Phys. Status Solidi RRL **8**, No. 6, 532–535 (2014) / **DOI** 10.1002/pssr.201409017

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| Part of Focus Issue on  **Functional Oxides** |

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| Eds.: T. Frauenheim, J. M. Knaup, P. Broqvist, S. Ramanathan |

Ferroelectric properties and switching

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endurance of Hf0.5Zr0.5O2 films on TiN bottom and TiN or RuO2 top electrodes

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Received 10 January 2014, revised 11 February 2014, accepted 12 February 2014 Published online 17 February 2014

**Keywords** Hf0.5Zr0.5O2 films, TiN electrodes, RuO2 electrodes, endurance switching, ferroelectric capacitors

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| The effect of the top electrode (TE) on the ferroelectric prop-erties and switching endurance of thin Hf0.5Zr0.5O2 films was examined. The TiN/Hf0.5Zr0.5O2/TiN capacitor can endure electric cycling up to 109 times, which is promising for the next-generation memory. RuO2 TE was reduced during an- | nealing due to the reactive TiN bottom electrode, resulting in the degradation of the ferroelectric properties and endurance. In addition, the endurance of the TiN/Hf0.5Zr0.5O2/TiN capaci-tors was optimized by changing the film thickness and the postannealing temperature. |

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**1 Introduction** The ferroelectric/electrode interface is one of the most important factors that affect the ferroelec-tric properties and endurance of ferroelectric devices [1]. Conventional materials, such as Pb(Zr,Ti)O3 (PZT), suf-fered from the insufficient switching endurance for work-ing memory application with the Pt electrode [2]. The origin of the degradation during electric-field cycling is generally thought to be related to the accumulation and possible ordering of oxygen vacancies in the region near the noble-metal electrodes, such as Pt [3, 4]. Therefore, adopting the oxide electrode, such as IrO2, is a promising method of enhancing the ferroelectric properties and the endurance of ferroelectric capacitors up to the 1014 cycles level [2–5]. The oxide electrode can work as an oxygen vacancy sink, allowing the endurance of ferroelectric ca-pacitors to be improved significantly [3, 4].For the case of Hf0.5Zr0.5O2 (HZO), which is one of the hottest materials in this field due to its excellent ferroelectricity with small film thickness (*t*f), Si-process compatibility, and matured deposition techniques, in contrast, the effect of the elec-trode on the ferroelectric properties and endurance has been rarely reported since the first report by Müller et al. [6]. Park et al. reported that the remnant polarization (*P*r)



of TiN/HZO/TiN capacitors was ~30% larger than that of the Pt/HZO/TiN capacitor, which means that the TiN/HZO interface was beneficial in achieving better ferroelectric performance compared with the Pt/HZO interface [7]. The reason for such an aspect of the TiN electrode, however, has not been clearly elucidated. Meanwhile, TiN is a reac-tive metal that could be relatively easily oxidized into TiO*x*N*y* or TiO2, which is not expected to be appropriate for achieving the optimum properties [8]. Changing the bot-tom electrode (BE), however, is a very challenging task given the fact that the HZO film showed the best ferroelec-tric properties when they were grown on TiN BE [9]. It was also noted that the formation energy of the oxide elec-trode, such as RuO2, is relatively smaller than that of TiO2 [10, 11]. This means that the severe loss of oxygen from RuO2 could be induced when it is adopted as the top elec-trode (TE) in TiN BE through the thin HZO layer. This in-dicates that adopting RuO2 as the TE material may not re-sult in the optimum endurance performance. Therefore, it is an important task to examine the interactions of oxide TE and TiN BE with the ferroelectric HZO thin films whose *t*f are only ~10 nm. In addition, the coercive field of HfO2-based thin films is larger than that of thin PZT films

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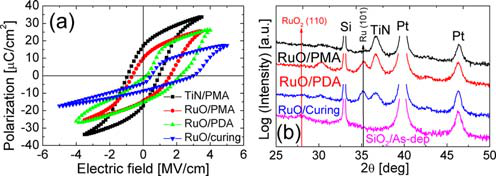
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by about one order of magnitude [7]. Such a large electric field is known to change the resistance state of oxide films through the motion of the defects, such as the oxygen va-cancy, which can also make a difference in terms of endur-ance compared to PZT [12]. In this study, the ferroelectric properties and the endurance of the TiN/HZO/TiN and RuO2/HZO/TiN capacitors were compared, and their dif-ferences were explained via structural and chemical analy-sis, which have not yet been reported in detail.

