Japanese Journal of Applied Physics

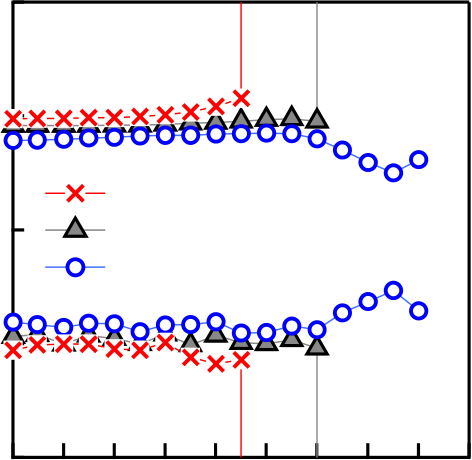


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Polarization switching behavior of Hf–Zr–O ferroelectric ultrathin films studied through coercive field characteristics

To cite this article: Shinji Migita *et al* 2018 *Jpn. J. Appl. Phys.***57** 04FB01

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| Japanese Journal of Applied Physics 57, 04FB01 (2018) | REGULAR PAPER | |
| <https://doi.org/10.7567/JJAP.57.04FB01>  Polarization switching behavior of Hf–Zr–O ferroelectric ultrathin films studied | |  |

through coercive field characteristics

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Received October 10, 2017; revised November 27, 2017; accepted December 20, 2017; published online March 5, 2018

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| The electrical properties of ferroelectric Hf–Zr–O ultrathin films, particularly the dependences of remnant polarization, leakage current, coercive |

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| field, and breakdown field on the metal composition and film thickness, are systematically examined. Physical analyses show that the Hf–Zr–O |

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| films in this experiment consist of polycrystalline grains and contain both ferroelectric and dielectric phases. It is found that changes in metal |

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| composition and thickness strongly influence the remnant polarization and the leakage current simultaneously. In contrast, the coercive field was |

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| relatively unaffected by these parameters. This particular behavior of the coercive field suggests that the polarization switching in Hf–Zr–O films is |

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| predominantly determined by the nature of nanometer-scale ferroelectric domains dispersed in the films. |

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| ©2018 The Japan Society of Applied Physics | | (a) | 2) | 40  20  0  -20  -40 |  | | | | | | 2 10 | 2) |
| 1. | Introduction |
| Since the first report of ferroelectricity in Si-doped HfO2 | |
| 0 10 |
| crystalline films, ferroelectric HfO2 films have been reported using many types of dopants, such as Si,1–6)Zr,6–10) | |
| Polarization (µC/cm |
| -2 10 |
| Current (A/cm |
| -4 10 |
| Y,4–6,11–13)Al,4–6,14)Gd,4,15,16)Sr,5,17)La,18,19)Sc,6)Ge,6) | |
| and N.6,20)Nondoped HfO2 films also show ferroelectricity when an appropriate amount of oxygen deficiency is | | -6 10 |
| -8 10 |
| introduced.12,21–23)It is widely recognized that the ferroelec- | |
| -10 10 |
| tricity in HfO2 is attainable in a particular range of dopant concentrations, and its spontaneous polarization is induced | |
| -12 10 |
| -4 | -2 | 0 | | 2 | 4 |
| by the displacement of oxygen ions in the noncenter | |
| V (V) | | | | | | |
| symmetric orthorhombic phase crystal.1,4,5)The ferroelec- | |
| tricity of HfO2 films is maximized in ultrathin films of around 10 nm thickness. Crystallization of HfO2 films begins at low annealing temperatures of around 400 °C,11)and the ferro- | | (b) | 2) | 40 | | | | | | |
| 20 | | | | | | |
| electric property is stable after annealing at 1000 °C.2,3) | |
| Currently, ultrathin HfO2 films are attainable by atomic layer deposition (ALD) and are already utilized as the major gate | |
| *P*r (µC/cm | 3.0 V | | | | | | |
| 0 | | 2.5 V | | | | |
| stack material for advanced metal–oxide–semiconductor field-effect transistors (MOSFETs) in largely integrated | | 2.0 V | | | | | | |
| -20 | | | | | | |
| circuits (LSIs). Developments in the fabrication of non- | |
| volatile memories using ferroelectric HfO2 films are therefore expected to be made in ferroelectric random access memories | | -40   0 10 | | 2 10 | 10 | 4 | 6 10 | 8  10 |
| (FeRAMs),24,25)ferroelectric gate-FETs (FeFETs),24,26–30) | |
| Pulse cycle | | | | | | |
| and ferroelectric tunneling junctions (FTJs).31,32) | |

