

Annealing Study of ALD Deposited Ferroelectric Aluminum-doped Hafnium Oxide

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ABSTRACT

With the acquisition of a Savannah ALD tool at RIT, it is now possible to deposit ferroelectric Al-doped HfO_2 (Al:HfO_2) in the SMFL. Recipes for Al:HfO_2 have been developed using tetrakis(dimethylamido)hafnium(IV) (TDMAHF) as a Hafnium precursor, and trimethyl aluminum (TMA) as an Aluminum precursor. Various percentages of Al in the Al:HfO_2 , controlled by the number of TMA cycles during the ALD deposition, were deposited in order to observe the effect of Al concentration on ferroelectricity. To determine the dependence of ferroelectricity on annealing conditions, samples underwent rapid thermal annealing steps at varying temperatures and times. The dependence of a top TiN electrode being present during then annealing step on ferroelectricity was also observed, as both Post-Metallization Anneal (PMA) and a Post-Deposition Anneal (PDA) process steps were performed for both Al concentration and annealing conditions. It was found that ferroelectricity was only observed in PDA devices, as it is likely that the top TiN layer was absorbing enough heat to prevent the domain sizes from growing in the Al:HfO_2 layer in the PMA devices. It was also observed that a longer annealing time yields higher remnant polarization values at similar coercive voltage values, which is likely due to larger domain sizes resulting from the longer anneal.

1. INTRODUCTION

The recent growth in desire for non-volatile memory in embedded systems has led to the increased interest and research in ferroelectric Hafnium Dioxide (HfO_2).¹⁻⁴ Traditionally, the problem with ferroelectric films, such as $\text{Pb}(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3$ (PZT), are that they are not compatible with typical CMOS fabrication processes and lose their ferroelectric properties when scaled down in size.² However, with recent advancements in Atomic

Layer Deposition (ALD) technology it has been found that it is possible to achieve ferroelectricity in HfO_2 through the combination of dopants introduced during film deposition, a mechanically confining top metal layer, and a subsequent annealing process.⁵ With this discovery it is now potential for ferroelectric films to be scaled down to sizes comparable with modern integrated circuits (IC), as HfO_2 is compatible with CMOS fabrication processes⁶ down to extremely thin thicknesses and is capable of achieving a relatively high coercive field at low operating voltages. The scalability of ferroelectric HfO_2 makes it possible for various ferroelectric devices such as ferroelectric tunnel junctions (FTJs), ferroelectric field effect transistors (FeFETs), negative capacitance field effect transistors (NC FETs), and ferroelectric random access memory (FRAM), to compete with modern devices.³

2. THEORY

2.1 Ferroelectricity

Ferroelectricity is a phenomenon observed in dielectrics, that depends on the crystallographic structure of the dielectric.⁷ All dielectrics are either centrosymmetric or they are non-centrosymmetric. Within the non-centrosymmetric dielectrics are ferroelectrics, which are a class of pyroelectrics, which in turn are a class of piezoelectrics. The hierarchy of these dielectrics can be seen below in figure 1. Ferroelectricity in particular is the phenomenon in which a dielectric has two stable polarization states, depending on the position of atoms in the crystallographic structure. When the ferroelectric is subject to an applied electric field, it is possible for the atoms to move between the two positions, or polarization states, depending on the ferroelectric nature of the dielectric and the electric field applied.

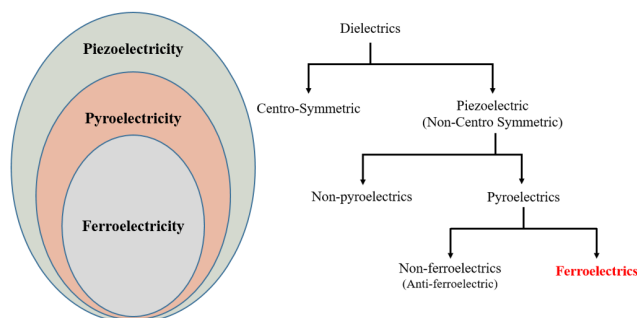


Figure 1. Ferroelectricity within the hierarchy of dielectrics

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Ferroelectricity can be observed in dielectrics through polarization vs. voltage measurements. If ferroelectric, these measurements should result in a hysteresis loop, an example of which can be seen below in figure 2.