**2 Experimental** HZO films were deposited on a sput-tered 50 nm thick TiN/Ti/SiO2/Si substrate via thermal atomic layer deposition (ALD) at a 280 °C wafer tempera-ture, using Hf[N(C2H5)CH3]4, Zr[N(C2H5)CH3]4, and ozone as the Hf precursor, Zr precursor, and oxygen source, respectively. As the growth per cycles of HfO2 and ZrO2 were almost identical (~0.12 nm/cycle), the HZO films with a Hf:Zr ratio of 0.5:0.5 could be deposited using a HfO2:ZrO2 ALD cycle ratio of 1:1. For the electrical characterization, Pt(60 nm)/TiN(20 nm) and Pt(60 nm)/ RuO2(20 nm) TEs were deposited via DC (reactive for RuO2 and TiN) sputtering through a shadow mask with a 300 μm hole diameter (TiN and RuO2 contacts HZO films). The TiN TE samples were annealed at 500 °C for 30 s in a N2 atmosphere after TE deposition (TiN/PMA). The details of the optimized RuO2 deposition condition were reported elsewhere [13]. For the RuO2 TE samples, on the other hand, the following three annealing conditions were adopted: (1) postmetallization-annealing (RuO/PMA) – annealing at 500 °C for 30 s in a N2 atmosphere after TE deposition; (2) postdeposition-annealing (RuO/PDA) – annealing at 500 °C for 30 s in a N2 atmosphere before TE deposition; and (3) PDA + curing (RuO/curing) – anneal-ing the PDA samples at 400 °C for 30 min in an air atmo-sphere after TE deposition. The cation composition and *t*f were examined via X-ray fluorescence (Quant’X, Thermo Scientific) and ellipsometry (L-116d, Gaetner), respec-tively. For the structural analysis, Pt(10 nm)/TiN(20 nm) and Pt(10 nm)/RuO2(20 nm) layers were deposited on HZO films with no patterning. The crystallographic phase of the films was examined through a normal θ–2θ scan and via grazing-angle incidence X-ray diffraction (GAXRD) using an X-ray diffractometer (Pananalytical X-pert Pro, Cu Kαradiation with a 0.15418 nm X-ray wavelength). Depth profiling was performed via Auger electron spec-troscopy (AES, Perkin–Elmer, 660). For electrical charac-terization, the polarization electric field (*P*–*E*) and capaci-tance–field (*C*–*E*) were measured at room temperature using a ferroelectric tester (TF Analyzer 2000, Aixacct Systems) with a 1 kHz frequency and an impedance ana-lyzer (4194A, HP) with a 10 kHz AC frequency. An en-durance test was performed using a ferroelectric tester (TF Analyzer 2000, Aixacct Systems) with a 100 kHz electrical cycling frequency.

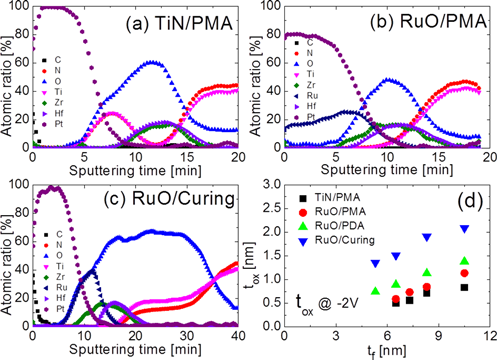
**3 Results and discussion** Figure 1a shows the *P*–*E* hysteresis curves for the capacitors with 10.5 nm thick

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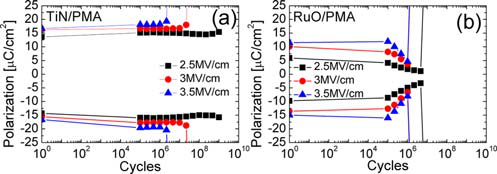
**Figure 1** (a) *P*–*E* hysteresis of 10.5 nm thick Hf0.5Zr0.5O2 capaci-tors with a TiN and RuO2 top electrode with various annealing conditions. (b) Glancing-incidence angle X-ray diffraction spec-tra of the Hf0.5Zr0.5O2 and SiO2 films with an RuO2 top layer with various annealing conditions.

