Atomic Layer Deposition of Ferroelectric HfO_2

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Outline

- Introduction
  - Background
  - Previous Work at RIT
  - Project Objectives
- Process
  - ALD Development
  - Fabrication of Capacitor Devices
- Results
  - TEM and EELS
  - CV Measurements
- Conclusions and Future Work

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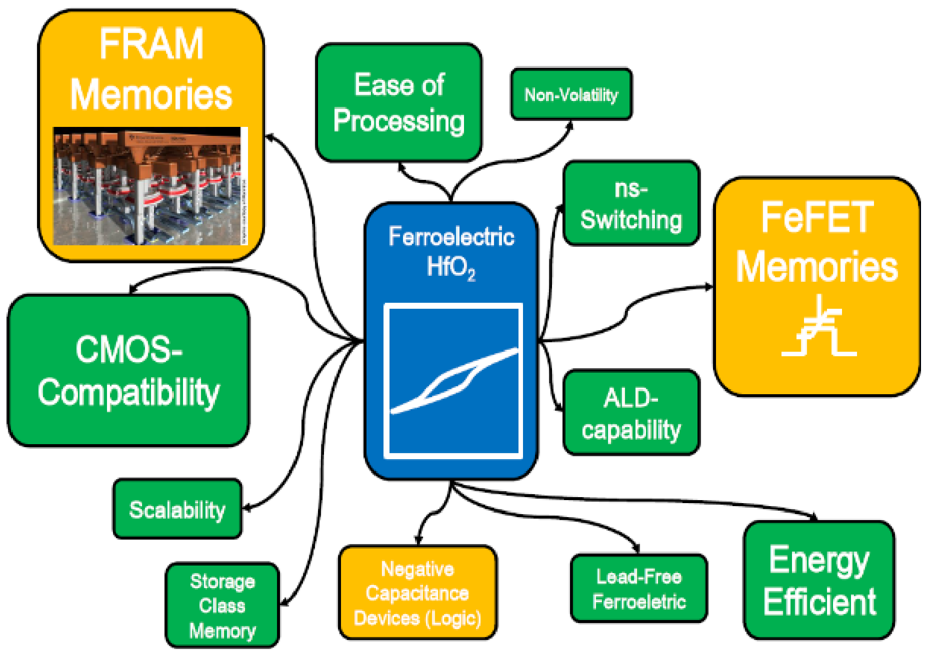
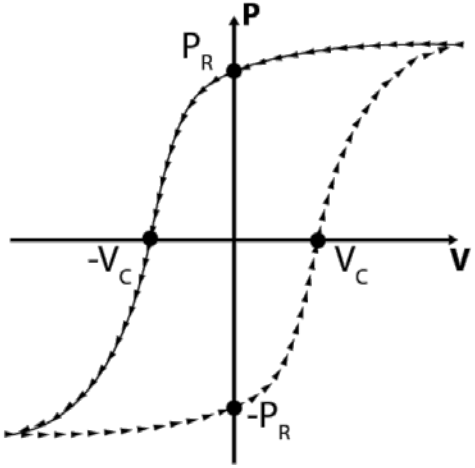
Background

- Hafnium oxide (HfO_2) is a high permittivity dielectric material (dielectric constant k~25)
- HfO_2 has replaced SiO_2 as the gate dielectric in silicon CMOS since the 45nm node
- Doped HfO_2 has shown to be ferroelectric in nature expanding its applications to devices such as FeFETs, FRAM, NC FETs, and FTJs



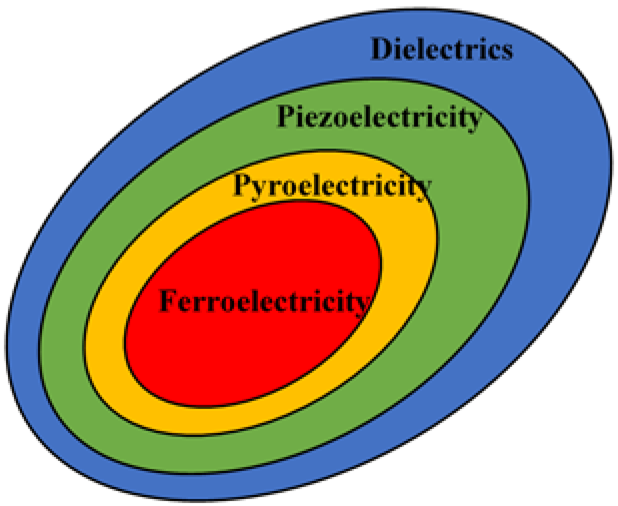
What is Ferroelectricity?