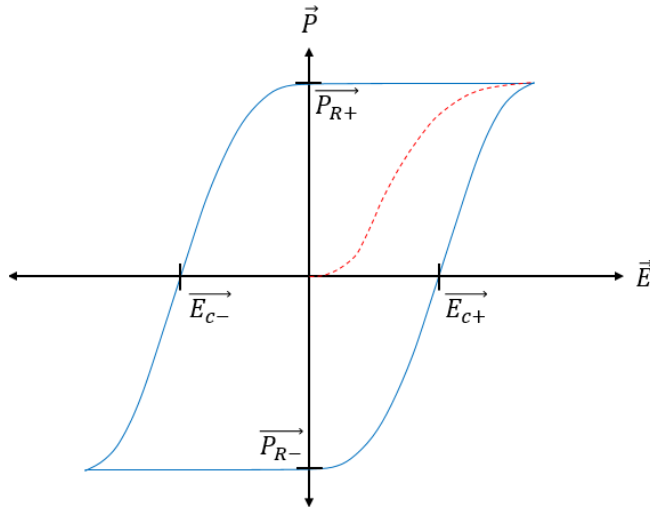


Figure 2. Basic hysteresis loop of ferroelectric material

The nature of how a generic ferroelectric material changes polarization states with applied electric field can be observed in figure 2. In order to initially polarize the material, the ferroelectric must be subject to an external electric field, which is typically done by applying a certain voltage. After a large enough voltage is applied, the ferroelectric will become polarized in either the up or down direction, depending on the voltage applied. Once polarized in either direction, the ferroelectric will maintain the polarization state, even when the external electric field is taken away from the dielectric. This polarization state maintained by the ferroelectric material is known as the remnant polarization, and is labeled as P_R in figure 2.

After being polarized in one direction, an external electric field can again be used to switch the polarization state of the ferroelectric material. For example, say a ferroelectric material is positively poled with a positive remnant polarization, (P_{R+}). If a negative electric field is applied to this material then the domains in the ferroelectric material, which were previously poled in the positive direction, will begin to switch polarization direction. Eventually, if the negative electric field applied is large enough, the material will lose its positive polarization. The magnitude of the electric field at this point is known as the coercive field, labeled as E_C in figure 2, which generally corresponds to a coercive voltage value (V_C). If the negative electric field is then further increased, then the ferroelectric material will

become negatively polarized, and maintain a negative remnant polarization (P_{R-}) after the external electric field is taken away. Thus, the polarization states of ferroelectric materials can be easily switched by applying an electric field.

For HfO_2 , ferroelectricity is observed when the HfO_2 film is in the orthorhombic crystalline phase. Typically, HfO_2 is only found in the natural centrosymmetric phase. However, it was recently discovered that the orthorhombic crystalline phase is achievable in HfO_2 through the introduction of different dopants. Among these dopants are Silicon (Si), Zirconium (Zr), Yttrium (Y), Strontium (Sr), Lanthanum (La), Gadolinium (Gd), and Aluminum (Al). The orthorhombic phase of ferroelectric HfO_2 depends heavily upon the concentration of the dopant in the HfO_2 film, as well as on a rapid thermal annealing (RTA) step that forms the ferroelectric domains in the film.

2.2 Atomic Layer Deposition

Atomic Layer Deposition (ALD) is a highly conformal deposition process that relies on self-limiting surface reactions to deposit one atomic layer at a time.⁸ These self-limiting reactions are performed by introducing different precursors that react with the surface of the wafer. Because each precursor will only react with the surface molecules of the wafer, only a monolayer will be deposited at time. After each self-limiting reaction, the excess precursor in the ALD chamber and the reacted by-products are purged from the chamber, and then the next precursor is introduced so that the next self-limiting reaction. This cycle can then be repeated as many times as need to achieve the desired thickness of the film, allowing for high quality films with accurate thicknesses to be deposited. A depiction of how a generic ALD process works can be seen below in figure 3.

