Atomic Layer Deposition of Ferroelectric HfO$_2$

Casey J Gonta
Department of Electrical and Microelectronic Engineering
Rochester Institute of Technology, 1 Lomb Memorial Drive, Rochester NY, USA

Abstract—Ferroelectric (FE) materials exhibit spontaneous polarization making them particularly attractive for non-volatile memory and logic applications. Recently, doped hafnium oxide has shown to be ferroelectric in nature expanding its applications to these areas of interest. Ferroelectricity has been reported in atomic layer deposition (ALD) of HfO$_2$ with Al, Y, or Si dopants. Previous work at RIT demonstrated functional ferroelectric field effect transistors (FeFETs) using silicon doped HfO$_2$ (Si:HfO$_2$) as the gate dielectric.

The new addition of a Savannah ALD system at RIT has made deposition of doped HfO$_2$ films possible. Recipes have been developed for deposition of aluminum doped HfO$_2$ using the hafnium precursor TDMAHf, tetrakis(dimethylamido)hafnium(IV), and the aluminum precursor TMA, trimethyl aluminum. Transmission electron microscopy (TEM) imaging and electron energy loss spectroscopy (EELS) were performed on the deposited Al:HfO$_2$ films. TEM images verified that the target of a 10nm film was achieved. The separate Al layers could faintly be seen in TEM images of unannealed samples. Capacitors with the deposited Al:HfO$_2$ were fabricated and tested. A small amount of ferroelectric behavior has been observed however with low breakdown voltage as well as high leakage current.

Index Terms—Atomic Layer Deposition, ALD, Hafnium, Ferroelectric, TEM, EELS

I. INTRODUCTION

MOORE’S law is the observed trend that the number of transistors per a given area in an integrated circuit (IC) doubles about every two years. The most impactful innovations in the microelectronics industry are those that keep this trend alive. As transistors have become smaller and smaller, silicon dioxide (SiO$_2$) has been replaced as the standard gate dielectric by materials that possess a higher relative permittivity or dielectric constant. These materials are referred to as high-k dielectrics.

Compared to SiO$_2$ which has a dielectric constant (k) of 3.9, hafnium dioxide (HfO$_2$) is a high permittivity dielectric material with a dielectric constant of approximately 25. HfO$_2$ and other hafnium based oxides have replaced SiO$_2$ as the gate dielectric in silicon CMOS devices since the 45nm node.

Recently, it has been proven that by doping the HfO$_2$ with a small atomic percent of materials such as aluminum (Al), yttrium (Y), or silicon, the dielectric shows ferroelectric behavior. Unlike ceramic materials like lead zirconate titanate (PZT) which have been known to show ferroelectric behavior, HfO$_2$ is CMOS compatible, scalable down to desired gate thicknesses, and atomic layer deposition (ALD) compatible. Ferroelectric HfO$_2$ has opened doors to many applications such as ferroelectric field effect transistors (FeFETs), negative capacitance FETs (NC FETs), ferroelectric tunnel junctions (FTJs), and ferroelectric random access memory (FRAM).

II. THEORY

A. Ferroelectricity

The crystal structure of hafnium oxide, whether bulk or thin film, is centrosymmetric and known to be non-ferroelectric. However, with certain amounts of dopant in the hafnium oxide, the proper annealing conditions, and stress from a capping layer, the material falls into the non-centrosymmetric orthorhombic crystal phase leading to ferroelectric behavior.

Normal dielectric materials cannot retain a polarization without voltage. A polarization vs voltage measurement of a capacitor with a normal dielectric would result in a line through the origin with a single slope. A ferroelectric capacitor measured in the same fashion results in a hysteresis
loop instead of a line. It can be seen in Figure 1 that in a measurement of this nature, two polarization states are present with zero applied voltage. A characteristic property of a ferroelectric material is this spontaneous polarization and the amount of charge due to this polarization is referred to as the remnant polarization. The electric field required to eliminate this polarization, and further reverse it, is called the coercive field.

Fig. 1. Polarization vs voltage of a capacitor showing ideal ferroelectric hysteresis behavior. The remnant polarization and coercive field are labeled.