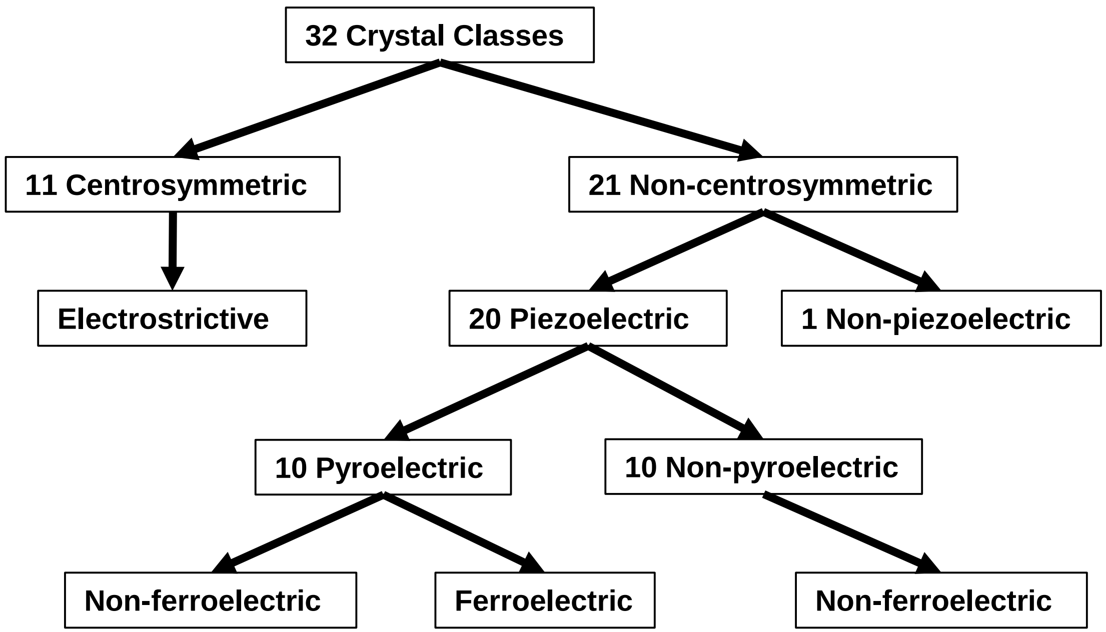
- **Ferroelectric (FE) materials exhibit spontaneous polarization making them particularly attractive for non-volatile memory and logic applications**
- **In ferroelectric material when no bias is applied, Remnant Polarization (P_R) is present**
- **With no polarization, a Coercive Field (V_C) is present**



What is Ferroelectricity?

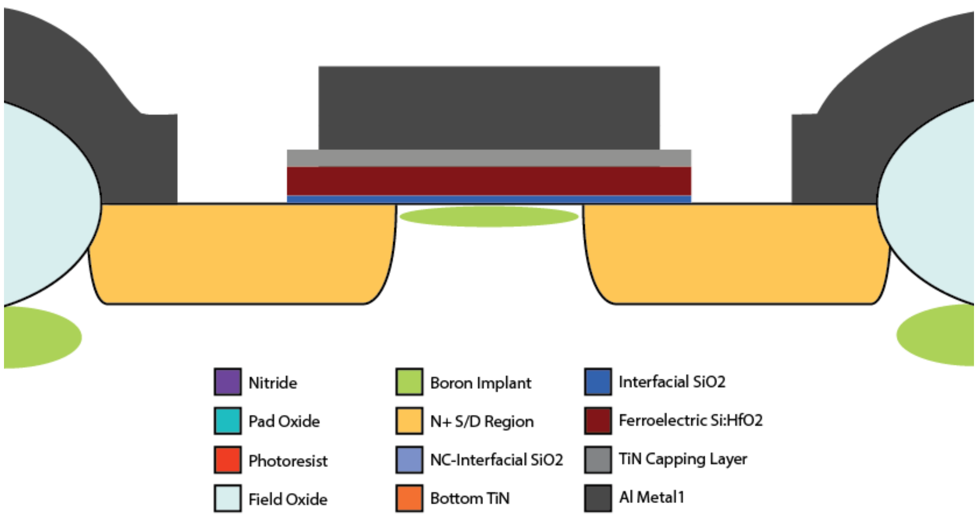
- **Within the realm of Dielectrics exist:**

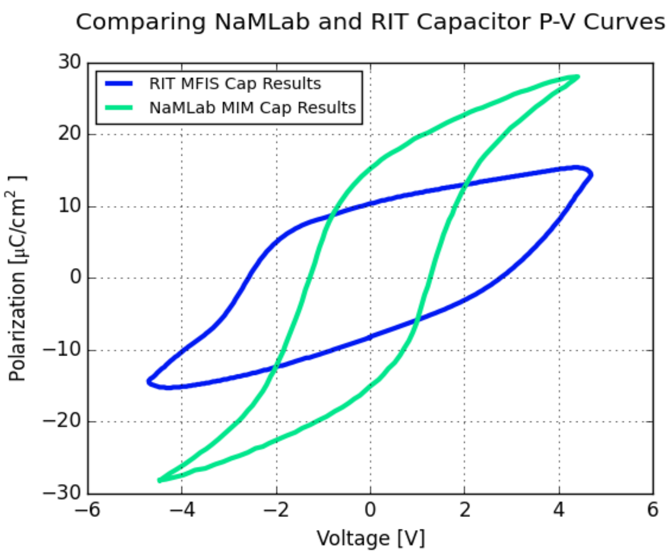




Previous Work at RIT

- Ferroelectric transistors (FeFETs) have been fabricated at RIT by Joe McGlone
- Collaboration and ferroelectric Si:HfO_2 depositions from NaMLaB in Dresden, Germany





