2023 International VLSI Symposium on Technology, Systems and Applications (VLSI-TSA/VLSI-DAT) | 979-8-3503-3416-6/23/$31.00 ©2023 IEEE | DOI: 10.1109/VLSI-TSA/VLSI-DAT57221.2023.10134407

Ultra High-k $HfZrO_4$ Thin Films Grown by Atomic Layer Deposition using Metal-Organic and Brute HOOH precursors

[1]Harshil Kashyap, [2]Marshall Benham [2]Jeffrey Spiegelman, [1]Andrew Kummel
[1]University of California San Diego
[2]Rasirc

Abstract

Lower leakage at low EOT is a requirement for DRAM application. High-k materials such as TiO_2 have shown low EOT (3.5A-4A) but suffer from small band gap and high leakage[1]. Ferroelectric/antiferroelectric $HfZrO_4$ films have shown high-k at 10nm but as the films are scaled, the dielectric properties of the films decrease[2,3]. The key to low EOT is to find a material with high-k at 5 nm or sub-5nm thickness with low leakage. In the present study, $HfZrO_4$ films were fabricated with HOOH and metal organic precursors which demonstrate very high-k (~88) at 5 nm thickness with TiN and W electrodes in metal-insulator-metal (MIM) device structure.

Experimental

Metal-Insulator-Metal were fabricated with $HfZrO_4$ thin films. 5nm $HfZrO_4$ was grown by ALD on sputtered TiN and W substrates at 275 °C using tetrakis(dimethylamino)hafnium (TDMAH), tetrakis(dimethylamino)zirconium (TDMAZ) and H_2O_2. $HfZrO_4$ thickness was determined by cross-sectional TEM and were between 5.0 and 5.5 nm. TiN and W electrodes were deposited by magnetron sputtering. Top electrodes were patterned by photolithography. Samples were annealed in N_2 at 600°C for 2 minutes. Control samples with H_2O were also fabricated for comparison with TiN and W electrodes The fabricated devices were characterized using Keithley 4200A parameter analyzer.

Results and Discussion

Fig 1 shows the C-V measurements for $HfZrO_4$ films deposited with HOOH. Control samples made with H_2O were used for comparison. For $HfZrO_4$ using HOOH with TiN electrodes, there are 4 switching peaks in the C-V consistent with presence of the AFE phase (Fig. 1a). HZO with 1:1 Hf:Zr ratio is known to show FE switching; however, use of HOOH precursor may lead to Ti diffusion from TiN substrate into the HZO film. Small amounts of Ti are known to stabilize the AFE phase in HZO[4]. To study the impact of metal electrodes, samples with sputtered W electrodes were fabricated since W is known to show enhanced FE/AFE switching in HZO films. Undoped HZO with 1:1 Hf:Zr and W electrodes grown with HOOH (Fig 1b) shows only FE switching and no AFE switching.

When using HOOH, both the samples with TiN and W electrodes show record high capacitance for 5 nm films (> 10 $\mu F/cm^2$). $HfZrO_4$ films in ferroelectrics literature show a wide range of k values. Extrinsic contributions to k value from domain walls play an important role. A higher vol% of domain walls may be key to the extremely high-k observed in films fabricated using HOOH vs H_2O. TEM will be performed to verify this hypothesis. Fig 2 shows suppressed polarization in domain walls which are very susceptible to eternal stimuli and thus show high permittivity

For DRAM application, it essential to have high-k near 0V. Fig 3 (a) shows a high-k benchmark of existing $HfZrO_4$ high-k literature. k@0V was extracted from C-V measurement. Both devices fabricated using HOOH show record high-k at (~58 with TiN, ~88 with W) 5 nm thickness which results in ultra-low EOT of ~3.5 A with TiN and ~2.5 A with W.

Fig 4. shows the leakage data. The sample with W electrode shows higher leakage in comparison with samples with TiN electrodes. This may be in part due to higher crystallinity in $HfZrO_4$ imparted by the W electrodes since major leakage pathway in crystalline $HfZrO_4$ thin films is grain boundaries.