### B. Atomic Layer Deposition

Atomic layer deposition (ALD) is a useful process for the fabrication of microelectronics due to its ability to produce accurate thicknesses and uniform surfaces in addition to high quality film production using various different materials. In microelectronics, ALD has been implemented as a technique to deposit high permittivity gate oxides, high permittivity memory capacitor dielectrics, ferroelectrics, and metals and nitrides for electrodes and interconnects.

ALD is a technique similar to that of chemical vapor deposition, but has specific differences. ALD is a method in which a thin film is grown on a substrate by exposing its surface to alternating gaseous species. Like chemical vapour deposition (CVD), it uses gaseous precursors, however the precursors are never present simultaneously. Instead, the gaseous precursors are inserted as a series of sequential, non-overlapping pulses. Each pulse is therefore a self limited reaction, terminating when surface reactions with the precursor and all of the available bonds on the surface have taken place.

### III. Experimental Details

#### A. Material Development

The first reports on ferroelectric HfO$_2$ were by NaMLab in Dresden, Germany in 2011. In 2015, previous studies were conducted at RIT by Joe McGlone, a Microelectronic Engineering student, on ferroelectric field effect transistors (FeFETs) with depositions of the ferroelectric material done in partner by NaMLab. In fabrication of these devices, the gate dielectric was silicon doped hafnium oxide (Si:HfO$_2$). The devices were fabricated up to the point of the gate stack deposition. At this point the devices were sent to NaMLab for atomic layer deposition of the Si:HfO$_2$ and a capping layer of TiN deposited by DC reactive sputtering. An anneal of the layers was also conducted by NaMLab and then returned. The final steps in fabrication of the devices were then done at RIT. The polarization vs voltage measurements of the RIT MFIS capacitors as well as NaMLab MFM capacitors, done by Joe McGlone, are shown in Figure 2.

![Comparing NaMLab and RIT Capacitor P-V Curves](image)

Fig. 2. Comparison between the NaMLab metal-ferroelectric-metal (MFM) capacitor and the RIT processed metal-ferroelectric-insulator-silicon (MFIS) (N+ Si) capacitor.

The new addition of a Savannah ALD system at RIT has made deposition of doped HfO$_2$ films possible. Although the most successful dopant reported on is silicon, the ALD system at RIT is currently only equipped with hafnium, titanium, and zinc precursors. Recipes have been developed for aluminum doped hafnium oxide (Al:HfO$_2$) ALD.
B. Process Details

For fabrication of capacitor devices with the Al:HfO$_2$ material, the substrate was degenerately doped ($\rho < 0.0012 \ \Omega \cdot \text{cm}$) p-type silicon for direct contact to the device when testing. For ALD of the Al:HfO$_2$ material, the hafnium precursor TDMAHf, tetrakis(dimethylamido)hafnium(IV), and the aluminum precursor TMA, trimethyl aluminum were used.

Starting with a freshly cleaned silicon substrate, hydroxyl groups are present on the silicon surface. To initiate the ALD, the hafnium precursor is pulsed into the chamber. Surface reactions then occur with the hafnium precursor and the exposed hydroxyl groups. The result of this is the hafnium atoms bonded to the oxygen atoms from the hydroxyl groups and dimethylamine, (CH$_3$)$_2$NH, as a by-product. The chamber is then purged, removing all unreacted hafnium precursor and dimethylamine by-product. DI water is then pulsed into the chamber to react with the rest of the exposed end groups from the initial precursor attached to the hafnium atoms. This reaction results in the formation of hafnium-oxygen-hafnium bridges. The chamber then contains unreacted water molecules as well as the by-product which is once again dimethylamine. Another purge is then performed to evacuate the unreacted water molecules and dimethylamine by-product, which then leaves the surface with exposed hydroxyl groups ready to accept the next layer of hafnium atoms. This sequence is depicted in Figure 3. This entire sequence is then repeated to form layer after layer of HfO$_2$. Each cycle deposits about 0.94 Å of HfO$_2$.