Project Objectives

Goal: To engineer ferroelectric HfO_2 solely at RIT by:

- **Developing a recipe for atomic layer deposition (ALD) of aluminum doped HfO_2**
- **Fabricating capacitor structures to characterize the performance of the doped and un-doped HfO_2**
- **Conducting polarization and current testing on capacitors to observe and verify ferroelectric properties**

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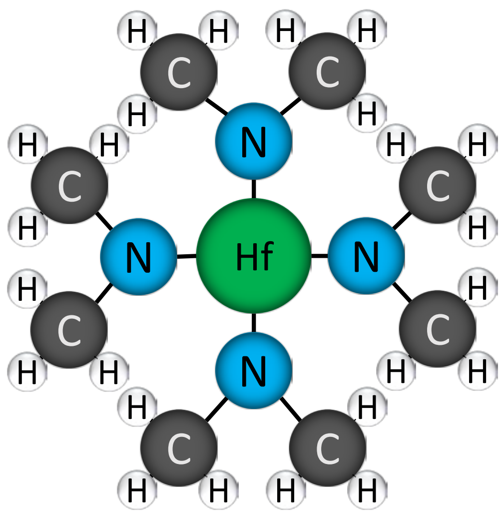
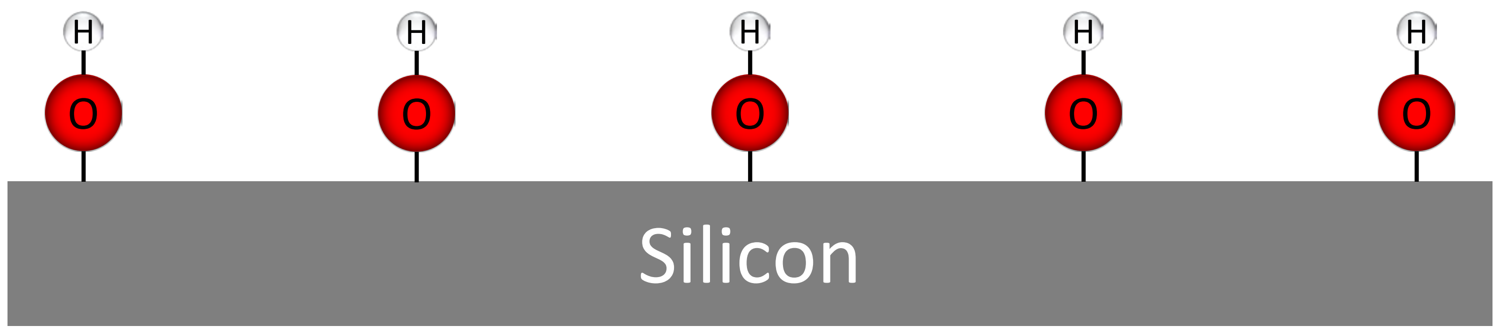
Introduce Hf Precursor to Starting Substrate



TDMAHf

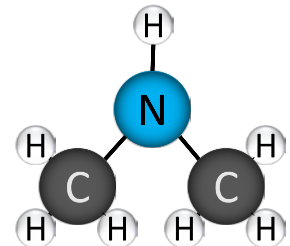
Tetrakis(dimethylamido)hafnium(IV)