HZO films with various TE and annealing conditions. The *P*–*E* loops of the capacitors with different *t*f values were included in the online Supporting Information (SI). The 2*P*r values of TiN/PMA and RuO/PMA were ~34 and ~24 μC/cm2, respectively, and the *P*–*E* loop of TiN/PMA was almost symmetric, whereas that of RuO/PMA was shifted to the positive bias direction by ~0.48 MV/cm, which might be related to differences in work function, charge injection barrier, or oxygen affinity of TE and BE [14–17]. This means that the RuO2 TE degraded the ferro-electric properties of the HZO capacitor, which is quite dif-ferent from the reports on the PZT capacitors [4, 5]. To elucidate this unexpected result, the crystal structure of RuO/PMA was analysed using GAXRD spectra, as can be seen in Fig. 1b. To confirm the deposition of the fully oxi-dized RuO2 TE, the Pt/RuO2 TE was also deposited on a 100 nm thick thermal SiO2/Si substrate, and no RuO2 re-duction was observed, as seen in Fig. 1b. For RuO/PMA, however, no diffraction peak was seen from both RuO2 and Ru. This means that there might be chemical reactions re-lated to the RuO2 layer. Figure 2a–c show the AES depth profile results. In Fig. 2b, it can be easily noticed that RuO2 was significantly reduced to Ru, and that the Ru



**Figure 2** Auger electron spectroscopy spectra of (a) TiN/PMA, (b) RuO/PMA, and (c) PDA/curing. (d) The change of the equi-valent oxide thickness from the *C*–*E* characteristics of various capacitors as a function of film thickness.

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atoms diffused into the Pt layer due to the RuO/PMA. Fig-  
ure 2a shows, on the other hand, that the Pt/TiN TE kept   
the structure intact even after the TiN/PMA. To address   
the problem related to the reduction of RuO2, the HZO film   
was crystallized before the deposition of RuO2 TE   
(RuO/PDA). The sample, however, showed an even more   
distorted *P*–*E* loop, which might have resulted from the

space-charge layer at the RuO2/HZO interface. In fact, the process of TE sputtering is well known as a source of inter-facial defects [13]. It is surprising to note that an Ru peak can be observed even for the GAXRD spectra of RuO/PDA, meaning that RuO2 is partly reduced during the sputtering process of RuO2 even without any thermal treatment. Therefore, the RuO/PDA capacitor was an-nealed in an air atmosphere to supplement the oxidation of the partly reduced RuO2. The *P*–*E* curve of the RuO/curing capacitor, however, shifted to the positive bias region even more. It can be understood that the oxidation of TiN BE as well as the reduction of RuO2 TE occurred during the cur-ing process from the decrease of the intensity of the TiN(111) peak and the increase of the Ru(101) peak in the GAXRD spectrum of the sample.

