# Ferroelectric Aluminum-Doped Hafnium Oxide for Memory Applications

Hojoon Ryu[1], Kai Xu[1], Ji Guo[1], and Wenjuan Zhu[1]
[1]*Univeristy Illinois at Urbana-Champaign, 208 North Wright Street, Urbana, IL 61801,USA*
*Email: wjzhu@illinois.edu / Phone: (217) 244-9456*

**Introduction**

Ferroelectric complex perovskites, such as lead zirconate titanate (PZT), strontium bismuth tantalate (SBT), and lead magnesium niobate-lead titanate (PMN-PT) have been widely used in ferroelectric devices. However, these traditional ferroelectric materials have a limitation in thickness scaling and are incompatible with CMOS processes. In the last few years, doped metal oxides, including hafnium oxide ($HfO_2$) and zirconium oxide ($ZrO_2$), were found to have ferroelectric phase [1-2]. Ferroelectric $HfO_2$ has the advantages of a high coercive field, excellent scalability (down to 2.5nm), and good compatibility with CMOS processing [3-7]. In this paper, we systematically investigate Al-doped $HfO_2$ with various electrodes, Al compositions and annealing temperatures. We found that Ti/Pd is a promising candidate as top electrode material for ferroelectric $HfO_2$.

**Experimental Process**

Planar ferroelectric MIS capacitors were fabricated on highly doped Si substrates, illustrated in Fig. 1. 20 nm thick $HfO_2$ doped with aluminum (Al) was deposited using an atomic layer deposition (ALD) system. The Al concentration was varied by tuning the cycle ratio between the Hf precursor [tetrakis(ethylmethylamino)hafnium (TEMAH)] and Al precursor [trimethylaluminium (TMA). The Ti/Pd and Ti/Au electrodes were deposited by e-beam evaporation, while TiN and W electrodes were deposited by sputtering. The encapsulated $HfO_2$ films were then annealed in a rapid thermal annealing (RTA) system.

**Device Results**

The dependence of top electrode, Al doping concentration and annealing temperature on the ferroelectricity in Al-doped $HfO_2$ were systematically investigated. We found that the top electrode plays a critical role in the ferroelectricity of the doped $HfO_2$. Fig. 2a and 2b show the polarization versus voltage (P-V) loops and the statistics of remanent polarization of the Al-doped $HfO_2$ capacitors with various electrodes. The capacitors with Ti/Pd show the highest remanent polarization. We speculate that the internal strain induced by Pd is in favor of forming ferroelectric phase in Al-doped $HfO_2$. With Ti/Pd electrode, the remanent polarization in Al-doped $HfO_2$ capacitor can reach 20 $\mu C/cm^2$. The remanent polarization is also very sensitive to the Al doping concentration. As shown in Fig. 3, the remanent polarization reaches maximum, when Hf to Al cycle ratio is around 23:1. In addition, the remanent polarization and the leakage current density can further be optimized by adjusting the annealing temperatures. Fig. 4a and 4b show the remanent polarization ($2P_r$) and the leakage current density as a function of annealing temperature. We can see that the remanent polarization reaches the peak value when the annealing temperature is around 900 $^oC$ – 950 $^oC$, while the leakage current density increases monotonically with increasing annealing temperature. This rising leakage current density at higher annealing temperatures may be caused by the increasing crystallization of the $HfO_2$ film, resulting in additional leakage path along the grain boundaries. With the optimized process conditions, the reliabilities of the Al-doped $HfO_2$ were also characterized. Fig.5a show the endurance of Al-doped $HfO_2$ capacitors with various electrodes. The capacitors with Ti/Pd electrodes show much higher endurance than those with TiN and W electrodes. At ±7 V program/erase pulses, the capacitors with Ti/Pd electrodes can endure more than $10^8$ cycles. The dependence of the endurance characteristics on the operating voltage is depicted in Fig 5b. At the ±7 V program/erase voltage, the ferroelectric Al-doped $HfO_2$ shows the characteristic fatigue behavior of ferroelectric materials. For higher voltages (±10 V), a hard break down becomes the limiting factor. The retention of the ferroelectric Al-doped $HfO_2$ with various top electrodes is shown in Fig. 6. The capacitors with Ti/Pd electrode show much longer retention as compared to those with W electrode.

**Conclusion**

We systematically investigated ferroelectric aluminum (Al)-doped hafnium oxide ($HfO_2$) with various top electrodes, Hf to Al ratios, and annealing temperatures. We found that the ferroelectric Al-doped $HfO_2$ capacitors with Ti/Pd electrodes have much higher remanent polarization, better endurance and longer retention as compared to those with TiN, W and Ti/Au electrodes. Based on the optimized process conditions, we demonstrated high-quality ferroelectric Al-doped $HfO_2$ with remanent polarization up to 20 $\mu C/cm^2$ and endurance higher than $10^8$ cycles.