There is a concern that the coercive field (EC) is close to the breakdown field (EBD) in ferroelectric HfO2 films.33,34) Figure 1 shows an example of the electrical properties of

10-nm-thick Hf0.5Zr0.5O2 capacitors, the fabrication process and measurement conditions of which are described in the

following section. A well-defined hysteresis behavior that

originates from the ferroelectric switching is observable from

the polarization–voltage (P–V) measurements in Fig. 1(a). The ferroelectricity almost saturates at swing voltages larger

than 2 V. The remnant polarization (Pr) under the saturated condition is about 20 µC=cm2. Using the polarity changes at

Fig. 1. (Color online) (a) P–V and I–V characteristics of 10-nm-thick Hf0.5Zr0.5O2 capacitors. I–V curves were measured using other devices on the same wafer. (b) Endurance characteristics of 10-nm-thick Hf0.62Zr0.38O2 capacitors. Swing voltages are ±2.0, 2.5, and 3.0 V.

attention must be paid to the maximum electric field in order to avoid breakdown. This becomes more problematic when the endurance of Hf–Zr–O capacitors is evaluated [Fig. 1(b)]. The endurance evaluations at peak voltages of 3.0 and 2.5 V resulted in a hard breakdown at less than 105and 106cycles, respectively. The endurance barely reaches 108cycles when

about ±1 V, EC is calculated to be 1 MV=cm. These values the peak voltage is 2.0 V. At peak voltages of less than 2.0 V,

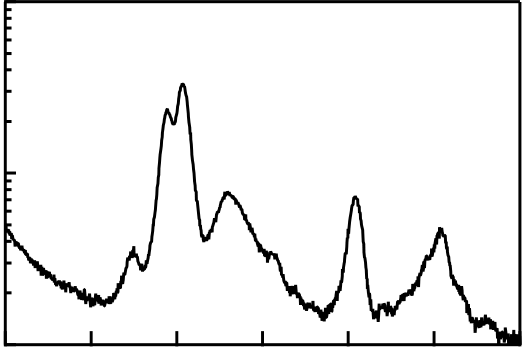
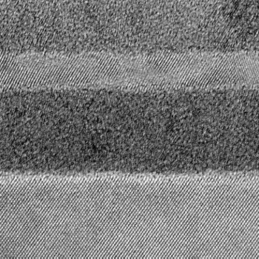
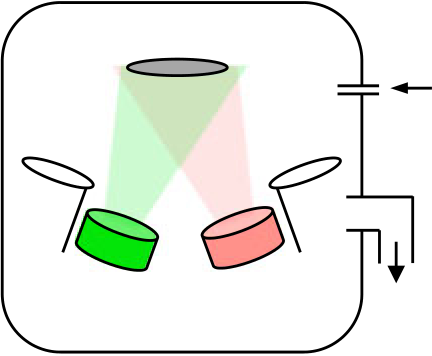
are consistent with those of other reports.6–10)In the current–voltage (I–V) measurement, however, a large leakage current is notable and a hard breakdown occurs at around ±4 V, that the memory window of Pr became very poor. Note that even

the best endurance so far achieved in ferroelectric HfO2

capacitors is 1010cycles.4,24)This value is low when

is, 4 MV=cm. In the operation of Hf–Zr–O capacitors, compared with the endurance of 1013cycles reported with

