27�–33�of GIXRD, where the diffrac-tion peaks of m(111) and o(111) are clearly distinguished, for the HZO and HZAHZ films as a function of their total tf. o(111) indicates the 111 diffraction peak from the o-phase (111) plane. The details of the quantitative analysis of the o-phase portion were reported elsewhere.24The relative ratio o(111) diffraction peak in HZO film was �94% when the tf was �10 nm, and it decreased to �82%, �70%, and �64% when tf increased to �20, �30, and �40 nm, respectively. On the other hand, the relative ratio of o(111) diffraction peak of HZAHZ film was �94% when the tf was 20 nm, and decreased to �84%, and �78% when tf increased to �30, and �40 nm, respectively, which are generally larger than that without the interlayer at similar tf. Next, the average grain size (Davg) of the two types of the films was examined from the plan-view SEM images. Figure 2(b) shows the vari-ation in the Davg of the HZO and HZAHZ films as function of tf. The Davg of the HZO films was �14.2 nm at the tf of�10 nm, and increased to �25.5, �34.3, and �43.1 nm when tf increased to �20, �30, and �40 nm, respectively. In contrast, Davg of the HZAHZ films was �14.4 nm at the tf of�20 nm, and increased to only �20.3, and �26.4 nm when tf increased to �30, and �40 nm, respectively. This suggests that the Al2O3 interlayer interrupts the continuous grain growth of bottom HZO films as shown in Figure 1(a), and

the Davg of HZAHZ films could be remained at small values that could suppress the transition to the stable m-phase.25 Next, the relative crystallographic orientations of the top and bottom HZO grains in HZAHZ films were examined by HRTEM and fast-Fourier transformation (FFT) of the lattice image to confirm that the physically separated grains are real crystallographically separate entity. Figure 2(c) shows the polycrystalline nature of the top and bottom HZO layers HRTEM image of the �30 nm-thick FE HZAHZ film. The could be confirmed from the lattice fringes with different ori-entations in the figure. Two inset figures are FFT image of top (upper inset) and bottom (bottom inset) HZO layers of the portion of HRTEM image indicated by arrows. The FFT patterns generally match with the o-phase, and the diffrac-tion spots from (111)-planes of the o-phase are marked by yellow circles in both FFT images. The o(111) d-spacing val-ues calculated from those spots were 2.93 and 2.94 A˚ , respectively, which are similar values achieved from the GIXRD in this work and previous studies.3,25–28The direc-tions of diffraction spots from two FFT images are signifi-cantly different from each other, suggesting that two grains in the top and bottom portions of the film had different crys-tallographic orientations although they are of commonly o-phase. This reveals that the insertion of 1 nm-thick Al2O3 layer effectively suppressed the continuous growth of the polycrystalline HZO grains and accompanying transition to the m-phase at total film thicknesses �20 nm. Next, the FE properties of these films are reported.

Figures 3(a) and 3(b) show the P-E hysteresis loops of the HZO and HZAHZ films, respectively, with different tf values. The P-E hysteresis loops from the initial measure-ment were presented, since the P-E characteristics of HZAHZ films were degraded during electric field cycling, which would be discussed in more detail in the later part of this letter and supplementary material. For the case of HZO films, the thinnest film (10 nm) shows a 2Pr value of 30.7 lC/cm2, but it decreased to almost negligible value (�2.1 lC/cm2) at a tf of 40 nm, which is comparable to the previous report.18This is believed to be due to the fast transition of

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| 192903-4 | Kim et al. | Appl. Phys. Lett. 105, 192903 (2014) | | |
|  | | FIG. | 3. Polarization-electric | field |
| curves of (a) the Hf0.5Zr0.5O2 films and | | |
| (b) | Hf0.5Zr0.5O2/Al2O3/Hf0.5Zr0.5O2 | |
| films with various thicknesses. | | |

the phase of the HZO film from the FE o-phase (thinner film) to non-FE m-phase (thicker film). In contrast, the HZAHZ film maintained the reasonably high 2Pr value (�22.7 lC/ cm2) up to the total thickness of 40 nm, thanks to the sup-pression of the grain growth and accompanying transition to m-phase. Surprisingly, 2Pr values of the 40 and 20 nm-thick HZAHZ film (22.7 and 31.5 lC/cm2) were almost equivalent with those of 20 and 10 nm-thick HZO films (20.6 and 30.7 lC/cm2). This means that the upper and lower HZO layers in HZAHZ films involves almost identical FE performances for the given thickness. However, the coercive field (Ec) of the HZAHZ film is generally higher than that of HZO film (0.98 MV/cm vs. 1.37 MV/cm). If two identical FE films simply stacked without any other adverse effects, their Ec must be invariant. Such increase in the Ec could be understood from the role of the thin Al2O3 layer as the tunneling barrier.29To further confirm the differences in the P-E hysteresis curves of HZO and HZAHZ capacitors, the transient switching cur-rents of the samples were also analyzed. The details of method and results of transient switching current analysis are included in the supplementary material.25The saturated 2Pr and Ec values from P-E hysteresis curve were also verified by pulse switching measurement, which were consistent with that from P-E hysteresis measurements. The role of Al2O3 layer as a series resistor during ferroelectric switching could be clearly confirmed by transient switching current analysis. The total resistance (RL) and interfacial capacitance (Ci) of Al2O3 interlayer can be calculated from the linear region of ln(switching current)–time curves, and the effect of Al2O3