Conclusion

HOOH is shown to be an excellent ALD precursor for growing high-k $HfZrO_4$ films. Films made with HOOH show a 2x boost in capacitance compared to films made with H_2O. This enables for ultra-low EOT films. These films are promising for next gen low-power high-density memory application.

References

(1)
Fröhlich, K.; Hudec, B.; Hušeková, K.; Aarik, J.; Tarre, A.; Kasikov, A.; Rammula, R.; Vincze, A. Low Equivalent Oxide Thickness TiO_2 Based Capacitors for DRAM Application. *ECS Trans.* **2011**, *41* (2), 73–77. https://doi.org/10.1149/1.3633656.

(2)
Zhou, J.; Zhou, Z.; Jiao, L.; Wang, X.; Kang, Y.; Wang, H.; Han, K.; Zheng, Z.; Gong, X. Al-Doped and Deposition Temperature-Engineered HfO_2 Near Morphotropic Phase Boundary with Record Dielectric Permittivity (~68). In *2021 IEEE International Electron Devices Meeting (IEDM)*; IEEE: San Francisco, CA, USA, 2021; p 13.4.1-13.4.4. https://doi.org/10.1109/IEDM19574.2021.9720632.

(3)
Das, D.; Jeon, S. High-k $Hf_xZr_{1-x}O_2$ Ferroelectric Insulator by Utilizing High Pressure Anneal. *IEEE Trans. Electron Devices* **2020**, *67* (6), 2489–2494. https://doi.org/10.1109/TED.2020.2985635.

(4)
Park, M.H., Lee, Y.H., Kim, H.J., Kim, Y.J., Moon, T., Kim, K.D., Müller, J., Kersch, A., Schroeder, U., Mikolajick, T. and Hwang,C.S. (2015), Ferroelectricity and Antiferroelectricity of Doped Thin HfO_2-Based Films. Adv. Mater., 27: 1811-1831. https://doi.org/10.1002/adma.201404531

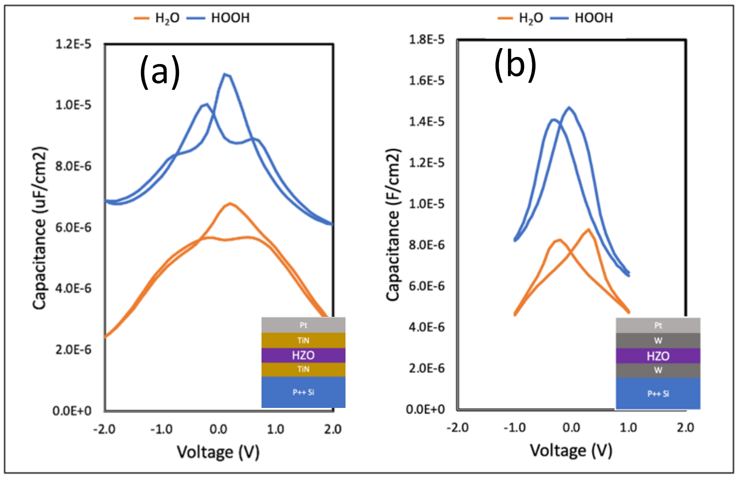

Fig 1 C-V: (a) MIM capacitors with TiN electrodes. Thicknesses were 5.0 nm (HOOH) and 5.5 nm (H_2O) (b) MIM capacitors with W electrodes. $HfZrO_4$ films fabricated with HOOH show a ~2x boost in capacitance over films made with H_2O. Thicknesses were 5.0 nm (HOOH) and 5.5 nm(H_2O)