Once every “N” cycles of hafnium precursor in this sequence, the aluminum precursor is pulsed instead of the hafnium precursor and reacts with the surface in the same fashion. “N” is calculated based on the desired dopant percent in the film. For example, a 4% Al doped film could be 96 pulses of the hafnium precursor and 4 pulses of the aluminum precursor for a targeted 100 Å film. The by-product of the reaction between the aluminum precursor trimethyl aluminum, Al(CH$_3$)$_3$, and the exposed hydroxyl groups, as well as the subsequent reaction with the water molecules, is simply methane: CH$_4$.

For the capacitor device structures, a DC reactive sputtered titanium nitride (TiN) capping layer was deposited on top of the Al:HfO$_2$. An aluminum layer
for top contact was then deposited by DC sputtering and a simple single expose and develop lithography process was performed. The final capacitor stack structures were then formed by reactive ion etching down to the silicon and stripping the photoresist.

Films were deposited with aluminum dopant concentrations ranging from 3% to 8% and different annealing conditions after TiN deposition were performed ranging from 800°C to 1000°C for either 1 or 20 seconds.

IV. RESULTS AND DISCUSSION

POLARIZATION vs voltage measurements were conducted on the fabricated Al:HfO₂ capacitors as well as regular HfO₂ capacitors with the same thickness dielectric. Figure 4 shows the polarization vs voltage measurements of a 4% Al:HfO₂ capacitor. It can be seen that when swept to ±1V, the device behaves like a normal capacitor (linear). Once voltage is swept higher than 1V, ferroelectric properties (hysteresis) should be able to be observed. However, this measured device, like many other devices tested, when a voltage higher than this is applied, breakdown of the dielectric is seen and the polarization curve approaches that of a resistor. Very inconsistently, devices tested resulted in shapes anywhere between that of what is depicted in Figure 4.

Transmission electron microscopy (TEM) imaging and electron energy loss spectroscopy (EELS) were performed on the deposited Al:HfO₂ films as well as the normal HfO₂ films. Figure 5 shows a TEM image of a capacitor with normal HfO₂ as the dielectric. It can be seen in this image that the targeted 10nm dielectric film was achieved. Figure 6 shows an EELS line profile of the same device shown in the TEM image in Figure 5. This EELS line profile shows the elemental composition of the different layers of the device, top aluminum, middle HfO₂ of approximately 10nm, and bottom silicon substrate, proving that the desired materials were successfully deposited.

Figure 7 shows a TEM image of an unannealed capacitor device with 4% Al:HfO₂. This image not only shows that the deposited dielectric layer is also approximately the targeted thickness of 10nm, but very faintly, four distinct layers of what is assumed to be aluminum can be seen.
approximately $2 \times 10^{-4} \text{cm}^2$, the thickness ($t$) of the Al:HfO$_2$ was approximately $1 \times 10^{-6} \text{cm}$, the relative permittivity of SiO$_2$ ($\epsilon_r$) is 3.9, and the known permittivity of free space ($\epsilon_0$) is $8.854 \times 10^{-14} \text{F/cm}$. Using these known values and the measured interfacial oxide thickness ($t_{\text{SiO}_2}$) of $2 \times 10^{-7} \text{cm}$, Equation 2 can be used where Equation 1 is used for the value of $C_{\text{Al:HfO}_2}$. The relative permittivity of the Al:HfO$_2$ calculated in this fashion is approximately 23.9.

V. CONCLUSIONS AND FUTURE WORK

HAFNIUM oxide (HfO$_2$) as well as aluminum doped hafnium oxide (Al:HfO$_2$) have both been successfully deposited by atomic layer deposition at RIT for the first time. Capacitors with the deposited dielectric materials were fabricated and tested. P-V testing of the devices however, resulted in low breakdown voltages observed at smaller voltages than ferroelectric behavior is reported to occur. TEM images and EELS analysis have proved that the deposited films are of the desired thickness and material composition. The deposited dielectrics also possess a calculated dielectric constant, relative permittivity, of approximately 23.9 which is very close to that of the reported value of 25.

This project has opened the door to a great amount of future work. Moving onward, fabrication variations will be considered to limit interfacial oxide. An in depth study of the annealing conditions will be done to achieve the proper orthorhombic crystal phase. X-ray diffraction will be conducted to calculate the exact crystal phase the materials exhibit after annealing.
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