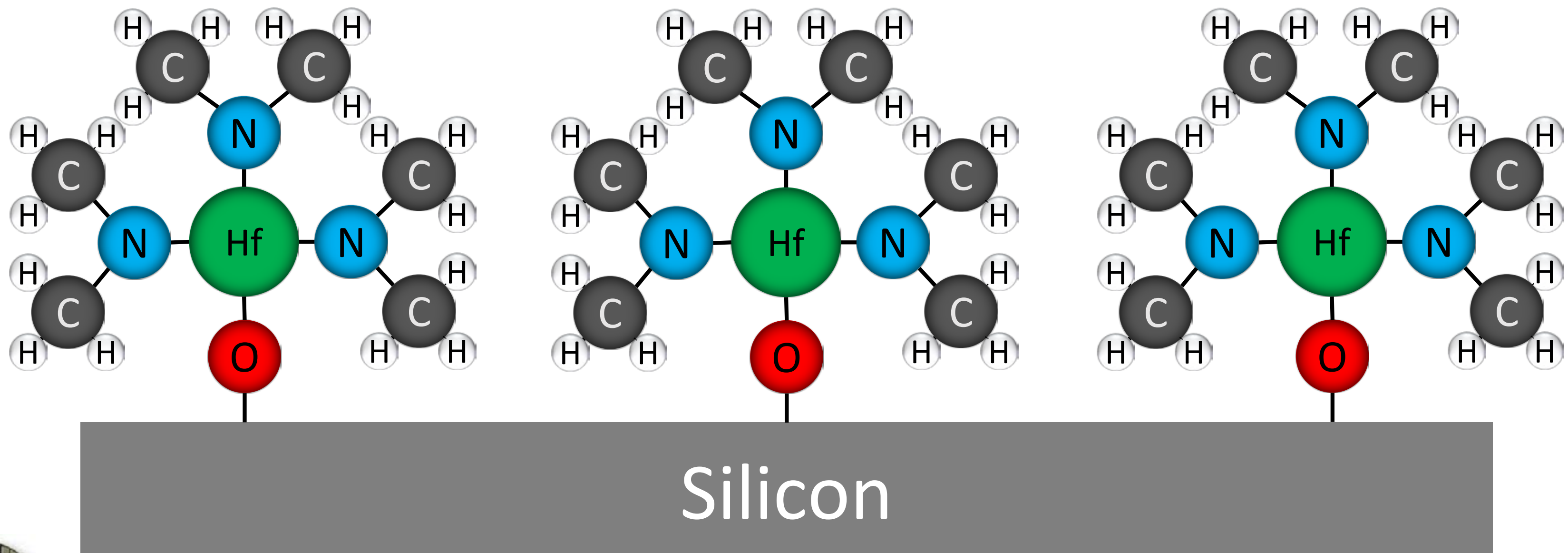
$Hf(N(CH_3)_2)_4$



Self Limiting Surface Reactions

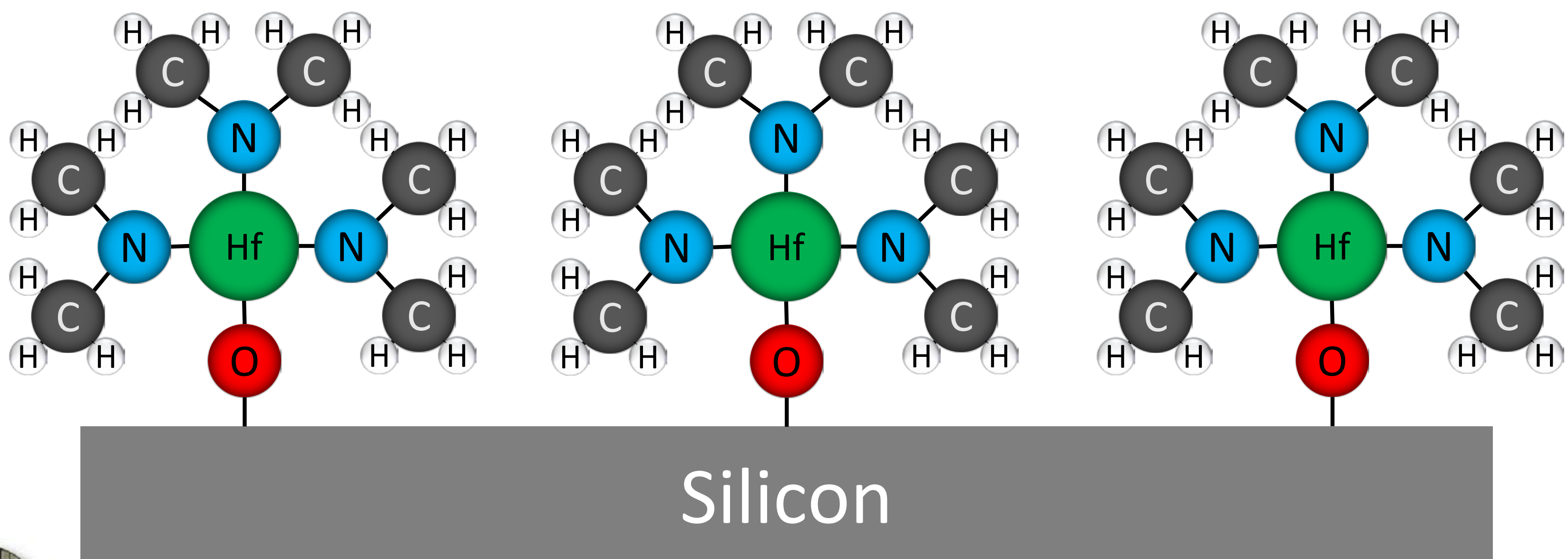
- **Surface reactions between OH groups and TDMAHf**
- **By-product is Dimethylamine: $(CH_3)_2NH$** →