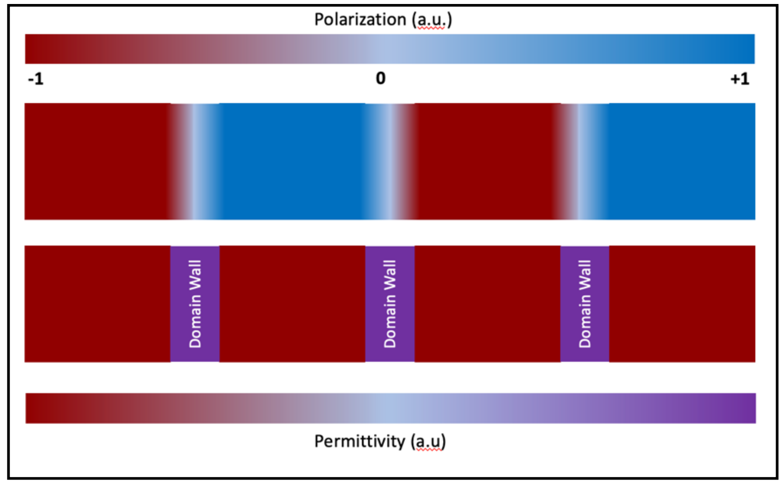

Fig 2 domain wall permittivity: model showing suppressed polarization in domain walls exhibit high permittivity.

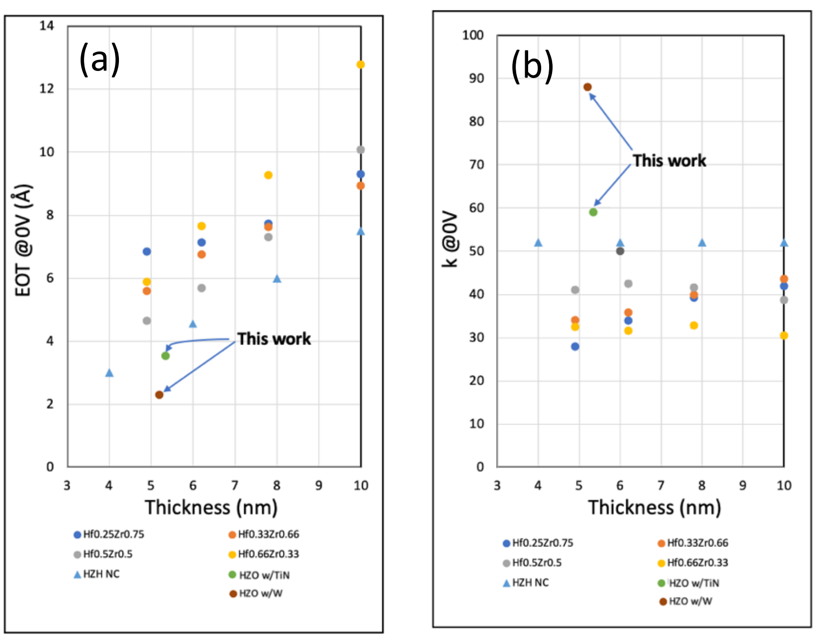

Fig 3 Benchmarking: (a) EOT @0V vs $HfZrO_4$ thickness. (b) k @0V vs HfZrO4 thickness. Record low EOT and high-k value $HfZrO_4$ sample fabricated using HOOH.

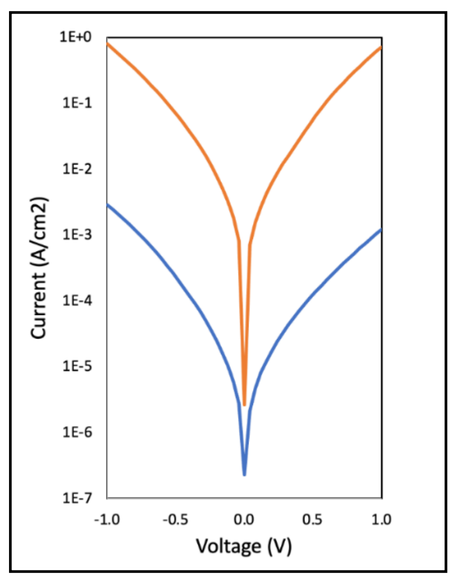

Fig 4 leakage: Higher leakage with W electrodes (orange) compared to TiN electrodes (blue) may be through grain boundaries.