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| Jpn. J. Appl. Phys. 57, 04FB01 (2018) | | | | | |  |  |  |  | S. Migita et al. | | | | | | |
| (a) | | Si substrate | | Ar gas | | (a) |  |  |  | **TaN** | | | | | | |
| Shutter | | | | | | **Hf0.5Zr0.5O2** | | | | | | |
| HfO2 | | | | ZrO2 | Vacuum  pump |
| **TaN** | | | | | | |
| RF sputtering sources | | | | | **10 nm** | | | | **Si** | | |
| (b) | | Shutter open | | | |
| HfO2  ZrO2 | | |  | | | (b) | 10 | 4 | 4 | -111m | | 111o  020o 200m  200o | | 220o 220m  022o | -302m | |
| Intensity (cps) |
| Cycle | | | | Time | | 10 | 3 | 2 |
| 110o 011m | |
| 311o | |
| Fig. 2. | (Color online) (a) Schematic of sputtering system for the | | | | | 2 | 4 | -211m  112o | |
| deposition of Hf–Zr–O films. (b) Shuttering program for the control of metal composition in Hf–Zr–O films. For the deposition of Hf-rich film, the shutter of HfO2 was open continuously, while that of ZrO2 was frequently closed. | | | | | |
| 2 |
| 10 | 10 | 20 | 30 | | 40 | 50 | 60 | 70 |
| The cycle of open=close was repeated during the deposition of the 0.5-nm- | | | | | |
| thick film in order to maintain a uniform composition through the thickness. | | | | | |
| 2theta (degree) | | | | | | |

Pb(Zr,Ti)O3.35)Therefore, ferroelectric HfO2 films require improvement that can be achieved through the detailed understanding of switching behavior.

the viewpoints of the coercive field36,37)and leakage We have been studying ferroelectric Hf–Zr–O films from

current.38)In this work, we systematically investigate these electrical properties and discuss the polarization switching behavior of Hf–Zr–O films. The remnant polarization, which is a measure of the ferroelectric phase in the film, changes with the metal composition and film thickness. Increasing remnant polarization accompanies increasing leakage current. In contrast, the coercive field is relatively unaffected by the metal composition and film thickness. On the basis of these results, we discuss the possibility that the polariza-tion switching behavior of Hf–Zr–O films is governed by the nanometer-scale ferroelectric domains dispersed in the

Fig. 3. (Color online) (a) Cross-sectional TEM image of TaN (10 nm)=

Hf0.5Zr0.5O2 (4.1 nm)=TaN (10 nm) stack deposited on Si substrate and annealed at 700 °C. (b) Diffraction pattern of Hf0.5Zr0.5O2 (10 nm)=   
TaN (10 nm)=Si sample measured by GIXRD. The sample was annealed at

600 °C. Diffraction peaks are indexed by monoclinic and orthorhombic

phases.

firmed by X-ray photoelectron spectroscopy. The metal composition in this work is expressed as the Zr content in the

formula of Zr=(Hf + Zr) (%). After the deposition of TaN= Hf–Zr–O=TaN stacked layers on Si substrates, the samples were annealed in the RTA system in vacuum (<1 Pa) at 600 and 700 °C. This is the “Cap-anneal” technique that we developed for the crystallization of metastable HfO2 phases with higher dielectric constant.39–41)After the deposition of thick aluminum layers on top of TaN films in another sputtering tool, capacitors of 100 × 100 µm2were fabricated

matrix. by lithography and dry etching.