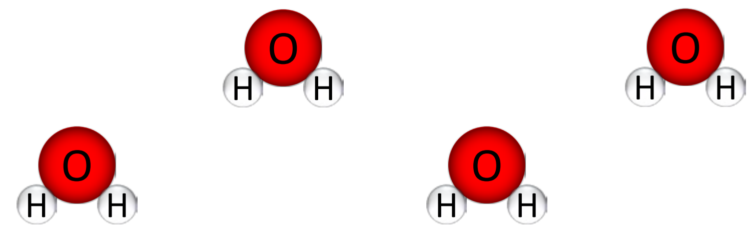
Purge

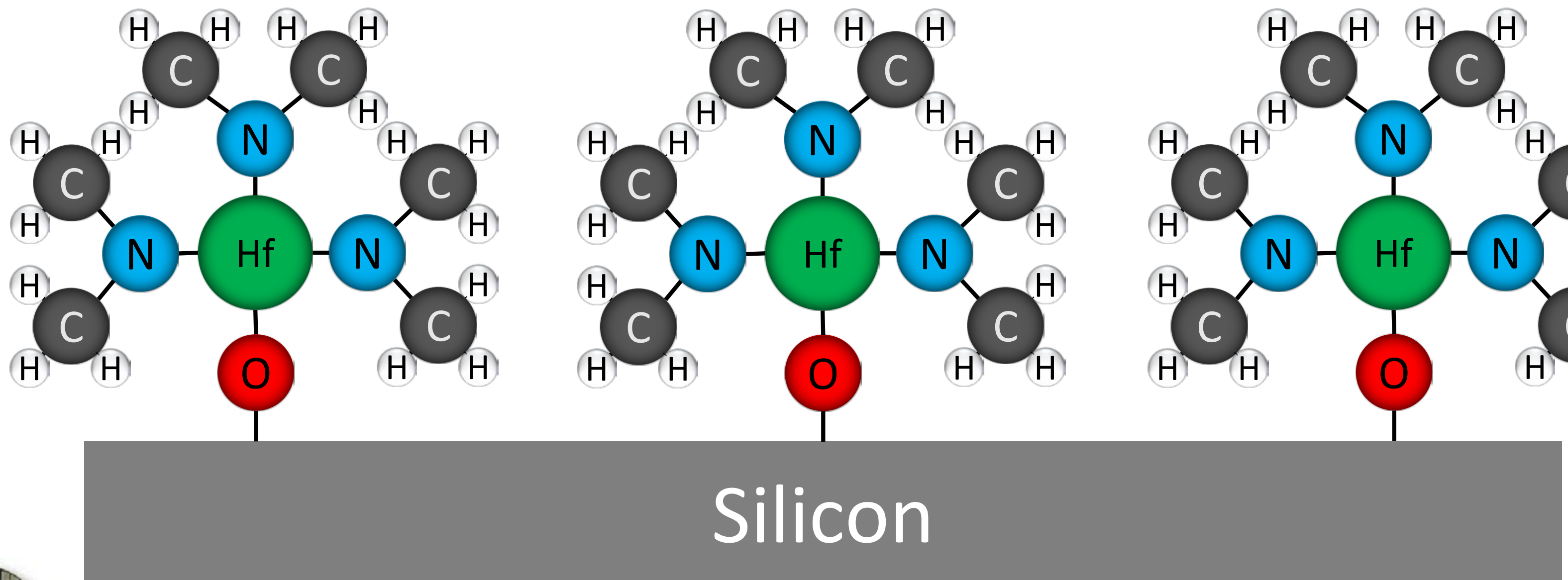
- **The chamber is then purged, removing all unreacted TDMAHf precursor and dimethylamine by-product**



Introduce H_2O

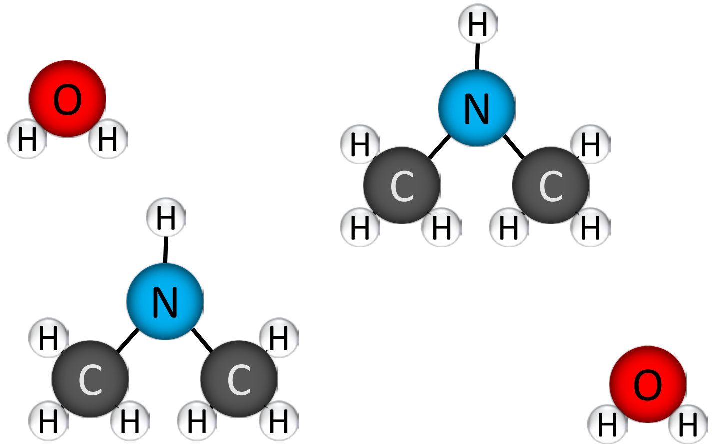
- **Water is then introduced to react with the exposed surface dimethylamine groups on the deposited hafnium atoms forming Hf-O-Hf bridges**