Figure 2d shows the change in the equivalent oxide thickness (*t*ox), which shows the thickness of the SiO2 film with the equivalent capacitance, from the *C*–*E* characteris-tics of various capacitors as a function of *t*f. The *C*–*E* curves of the various samples were included as Fig. S2 in the online SI. The *t*ox values were extracted from the ca-pacitance value measured at –2 MV/cm to exclude the effect of ferroelectric switching. Generally, the thickness of the interfacial low-*k* layer (*t*i) can be extracted from the *y*-axis intercept of the linear fitting of the *t*ox–*t*f plot. Park et al. reported, however, that a change in the value of *t*f will affect the competition of the polymorphs of HZO [18]. In their report, the portion of the polymorphs of HZO changed with the changing *t*f. Therefore, *t*i cannot be di-rectly extracted from the *y*-axis intercept, but the obviously different *y*-axis intercept indicated that there were signifi-cant changes in the interfacial state depending on the TE material as well as the annealing conditions. As expected from the *P*–*E* characteristics, the adverse contribution from the interface of RuO/curing was the largest, whereas that in TiN/PMA was the smallest among the samples. The *t*ox values of RuO/PMA, RuO/PDA, and RuO/curing were lar-ger than that of TiN/PMA by ~0.2, ~0.4, and ~1.1 nm. Such an increase in *t*ox could be attributed to the oxidation of the TiN electrode. Assuming that the dielectric constant (εr) of TiO2 is ~40, 1.1 nm *t*ox corresponds to ~11 nm [19]. The significant oxidation of TiN BE to TiO2 (or TiO2–*x* or TiO*x*N*y*) could be observed in the AES spectra in Fig. 2c. For RuO/PMA, in contrast, the mixing of the reduced Ru and Pt could be observed, which interferes with the crystal-lization of RuO2 and Ru, as shown in Fig. 1b. This means that the TE of the RuO/PMA sample was the mixture of Pt and Ru, which is not favorable for the optimal ferroelectric properties of the HZO film. The formation enthalpy of RuO2 was much smaller (~–280 kJ/mol at 773 K) [10] than

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**Figure 3** Endurance properties of (a) TiN/PMA and (b) RuO/PMA with 2.5 MV/cm, 3 MV/cm, and 3.5 MV/cm electric-field cycling, respectively.

that of TiO2 (~–907 kJ/mol at 773 K) [11], which is the fundamental driving force that induces such a significant reaction. It is also interesting to note that oxygen atoms could be observed in the TiN TE and BE. It is generally known that the electrode with oxygen can work as an oxy-gen vacancy sink, which is known as the degradation due to electric-field cycling. Therefore, the TiN electrodes are also expected to work as oxygen vacancy sinks and are ex-pected to show promising endurance properties, although they are not oxide electrodes.

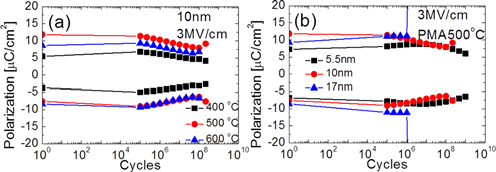
Figure 3a and b shows the switching endurance proper-ties of TiN/PMA and RuO/PMA, respectively. TiN/PMA shows robust *P*–*E* characteristics up to 109 cycles, with a large *P*r (>15 μC/cm2) when the switching field was 2.5 MV/cm, which is much higher than the usual switching field for the endurance test for PZT. Another notable fea-ture from this endurance test was that the HZO film usually broke down after endurance failure, which is usually not the case for PZT. The large coercive field of ~1 MV/cm and the small *t*f of ~10 nm might be the rea-sons for such hard breakdown with the formation of a per-manent leakage path through the films. The number of cy-cles for the breakdown decreased with increasing electric field, and the number of electric cycles was ~107 and ~106 for 3 MV/cm and 3.5 MV/cm electric fields, respectively. These levels of endurance properties of HZO were as good as those of the Si-doped HfO2 films reported by Müller et al. [20]. In the case of RuO/PMA, however, its endur-ance was worse than that of TiN/PMA. Even for the case of electric cycling with an electric field of 2.5 MV/cm, the hard breakdown with significant leakage current degrada-tion could be observed before the number of switching cycles increases to 107. This degradation might have re-sulted from the RuO2 reduction and from the mixing of the reduced Ru and the Pt TE, as already observed in Fig. 2b, which could enhance the roughening and the formation of local current paths. The endurance properties of the RuO2 TE samples with other annealing conditions could not be tested because their *P*–*E* curves were overly imprinted in the positive bias direction. As a result, TiN/PMA showed the best endurance among the samples.