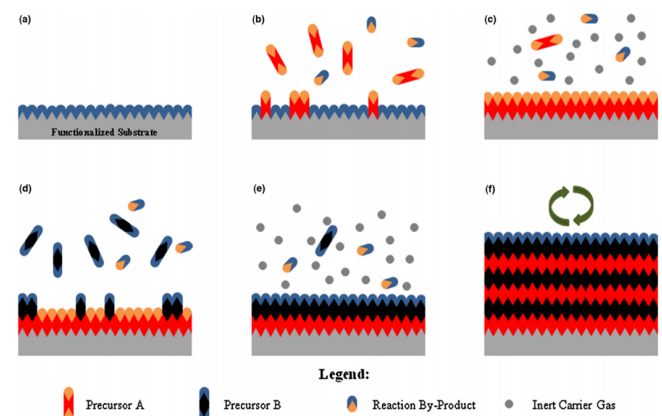


Figure 3. Self-limiting reactions in basic ALD process⁸

Tetrakis(dimethylamido)hafnium(IV)(TDMAHf) is used as the hafnium precursor and H_2O is used as the oxygen precursor for the HfO_2 ALD process performed in this project. Starting with a Si substrate, H_2O is pulsed into the chamber to initialize the surface of the wafer with hydroxyl groups. After a subsequent chamber purge, the hafnium precursor is then pulsed, and the self-limiting reactions between the surface hydroxyl groups and the TDMAHf occur. These self-limiting reactions form a dimethylamine $[(\text{CH}_3)_2\text{NH}]$ as a by-product, and also leave dimethylamine groups around the surface of the wafer. Once the self-limiting reactions have occurred around the surface of the wafer, the by-product dimethylamine groups and the unreacted TDMAHf are purged from the chamber. H_2O is then pulsed into the chamber where it reacts with the dimethylamine groups on the surface of the wafer. This reaction leaves behind Hf-O-Hf bridges along with hydroxyl groups on the surface of the wafer, along with H_2O and dimethylamine by-products. The by-products are then purged from the chamber, and the process is repeated until the desired thickness of HfO_2 is achieved. A depiction of this process can be seen in figure 4.

In order to introduce the Al dopant into the HfO_2 film, trimethyl aluminum (TMA) is used as an Al precursor that is introduced every "X" cycles, where "X" is a predetermined number of Hf precursor cycles. In this case, "X" is what determines the concentration of Al in the HfO_2 film, where a large "X" value corresponds to a low Al concentration, and a small "X" value corresponds to a high Al concentration. In order to achieve ferroelectricity in the HfO_2 layer, a 3%-6% concentration of Al is needed. Thus, "X" is chosen based upon the desired Al concentration and thickness of the film. Like TDMAHf, TMA will react with the hydroxyl groups present on the surface of the wafer, and any TMA groups present on the surface of the wafer will react with H_2O when pulsed. The by-product of these two reactions is methane (CH_4), which is subsequently purged the chamber after the self-limiting have occurred.

2.3 Annealing Conditions

Along with dopant concentration, the ferroelectricity of HfO_2 films depend heavily upon the rapid thermal annealing (RTA) conditions. The annealing step is what allows for the ferroelectric domains to form in HfO_2 layer, thus the size and nature of the ferroelectric domains depend heavily upon the annealing temperature and time. Generally, a metal capping layer deposited before the RTA step is required to obtain ferroelectricity in HfO_2 , which is needed to mechanically confine