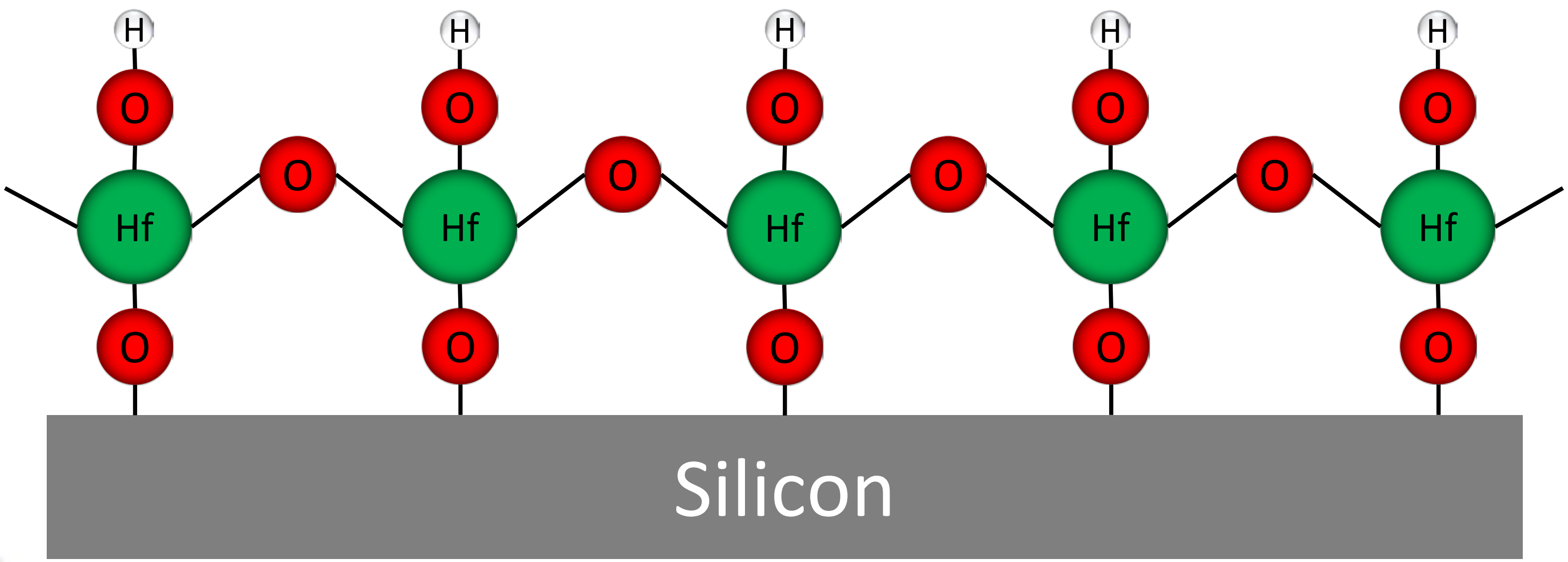




Reaction

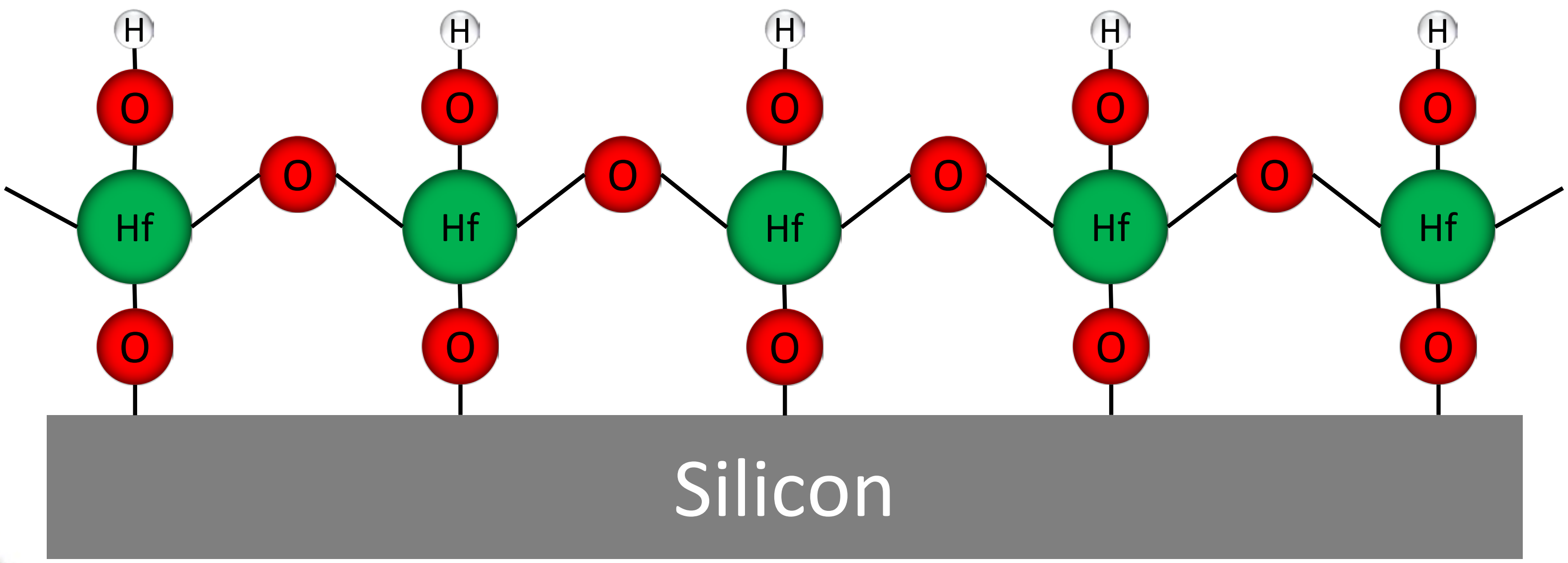
- **The resulting reaction leaves the surface with hydroxyl groups and Hf-O-Hf bridges**
- **The chamber then contains unreacted water molecules and the by-product which is once again dimethylamine**