2. Experimental procedure

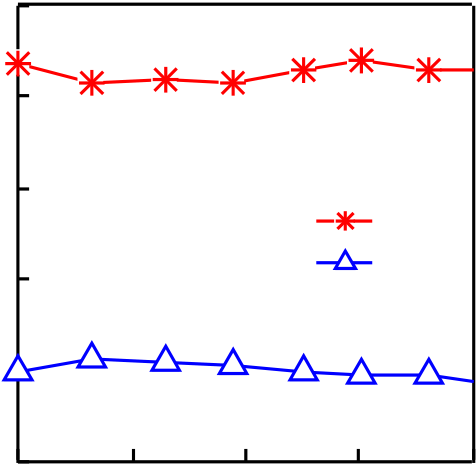
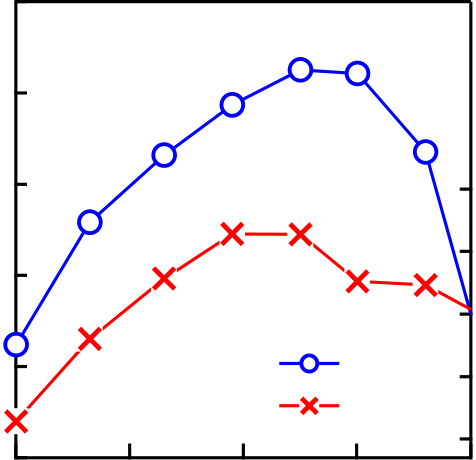
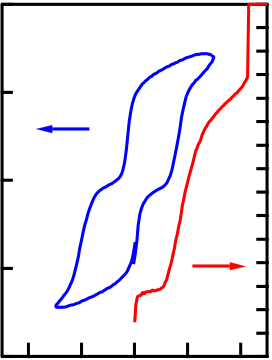
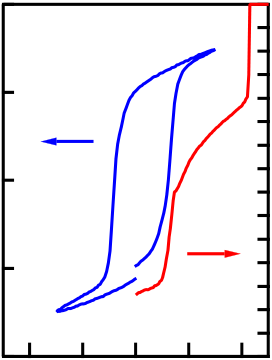
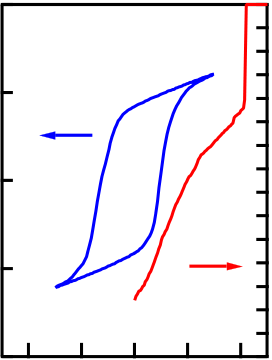
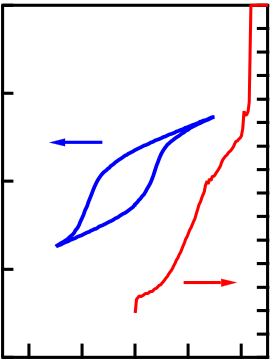
Stacked layers of metal and ferroelectric films in this experiment were fabricated in a cluster tool, which is equipped with a DC sputtering chamber, an RF sputtering chamber, a rapid thermal anneal (RTA) chamber, and a vacuum load lock. Heavily doped n-type Si wafers were cleaned with dilute HF solution and used as substrates. TaN electrode films were deposited in the DC sputtering chamber using an Ar=N2 gas mixture and a Ta metal target. The thickness of the TaN films was set to 10 nm. Hf–Zr–O films were deposited in the RF sputtering system [Fig. 2(a)] using Ar gas and HfO2 and ZrO2 targets. Metal composition was controlled by sputtering both targets simultaneously and frequently closing the mechanical shutters [Fig. 2(b)]. The shuttering cycle was set to be less than the deposition time of 0.5 nm (about 10 s), which corresponds to the unit cell size of the HfO2 crystal. In this manner, a uniform metal composition of the Hf–Zr–O films over a range of the thicknesses is obtained. The metal composition was con-

The electrical properties of capacitors were measured at room temperature. The P–V characteristics were measured using the TOYO FCE system at 1 kHz. The endurance properties in Fig. 1(b) were measured at 100 kHz. The I–V characteristics were measured using Agilent 4156C. Apart from the endurance properties, P–V and I–V characteristics were evaluated at under the initial conditions of capacitors without the wake-up treatment.

3. Results and discussion

A high-magnification cross-sectional transmission electron microscope (TEM) image of the TaN=Hf0.5Zr0.5O2=TaN stack prepared on a Si substrate and annealed at 700 °C is shown in Fig. 3(a). The 4.1-nm-thick Hf0.5Zr0.5O2 film is completely crystallized, while both the top and bottom TaN films remain in amorphous phase after annealing. The interface roughness is small and the thickness of the Hf0.5Zr0.5O2 film is uniform. The crystalline grains of the 4.1-nm-thick Hf0.5Zr0.5O2 film have a plate-like shape. Their heights correspond with the film thickness, and the in-plane