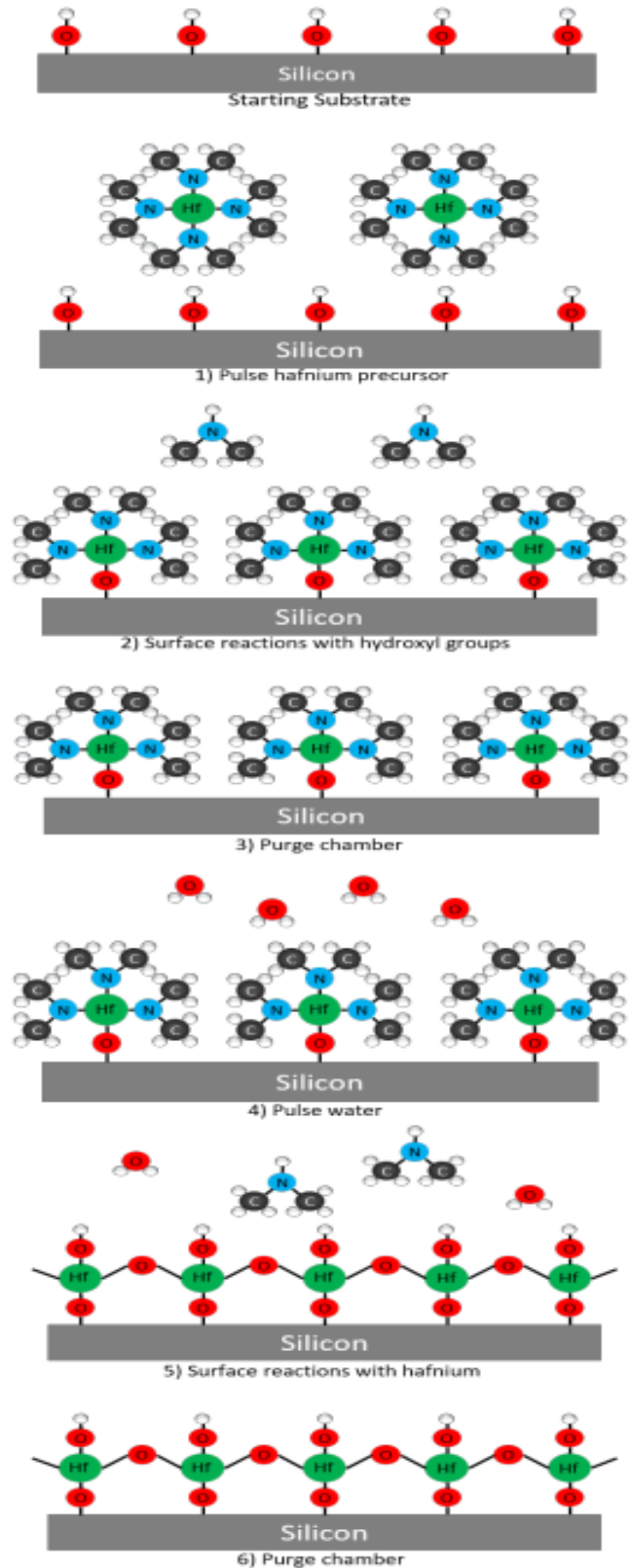


Figure 4. Depiction of self-limiting reactions during HfO_2 ALD cycle⁹

the crystallographic structure to the orthorhombic phase. However, it has recently been discovered that it is possible to achieve ferroelectricity in Al-doped HfO₂ without the presence of a metal capping layer, which was previously thought to only be possible when using rare-earth dopants.

3. EXPERIMENTAL DETAILS

In order to test ferroelectricity in Al-doped HfO₂ films, simple capacitor devices were fabricated. Five p-type degenerately doped silicon wafers ($\rho < 0.005 \Omega\text{-cm}$) were used so that a backside-chuck contact could be used during device testing. After initial wafer cleaning, a reactive sputter process was used to deposit a 20nm - 30nm bottom TiN layer on the bare Si wafers.

Two different Al concentrations, 3.03% and 2.70%, were deposited using an Ultratech Savannah ALD system. As discussed in the theory section, TDMAHf was used as a Hf precursor and TMA was used as Al precursor. Al concentration values were based upon the assumption that TDMAHf and TMA precursors had the same deposition rate, which was assumed to be around 0.94Å/sec at 200°C.