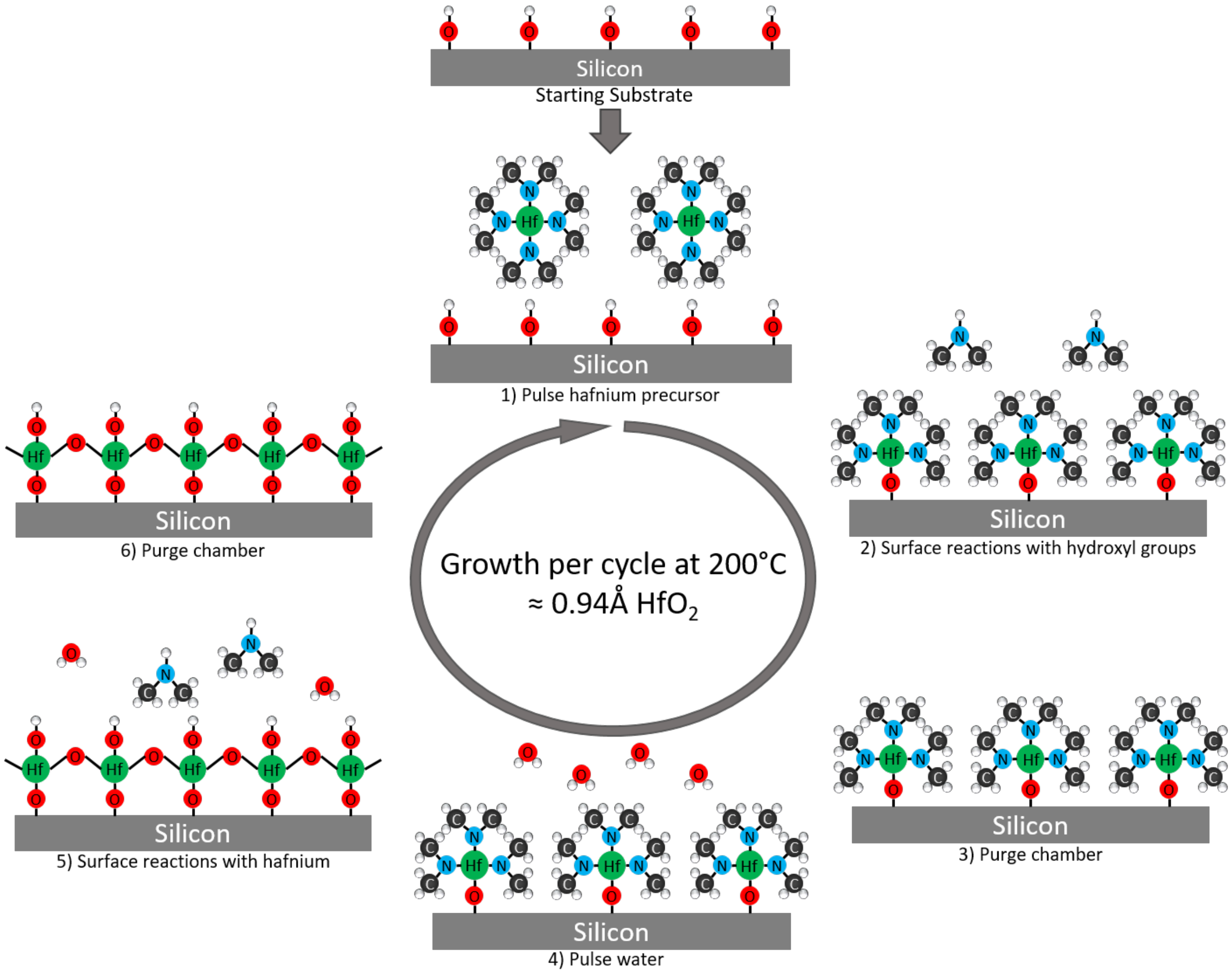
Purge

- **Another purge is done to evacuate the chamber of unreacted water molecules and the dimethylamine by-product**
- **The surface is then ready to accept the next layer of hafnium atoms**



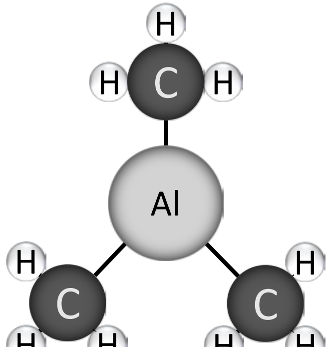
Repeat

- **The whole sequence is then repeated to form layer after layer of HfO_2**

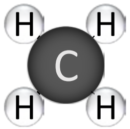


How is the Aluminum Dopant Introduced?

- **Once every "X" cycles of hafnium precursor, an aluminum precursor is pulsed and reacts with the surface in the same fashion**
- **The aluminum precursor used is TMA – trimethyl aluminum: $Al(CH_3)_3$**

