Ferroelectric Zr-doped Hafnium Oxide for Memory Applications

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Introduction: In the last few years, doped metal oxides, including hafnium oxide (HfO_2) and zirconium oxide (ZrO_2), were found to have a ferroelectric phase [1-2]. As compared to traditional ferroelectric materials, ferroelectric doped HfO_2 has the advantages of high coercive field and good compatibility with CMOS processing [3-7]. Among various ferroelectric doped HfO_2 candidates, zirconium (Zr) doped HfO_2 is one of the most promising, with benefits including excellent scalability and low annealing temperature. In this paper, we systematically investigate Zr-doped HfO_2 with various process conditions and demonstrate high-performance ferroelectric capacitors based on Zr-doped HfO_2.

Experimental process: Planar metal-ferroelectric-semiconductor (MFS) capacitors were fabricated on highly doped Si substrates as illustrated in Fig. 1(a). 12 nm thick Zr-doped HfO_2 was deposited via atomic layer deposition (ALD). The Zr concentration was varied by tuning the cycle ratio between the Hf and Zr precursors. The Ti/Au electrodes were deposited by e-beam evaporation. The encapsulated HfO_2 films were then annealed in a rapid thermal annealing (RTA) tool.

Results and discussion: We systematically investigated the ferroelectricity and leakage current density of Zr-doped HfO_2 capacitors with various ALD deposition temperatures, Hf-to-Zr cycle ratios, annealing temperatures/time, thicknesses, top electrodes, and interfacial layers. Interestingly, we found that the deposition temperature during the ALD process can significantly influence the ferroelectricity of the Zr-doped HfO_2. Figure 2 shows the remanent polarization (P_r) as a function of ALD deposition temperature. We can see that the samples deposited at a higher ALD deposition temperature show higher P_r, even when all samples were annealed at the same temperature (550 °C) after deposition. We speculate that ferroelectric phase formation is facilitated in the Zr-doped HfO_2 film deposited at higher temperature because it contains less carbon contamination and fewer bulk traps. In addition, we found that the optimal Hf-to-Zr cycle ratio is around 3:1 when the ALD deposition temperature was set at 200 °C, as shown in Fig. 3. Moreover, the remanent polarization and the leakage current density can be optimized by tuning the annealing temperature. Figure 4(a) and 4(b) show the remanent polarization and the leakage current density as a function of annealing temperature. When the annealing temperature increases, the remanent polarization increases gradually. However, the leakage current density also increases with increasing annealing temperature. If we consider both the remanent polarization and leakage current density, the optimal annealing temperature is around 550–600 °C. With the optimized process conditions, the reliabilities of Zr-doped HfO_2 capacitors were characterized. Figure 5 shows the endurance of Zr-doped HfO_2 capacitors with two annealing times. The capacitor annealed for 30 seconds shows higher endurance than those annealed for 1 second. After 10^9 cycles, the remanent polarization reduces to 30% of initial value for the capacitor annealed for 30 seconds, while it drops to 19% for the capacitor annealed for 1 second. At the ±5 V and ±4 V program/erase voltage, the ferroelectric Zr-doped HfO_2 shows the characteristic fatigue behavior of ferroelectric materials, while at ±6 V program/erase voltage, hard breakdown becomes the limiting factor for the endurance. The retention of the Zr-doped HfO_2 with the two annealing times is shown in Fig. 6. After 10^4 seconds, 76.5% of initial polarization window remains for the capacitor with 30 second annealing, while 71% of initial polarization window remains for the capacitor with 1 second annealing. The retention shows asymmetric behavior for the program and erase pulses, which may due to the asymmetric depolarization fields at the top and bottom interface in the MFS capacitor.

Summary: We studied the impact of device structure and process conditions on the ferroelectricity and leakage current density of Zr-doped HfO_2. We found that the ALD deposition temperature plays an important role in the ferroelectricity of Zr-doped HfO_2 and a 3:1 Hf-to-Zr cycle ratio gives the optimal remanent polarization. With optimized process conditions, we were able to demonstrate Zr-doped HfO_2 with 17.5 μC/cm^2 remanent polarization and more than 10^9 cycle endurance.

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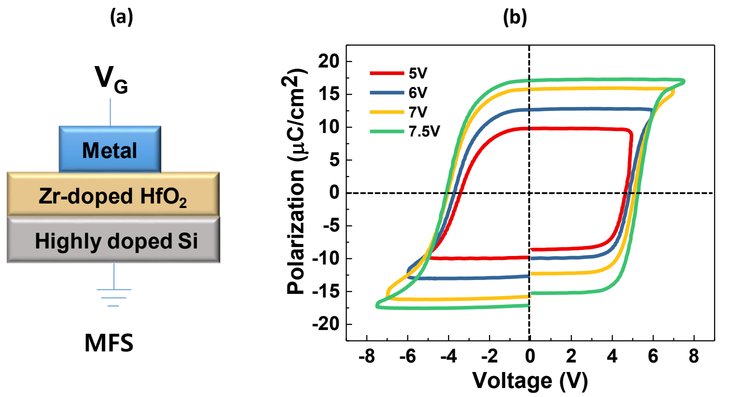
References: [1] T. S. Boscke et al., App. Phys. Lett., 99, 112904 (2011). [2] S. Mueller et al., Adv. Func. Mat., 22, p.2412 (2012). [3] J. Muller et al., IEEE IEDM, 10.8 (2013). [4] E. Yurchuk et al., IEEE TED, 61, p.3699, (2014). [5] M. Si et al., 2017 IEEE IEDM, 23.5 (2017). [6]Y.-C. Lin, et al., J. Vac. Sci. Technol. B, 36, p011204 (2018). [7] W. C. Yap et al., Appl. Phys. Lett., 111, 013103 (2017).