Inclusion of a TiN capping layer was also varied between devices. Like the bottom TiN, a reactive sputter process was used to deposit the capping TiN layer on three of the five wafers. The capping TiN layer was deposited prior to the annealing step to help mechanically confine the Al-doped HfO₂ layer. This capping TiN was not deposited at all on the other two wafers, which underwent a RTA step directly after the HfO₂ deposition. To be consistent with previous literature,¹ the process in which a capping TiN layer was deposited before the RTA step will be referred to as a post-metallization annealing (PMA) process, and the process in which no capping TiN layer is deposited will be referred to as a post-deposition annealing (PDA) process. RTA conditions were varied between both PDA and PMA processed wafers, as annealing temperature was varied between 800°C or 1,000°C and annealing time was varied between 30 seconds or 60 seconds for both PMA and PDA processes.

After annealing, a top contact Al layer was thermally evaporated on to both the PMA and PDA processed wafers. Capacitors were then patterned using a single photolithography step, and the pattern was transferred into the Al using a chemical wet etch process. A wet etch was also used to pattern the TiN capping layer on PMA devices to avoid capacitor shorting. A depiction of both the PMA and PDA process flows can be seen in figure 5.

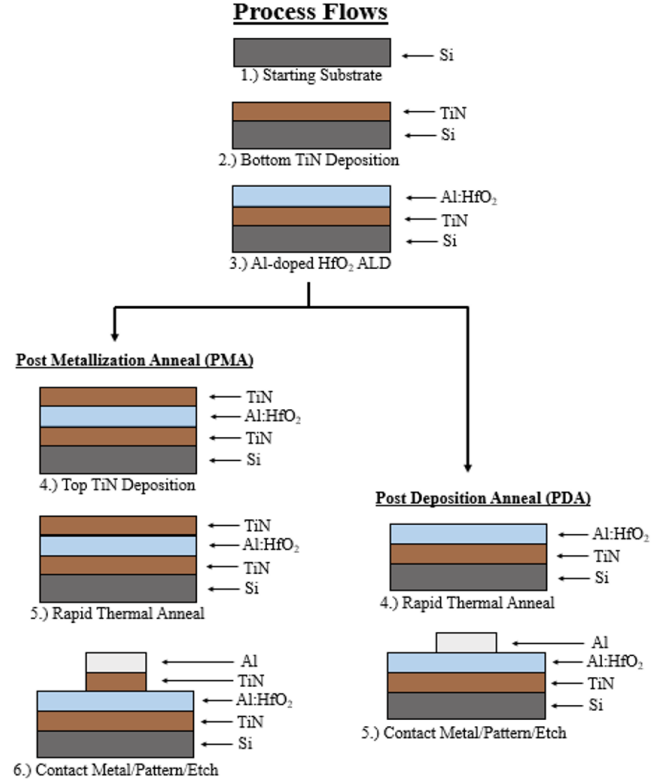


Figure 5. PMA and PDA Capacitor Process Flows

4. RESULTS AND DISCUSSION

An aixACT TF Analyzer 1000 was used to perform polarization vs. voltage testing on the fabricated PMA and PDA Al:HfO₂ capacitors to observe whether or not devices were ferroelectric. A summary table of the various devices fabricated and whether ferroelectricity was observed in them can be seen below in figure 6.

Sample	Process	Al Percentage	RTA Temp [°C]	RTA Time [s]	Ferroelectric
1	PMA	3.03%	800	60	No
2	PMA	3.03%	1000	30	No
3	PDA	3.03%	1000	30	Yes
4	PMA	2.70%	1000	60	No
5	PDA	2.70%	1000	60	Yes