paraelectric layer, the P-E hysteresis loop must become more with slanted shape and Pr should have been decreased. Therefore, the electrical role of Al2O3 in the HZAHZ stacked film is a series resistor, which increases the apparent Ec.29 One of the problems in the electrical performances of the HZO films is their exceptionally high Ec (�1 MV/cm) which is higher than that of conventional FE materials by almost one order of magnitude. This requires application electric field with a magnitude of several MV/cm to observe fully saturated P-E hysteresis loops, which is generally too severe to safely measure the reliability the HZO FE films, such as fatigue resistance. In fact, the authors reported a fa-tigue test results of several HZO films recently,30but the genuine fatigue property could not be accurately estimated due to the involvement of sudden dielectric break down after certain number of switching cycles, although initial fatigue performance was quite impressive. Both HZO and HZAHZ samples could endure up to �106cycles with the pulse height of 2.5 MV/cm and frequency of 100 kHz. However, the Pr of HZAHZ films further decreased with increasing number of field cycling compared to that of HZO films. It is believed that Al2O3 interlayer can make charge trap sites in HZO layer, which degraded the endurance of HZAHZ films. (See the supplementary material.) However, the 106cycle of field cycling might not be an intrinsic endurance limitation of HZAHZ capacitor, which could be improved by optimiz-ing fabrication process. Therefore, suppressing the leakage current is another critical issue for the HZO film for both the property estimation and stable operation of the integrated FE

layer on RL and Ci could be examined by comparing those of devices.

10 nm-thick HZO and 20 nm-thick HZAHZ films. From the analysis, calculated RL of 20 nm-thick HZAHZ film was larger than that of 10 nm-thick HZO film by �18 X, which is similar to the resistance of 1 nm-thick Al2O3 film in the pre-vious report (�15 X).29However, Ci values of 10 nm-thick HZO film and 20 nm-thick HZAHZ film are �33 nF and�32 nF, respectively. Since these values are much larger than the theoretical capacitance of 1 nm-thick Al2O3 (�8 nF with er of 9), the Al2O3 layer did not work as a series capaci-tor. Thus, these results suggest that the Al2O3 interlayer works as a series resistor during domain switching, not as a dielectric layer. The thinness of the Al2O3 layer allows fluent carrier transport across the layer, which does not interfere with the polarization of the HZAHZ film across the entire film thickness. If the Al2O3 layer played role as an insulating

Figures 4(a) and 4(b) show the J–E curves of the HZO and HZAHZ films with the various tf values. While the J level of the thicker (>30 nm) HZO films were low enough up to 2 MV/cm for both bias polarities that of the thinner HZO film was largely degraded due to the involvement of possible defects and surface roughness. However, for the HZAHZ films, the J level is highly low with almost no change with the film thickness. It is notable that the J level of 20 nm-thick HZAHZ film is lower than that of single layer HZO layer with the identical thickness by several orders of magnitude over wide field region. As aforementioned, this is not due to the insulating property of the thin Al2O3 layer since it plays a role as the series resistor via the probable involvement of tunneling mechanism. The interruption of straight grain boundaries across the film thickness, which

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| 192903-5 | Kim et al. | Appl. Phys. Lett. 105, 192903 (2014)  FIG. 4. The current density-electric  field curves of (a) the Hf0.5Zr0.5O2 | | | | | |
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| films | and | (b) | Hf0.5Zr0.5O2/Al2O3/ | | |
| Hf0.5Zr0.5O2 | | films | | with | various |
| thicknesses. | | | | | |

could play a role as the local leakage current path,31could be critical reason for such improvement in the J-E performance. Further details for the leakage current conduction mecha-nism and evaluation of the reliability performance based on this improvement will be reported in subsequent works.

In conclusion, the problem of degrading ferroelectric performance of the HZO films with increasing tf, which

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| could | be | ascribed | to | the | increased | portion | of | non- |

ferroelectric m-phase at higher tf could be resolved by inter-posing the Al2O3 interlayer at the middle position of HZO film. The Al2O3 interlayer interrupted the continuous grain growth HZO film, which was accompanied with the decrease in the average grain size. Therefore, the higher portion of ferroelectric o-phase could be retained up to the film thick-ness of 40 nm. The two portions of the HZO films at upper and lower position appear to have identical ferroelectric per-formances even though the lower portion was grown on TiN BE, while the upper portion was grown on the inserted thin Al2O3 layer. This implies that the repetition of even higher number of stacking might be possible without degrading the ferroelectric performance, which is under investigation. The insertion of thin Al2O3 layer was also highly effective to largely decrease the leakage current, which will greatly facil-itate the stable operation of integrated device as well as the precise evaluation of the reliability of this ferroelectric layer.

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