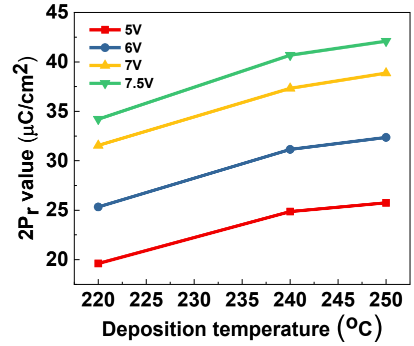


Fig 1. (a) Illustration of a MFS capacitor with ferroelectric Zr-doped HfO_2 on a silicon substrate. (b) Representative polarization-voltage (P-V) loops of Zr-doped HfO_2 capacitor deposited at 220 ℃.

Fig 2. Effect of ALD chamber temperature during film deposition on the remanent polarization.

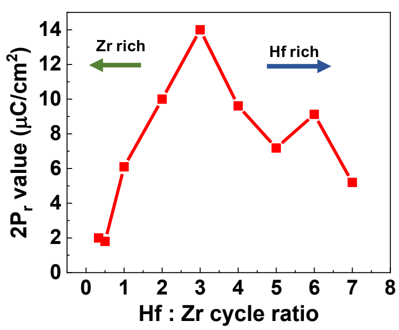


Fig 3. Remanent polarization as a function of Hf-to-Zr cycle ratio for 12 nm Zr-doped HfO_2 capacitors.

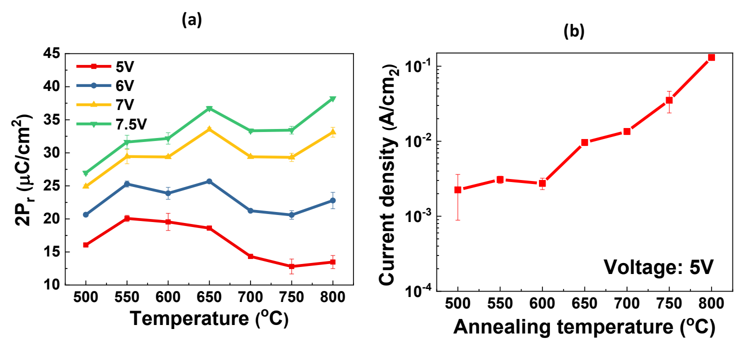


Fig 4. (a) Effect of annealing temperature on (a) remanent polarization and (b) leakage current density of the Zr-doped HfO_2 capacitors.

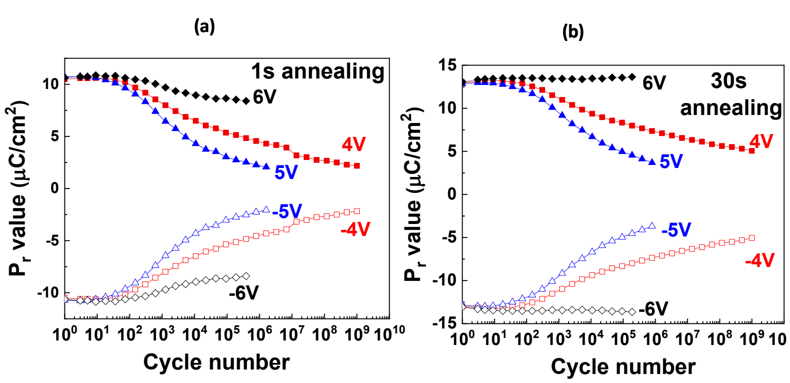


Fig 5. Endurance at various program/erase pulse amplitudes tested on the Zr-doped HfO_2 capacitors annealed for (a) 1 second and (b) 30 seconds.

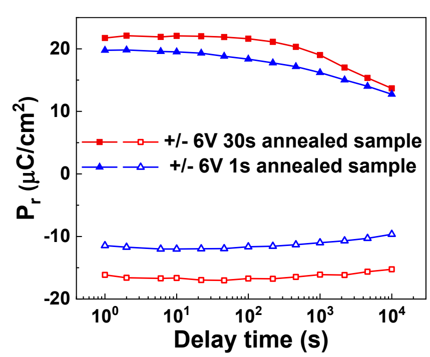


Fig 6. Retention of Zr-doped HfO_2 capacitors annealed for 30 seconds and 1 second.