Figure 6. Summary Table of Fabricated Capacitor Devices

As seen in the summary table, ferroelectricity was observed on both PDA processed wafers, but not on any of the PMA processed wafers. The two PDA wafers displayed similar positive and negative coercive voltage values ($|V_C| \approx 2V$), however larger positive and negative remnant polarization values ($P_{R+} = 5.83 \mu\text{C}/\text{cm}^2$, $P_{R-} = -5.53 \mu\text{C}/\text{cm}^2$) were observed in the 2.70% Al

sample annealed at 1,000°C for 60 seconds (sample 5) compared to 3.03% Al sample annealed at 800°C for 60 seconds (sample 3), which had positive and negative remnant polarization values $P_{R+}=2.29 \mu\text{C}/\text{cm}^2$ and $P_{R-}=-2.32 \mu\text{C}/\text{cm}^2$. The polarization vs. voltage plots for both samples can be seen below in figures 7 and 8.

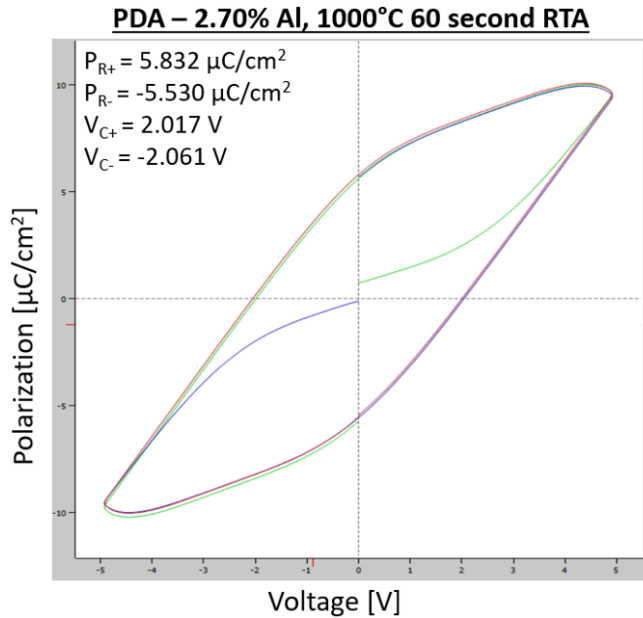


Figure 7. Ferroelectric Hysteresis from Polarization vs. Voltage measurement on 2.70% Al PDA Device

The larger observed P_R values in the 2.70% PDA sample is likely due to the 30-second longer annealing time allowing for an increased amount of ferroelectric domain formation in the Al:HfO₂ layer. Though it is possible that the difference in dopant concentration also caused the difference in P_R values, it can not be concluded for certain as the assumed concentration values are based upon believed growth rates and not verified with measurement.

The polarization vs. voltage measurements indicated no ferroelectricity in the PMA fabricated devices, which instead just show capacitor characteristics. There were two imperfections in the top TiN deposition process that may have attributed to the lack of ferroelectricity in the PMA devices. The first potential issue is the relatively high base pressure reached before sputtering, as the remnant O₂ in the chamber may have resulted in a TiON layer being deposited rather than a pure TiN. The other potential issue is the introduction of trap charges during the deposition process that inhibit ferroelectricity. Though the use of a TiN reactive sputter process made the introduction of trap charges into the Al:HfO₂ layer inevitable, the amount introduced was minimized by the use of low-power sputter process. It is also possible that the top TiN layer on the PMA devices absorbed some of the heat during the RTA step, inhibiting the formation of ferroelectric domains in the layer. An example of a polarization vs. voltage measurement taken on a PMA fabricated device can be seen in figure 9.