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| Jpn. J. Appl. Phys. 57, 04FB01 (2018) |  | 40 | Zr 0 %, | | | | | |  |  | 3 | | |  | 40 | S. Migita et al. | | | | | | | | |
| grain sizes estimated using a low-magnification TEM image | (a) | 4 | 10 | (b)  ) | Zr 26 %, | | | 10 | | | 3 | | |
| are about 50 nm (not shown). This in-plane grain size |
| prepared by sputtering in this experiment appear to be larger | 2 | | 10 nm | | | | | | 10 10 10 10 | 0 | 2) | | 2 | | 10 nm | | | 10 | | | 0 | 2) | |
| Polarization (µC/cm   20  0  -20 | | Polarization (µC/cm   20  0  -20 | |
| than those obtained by ALD.42)Additionally, we analyzed a | -3  -6  -9 | Current (A/cm | | -3  -6  -9 | | Current (A/cm |
| 10 | | |
| cross-sectional TEM image of the 40-nm-thick Hf0.5Zr0.5O2 |
| film prepared by the same process (not shown). This image | 10 | | |
| confirmed that the height of grains corresponds with the film |
| 10 | | |
| thickness in most cases while a few grains have smaller |
| height than the film thickness. In contrast, the in-plane grain | -40 | | -4 | -2 | 0 | | 2 | | 10 | -12 | | | -40 | | -4 | -2 | 0 | 2 | 4 | 10 | -12 | | |
| size of the 40-nm-thick Hf0.5Zr0.5O2 film is as small as 10 nm, smaller than that in the case of the 4.1-nm-thick film. The |
| (c) | 40 | Voltage (V) | | | | | | 4 | 10 | 3 | | | (d) | 40 | Voltage (V) | | | | | | | | |
| Zr 72 %, | | | 10 | | | 3 | | |
| crystal shape seems to become columnar with increasing film | Zr 50 %, | | | | | |
| thickness. |
| 2) | | 2) | |
| 10 nm | | | | | | 10 10 10 10 | 0 | 2) | | 10 nm | | | 10 | | | 0 | 2) | |
| The crystalline structure of the 10-nm-thick Hf0.5Zr0.5O2 | Polarization (µC/cm   20  0  -20 | | Polarization (µC/cm   20  0  -20 | |
| -3  -6  -9 | | Current (A/cm | -3  -6  -9 | | Current (A/cm |
| film was analyzed by grazing incident X-ray diffraction | 10 | | |
| (GIXRD), using Rigaku Smart Lab with 45 kV and 200 mA |
| 10 | | |
| at 0.45° grazing angle. This sample was prepared on a TaN= |
| -4 | -2 | | 0 | | 2 |
| Si substrate without the deposition of a top TaN film and | 10 | | |
| annealed at 600 °C. The result shown in Fig. 3(b) indicates |
| 10 | -12 | | | -4 | -2 | 0 | 2 | 4 | 10 | -12 | | |
| -40 | | -40 | |
| that the film consists of several phases such as orthorhombic |
| and monoclinic. Because most of the diffraction peaks of | Voltage (V) | | | | | | Voltage (V) | | | | | | | | |

orthorhombic, tetragonal, and cubic phases appear at similar

angles, it is difficult to distinguish these phases. In our

experiment, the ferroelectric properties of Hf0.5Zr0.5O2

capacitors did not differ significantly between the Cap-anneal

Fig. 4. O capacitors annealed at 700 °C. Zr compositions are (a) 0, (b) 26, (c) 50, and (Color online) P–V and I–V characteristics of 10-nm-thick Hf–Zr–

(d) 72%.