Next, the effect of the annealing temperature (*T*anneal) and *t*f on the endurance properties were examined to opti-mize the endurance properties of the TiN/PMA samples. Figure 4a shows the endurance test results of the TiN/PMA

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**Figure 4** Endurance properties of (a) TiN/PMA with a 10 nm film thickness and annealed at 400 °C, 500 °C, and 600 °C, and (b) TiN/PMA with 5.5 nm, 10 nm, and 17 nm film thicknesses and a 500 °C annealing temperature, respectively.

samples with 10 nm thick HZO films whose *T*anneal values were 400 °C, 500 °C, and 600 °C, respectively. The physical and ferroelectric properties of the samples were reported elsewhere [18]. With an electric field for cycling of 3 MV/cm, the initial *P*r of the sample annealed at 500 °C was the largest, whereas that of the sample annealed at 400 °C was the smallest. It is believed that *T*anneal affects the crystalline quality of the ferroelectric film, and that *T*anneal of 400 °C is too low to produce a high-quality film with a low density of defects. In addition, the interface between the ferroelectric film and the electrode could also be affected by *T*anneal. Meanwhile, an increase in *T*anneal can result in the formation of the partial monoclinic phase (m-phase), which can also affect the ferroelectric properties and endurance. Especially, a double-layered structure with an upper m-phase and a lower ferroelectric orthorhombic phase can be formed partly with the increasing *T*anneal or *t*f of the HZO films [18]. The effect of the m-phase formation can be ob-served more clearly in Fig. 4b. TiN/PMA, whose *t*f is 17 nm, contains more m-phase than the thinner films do, which is consistent with the previous report [11]. The m-phase can work as a dead layer in ferroelectrics and would thus de-grade both the ferroelectric properties [18] and the endur-ance of the HZO capacitors. For the endurance, the problem can be even worse because the loss of the switching electric field across the m-phase with a low εr must be more severe, and an even higher voltage is necessary to induce sufficient electrical switching. The concentred electric field across the low-εr region can more easily result in a hard breakdown. As seen in Fig. 4b, the TiN/PMA sample, whose *t*f was 17 nm, was broken down at an electric cycling of only 106 times, whereas the samples whose *t*f values were 10 nm and 5.5 nm showed robust ferroelectric characteristics up to ~108 and ~109 cycles, respectively. Even though the 5.5 nm thick TiN/PMA could switch to a cycle number more than 10 nm thick one, its *P*r was much smaller than that of the 10 nm thick one. This might have been due to the increase of the portion of nonferroelectric tetragonal phase or the increase of the low-εr interfacial layer. Therefore, the ~10 nm of *t*f was found to be the best for the optimum ferroelectric prop-erties and endurance.

**4 Conclusions** In conclusion, unlike the conventional ferroelectrics, such as Pb(Zr,Ti)O3 with a noble-metal BE, the RuO2 electrode could not improve the ferroelectric

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properties and endurance of the HZO capacitors with the TiN BE. The reason for this was the reduction of the RuO2 TE by the chemical reaction with the reactive TiN BE. However, this does not mean that an oxide electrode cannot work with HZO film, and it is still expected to improve the endurance HZO capacitors, if there is no fab-rication issue. TiN appears to be the best and only BE material that is known to work well with ferroelectric HfO2-based films, and as such, it seems unlikely that TiN BE will be replaced with another electrode material. Mean-while, the TiN electrode contained a significant amount of oxygen atoms, which may decrease the oxygen vacancy concentration in the HZO layer during the repeated switch-ing, which in turn can improve the endurance of the ferro-electric capacitors. The TiN/PMA sample showed robust ferroelectric properties even after electric cycling for 109 times with a switching field of 2.5 MV/cm. The effect of *T*anneal and *t*f were also examined. With a 3 MV/cm electric field for cycling, the 500 °C *T*anneal showed the best endur-ance, which can be ascribed to the minimized m-phase formation and the improved crystalline quality of the HZO film.

**Acknowledgements** This work was supported by the Con-verging Research Center Program (2013K000158) and the Global Research Laboratory Program (2012040157) through the Minis-try of Science, ICT, and Future Planning, Republic of Korea.

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