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**References**:

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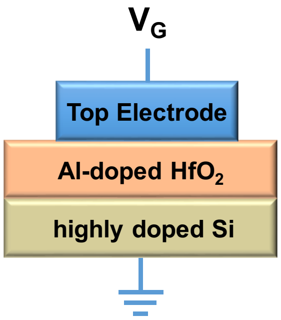


**Fig. 1.** Illustration of the metal-insulator-semiconductor (MIS) capacitors with ferroelectric $HfO_2$.

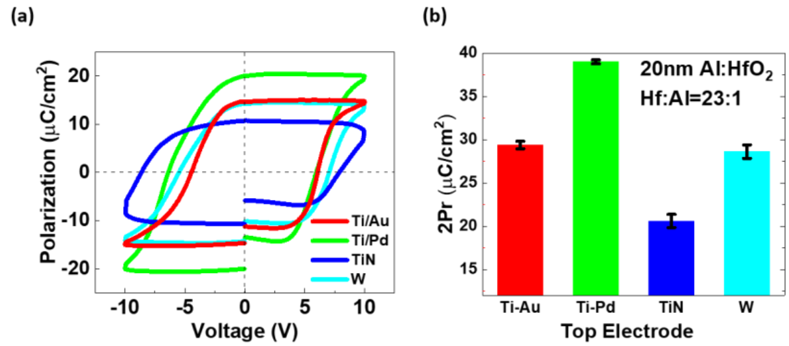


**Fig. 2.** (a) Polarization-voltage (P~V) loops of Al-doped $HfO_2$ capacitors with various top electrodes (TiN, W and Ti/Pd). (b) Statistic remanent polarization for various types of top electrodes.

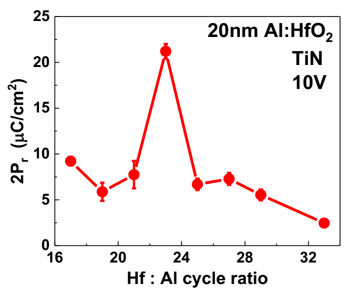


**Fig. 3.** Remanent polarization ($2P_r$) as a function of Hf to Al cycle ratio for 20nm Al-doped $HfO_2$ with TiN electrode.

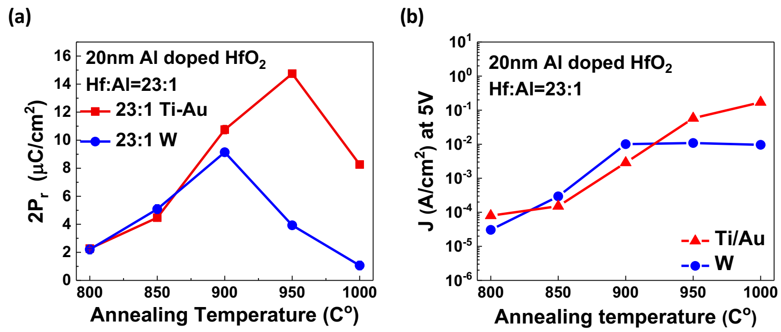


**Fig. 4.** (a) Effect of annealing temperature on the remanent polarization. (b) Effect of annealing temperature on leakage current density of the capacitor.

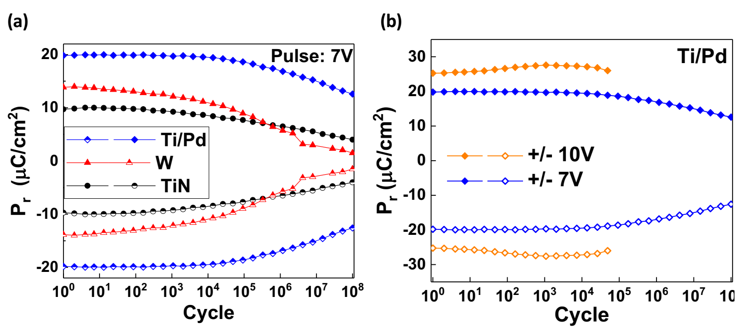


**Fig. 5.** (a) Endurance test of samples with diverse kinds of top electrode materials. (Fatigue voltage amplitude is 7V) (b) Endurance test result of Ti/Pd samples with changing the amplitude of fatigue voltage applied

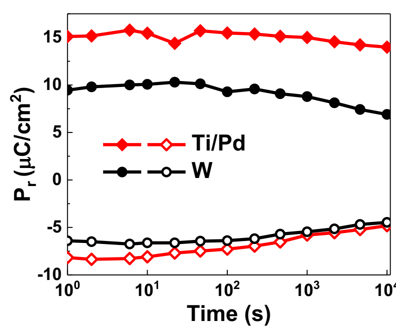


**Fig. 6.** Retention of Al-doped $HfO_2$ with Ti/Pd and W top electrodes.