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| and non-Cap-anneal processes (not shown). Therefore, we | | | | | | | (a) | 25 | 0 | *P*r | | | | | *E*BD | -3 10 | 2) |
| consider that the diffraction pattern in Fig. 3(b) is applicable | | | | | | |
| to the Cap-anneal films. In this manner, physical analyses | | | | | | | 2) | 20 |
| using TEM and GIXRD clarified that the Hf–Zr–O films in this experiment consist of polycrystals and contain several | | | | | | |
| *J* at 2 MV/cm (A/cm |
| *P*r (µC/cm | 15 |
| phases. This is consistent with previous results.1,8,10,11,15) | | | | | | |
| First, the emergence of the ferroelectric phase in HfO2 films was discussed on the basis of mechanical stress through the | | | | | | | 10 | -4 10 |
| -5 10 |
| TiN electrodes at the bottom and top of HfO2 films.3)Later, it was demonstrated that the top TiN capping layer is not | | | | | | | 5 |
| -6 10 |
| *J* | | | | |
| -7 10 |
| necessary, although it affects the volume fraction of the | | | | | | | (b) | 0 | 20 | 40 | | 60 | |
| ferroelectric phase in the film.11)Furthermore, ferroelectric | | | | | | | 80 |
| Zr/(Zr+Hf) (%) | | | | |
| HfO2 films are demonstrated on Ge substrates without Cap-anneal.6,20)Therefore, it is concluded that the mechanical | | | | | | |
| 5 |
| stress through metal electrodes is not the main factor of the | | | | | | |
| formation of the ferroelectric phase in the films. | | | | | | | *E*C, *E*BD (MV/cm) | 4 | 0 | 20 | | 40 | | 60 | 80 |
| annealed at 700 °C are shown in Fig. 4. From among the Electrical properties of 10-nm-thick Hf–Zr–O films | | | | | | |
| 3 |
| many | experiments | conducted | to | investigate | the | metal |
| 2 |
| composition variation, the results of 0, 26, 50, and 72% Zr | | | | | | | *E*C |
| concentration are presented. A small ferroelectric hysteresis | | | | | | |
| 1 |
| loop is observable in the nondoped HfO2 film (Zr 0%). In the sputtering process using Ar gas in this experiment, it is | | | | | | |
| 0 |
| considered that the HfO2 film is prepared under an oxygen-deficient condition. This situation may induce the formation | | | | | | |
| Zr/(Zr+Hf) (%) | | | | |
| of orthorhombic, tetragonal, and cubic crystalline phases that | | | | | | |

have smaller crystal volumes than the monoclinic phase. Anion deficiency in the HfO2 film appears to have a similar effect to cation doping. Polarization increases as the Zr composition increases to 50%. When the Zr composition is larger than 50%, the hysteresis loop splits into two. This behavior is caused by the transition from the ferroelectric phase to the anti-ferroelectric phase.8)   
 The relationship of the remnant polarization (Pr) and the leakage current (J) with the metal composition in Hf–Zr–O films is shown in Fig. 5(a). The leakage currents are

Fig. 5. (Color online) Metal composition dependences of electrical

properties of 10-nm-thick Hf–Zr–O films prepared by annealing at 700 °C.

(a) Pr and J at 2 MV=cm. (b) EC and EBD.

compared at an electrical field of 2 MV=cm. Pr increases

with increasing Zr composition up to around 60%, and then

decreases. This is consistent with the preceding work.8)The

increase in Pr with Zr composition suggests the increase in

the volume of ferroelectric phase in the film. The volume of

the ferroelectric phase seems to be the largest at 50% Zr.

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| Jpn. J. Appl. Phys. 57, 04FB01 (2018) | | | | | | | | | | | | | | | | | | S. Migita et al. | | | | | | | | | | |
| (a) | Zr 50 %, | | | 3  10 | | | | | (b) | Zr 50 %, | | | 3  10 | | | | | (a) | 30 | | |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | |  |  |  |  |  |  | | | | | | |  |  |
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| explained by the domain nucleation model62)using the following formula: | distinguishable by electrical measurement, because the dielectric constants of paraelectric and ferroelectric phases |

EC � d�2=3: ð1Þ In the sequence of ferroelectric switching cycles, a reversely polarized domain can grow in the polarized matrix when it exceeds the “critical” nucleus size with the assistance of an external electric field. Roughly, the critical nucleus size correlates with the film thickness, and the external field required to overcome this size corresponds to EC. In the case of perovskite type ferroelectrics, the data fits very well with this formula. In the case of HfO2 ferroelectrics shown in Fig. 8, it is not applicable. Including our work, the results of three different research groups using HfO2 films prepared using different dopants and deposition processes show that EC is thickness-independent. The polarization switching behavior of ferroelectric HfO2 films cannot be explained by the domain nucleation model.