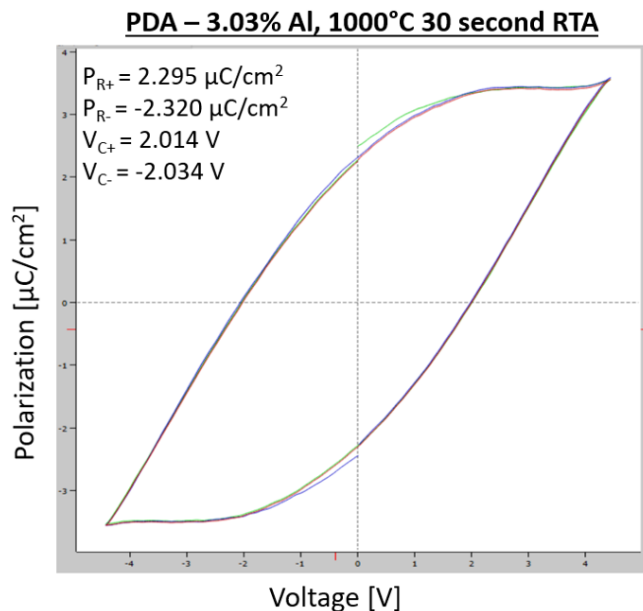


Figure 8. Ferroelectric Hysteresis from Polarization vs. Voltage measurement on 3.03% Al PDA Device

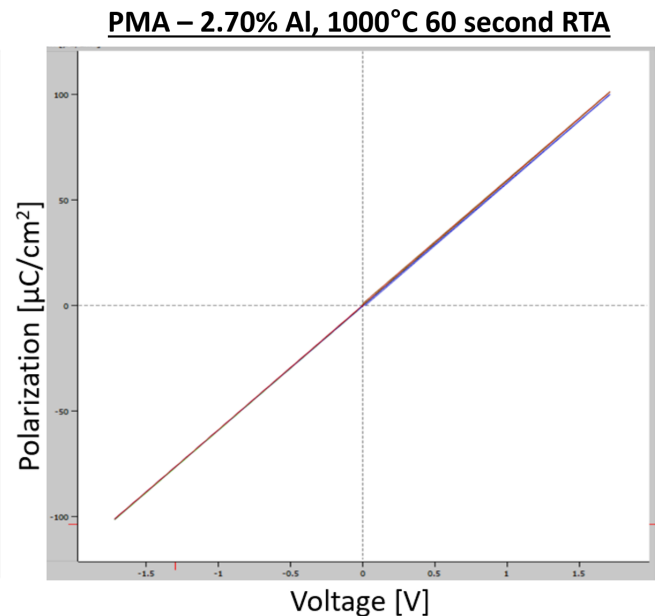


Figure 9. Basic Capacitor Characteristics seen in Polarization v. Voltage measurement of 2.70% Al PMA device

5. CONCLUSION

Ferroelectric Al:HfO₂ capacitors were fabricated using an ALD process at RIT. Al dopant concentration, annealing temperature and annealing time were varied between PMA processed devices and PDA processed devices to study their effects on ferroelectricity. Polarization vs. Voltage testing using an aixACT TF Analyzer 1000 indicated the presence of ferroelectricity in PDA fabricated devices, but only capacitor characteristics in PMA fabricated devices. Both PDA devices displayed positive and negative coercive voltage magnitudes with values around $|V_C| \approx 2\text{V}$, however the PDA device with 2.70% Al concentration annealed for 60 seconds at 1,000°C displayed higher P_R values than the PDA device with 3.03% Al concentration annealed for 30 seconds at 1,000°C. The larger P_R values seen in the 2.70% Al PDA fabricated devices is attributed to the longer annealing step allowing for more ferroelectric domain growth, though the difference in Al dopant concentration may have also played a role. The lack of ferroelectricity in the PMA fabricated devices was assumed to be a result of an imperfect top TiN reactive sputter process.

These results have opened the doors for all sorts of new projects to be performed at RIT, as the ability to deposit ferroelectric Al:HfO₂ makes the fabrication of numerous different ferroelectric devices possible. Optimization of the ALD process and the subsequent RTA conditions is still needed, and investigation into a new method of deposition for the top TiN layer can still be performed. On top of this, a thickness study to determine the minimum thickness in which ferroelectricity is still achieved in Al:HfO₂ would be useful for the future fabrication of FTJ devices. Also, investigation of a etching technique to pattern Al:HfO₂ without inhibiting the ferroelectric properties of the film will be required to fabricate ferroelectric devices such as FeFETs or NC FETs.

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