The unique switching behavior of HfO2-based ferro-electrics has also been examined by the measurement of switching response against the pulse period in capacitors63) and discrete threshold voltage shifts observed in FeFETs with small channel size.64,65)These behaviors were explained by the “nucleation-limited” mechanism. On the basis of these reports, in order to understand our results in detail, we suggest that ferroelectric domains are confined to the nanometer scale and dispersed in the matrix of a dielectric film. In other words, ferroelectric domains are isolated from each other in the film, and the number of ferroelectric domains changes with parameters such as metal composition and film thickness. In the reports utilizing high-resolution is found that orthorhombic, TEM observation,66,67) it   
monoclinic, and tetragonal crystals are tightly bonded while maintaining smooth interfaces. Because the orthorhombic crystal is a metastable phase,3)it may be stable when it is surrounded by stable phases. The similarity in lattice size between them also supports the matching of interfaces. Therefore, we speculate that ferroelectric domains made of

are largely different. In HfO2 systems, however, the dielectric constants of both paraelectric and ferroelectric phases are almost the same. Therefore, the capacitors show similar electrical performance whether the ferroelectric domain has a slim columnar or small spherical shape in the films. This topic remains to be studied in the future.

The leakage current is one of the concerns in ferroelectric capacitors. In our experiment, the J (at 2 MV=cm) increases markedly with increasing Zr composition in the Hf–Zr–O films, in correlation with the evolution of the ferroelectric phase [Fig. 5(a)]. In contrast, the thickness of Hf0.5Zr0.5O2 films has little influence on the leakage current at the same electric field, although the volume of the ferroelectric phase changes significantly [Fig. 7(a)]. It is difficult to explain these discrepant results consistently. In general, the leakage currents in polycrystalline films are mainly governed by the components through grain boundaries and inside grains. Further analysis is necessary to understand the origins of these behaviors. Practically, preparation of laminate films is expected to effectively reduce the leakage current.25,68)The constant EBD irrespective of Pr [Fig. 5(b)] seems to indicate that the breakdown occurs in non-ferroelectric regions in the films, such as grain boundaries. Thus, the improvement in EBD is possible by techniques such as annealing. The last subject to consider is the engineering of EC. EC values so far reported change depending on the kind of dopant used. Although the guiding principle of EC engineering has not been clarified yet, a combination of dopant exploration experiments and the concept of ferroelectric domain size proposed here will lead to the development of more reliable HfO2-based ferroelectrics.

4. Conclusions

Electrical properties of Hf–Zr–O films, i.e., remnant polar-ization, leakage current, coercive field, and breakdown field, are strongly affected by the metal composition and film

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| orthorhombic crystals exist in the grains mainly made of | thickness. | Although | the | best | ferroelectric | behavior | is |

paraelectric phases. Changes in dopant concentration alter the lattice parameters and induce distortion, and the number of ferroelectric domains changes. This appeares as the metal composition dependence of Pr. When the film becomes thick, the stability of paraelectric crystals increases and, as a result, the number of ferroelectric domains decreases. In this model, because the size of the ferroelectric domain is identical irrespective of the film parameters, EC is constant. In the case of HfO2 ferroelectrics, d in Eq. (1) may correspond to the domain size. Even in the maximum Pr film obtained with 50% Zr, the ferroelectric domains appear to be isolated and EC does not change. At present, it is difficult to examine how the ferroelectric domains are distributed in polycrystal-line films. We consider two extreme cases. One is that the ferroelectric phase has a slim columnar shape along the film thickness, sandwiched by the paraelectric phases, and connects to the top and bottom electrodes. The other is that

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| the | ferroelectric | phase | has | a | small | spherical | shape, |

obtained by a 10-nm-thick Hf0.5Zr0.5O2 film, the leakage current is very high. A particular behavior is that the coercive field is not changed by both the metal composition and the film thickness. The trends of these electrical properties are discussed from our theory that the ferroelectric domains are confined to the nanometer scale and dispersed in the matrix of dielectric grains. In order to apply HfO2-based ferro-electrics in advanced electron devices such as FeRAMs and FeFETs, development of the EC engineering technology is indispensable.

Acknowledgment

This work was supported by JST CREST, JPMJCR14F2.

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| sometimes localized at the interfaces with the electrodes. In conventional ferroelectric oxides, the difference between | 4) |
| the ferroelectric domain shapes mentioned above is clearly 04FB01-5 | |

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