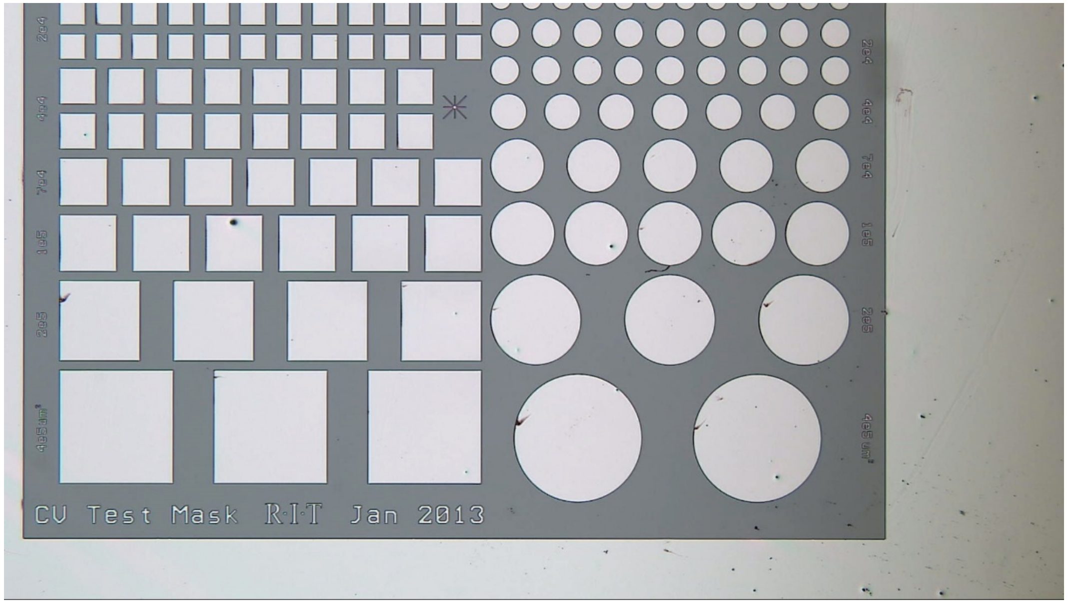


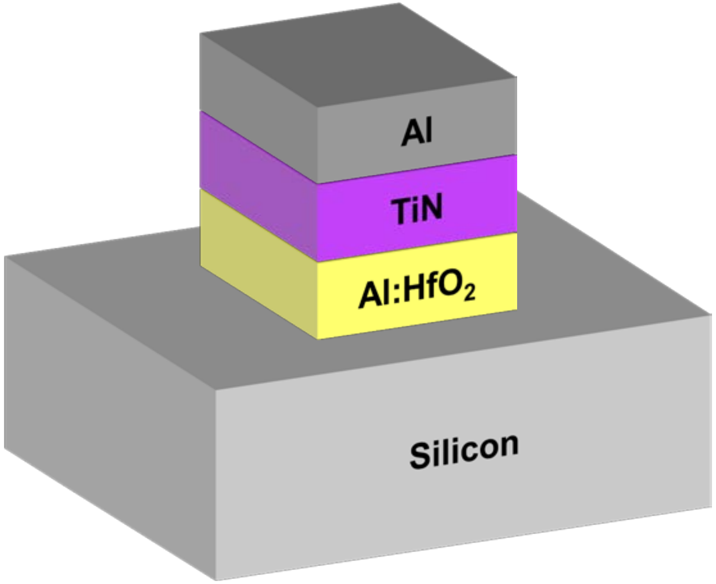
- **The by-product of this reaction with the exposed hydroxyl group, as well as the subsequent reaction with water, is simply methane: CH_4**



Fabrication of Capacitor Devices

- **Capacitor devices were fabricated for electrical testing**





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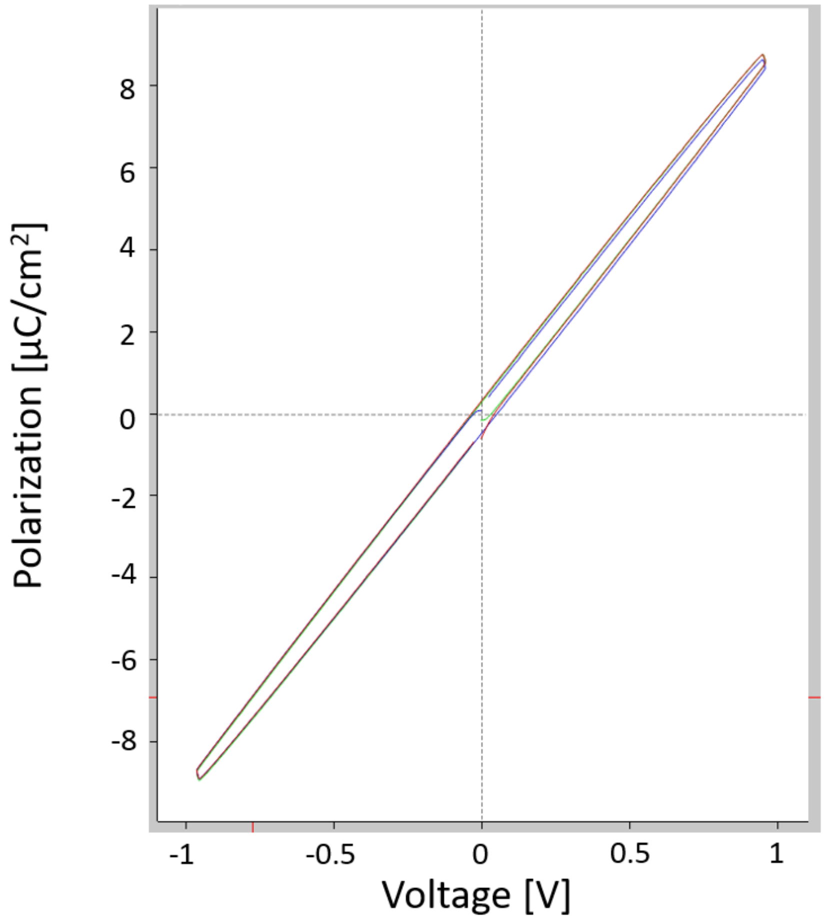
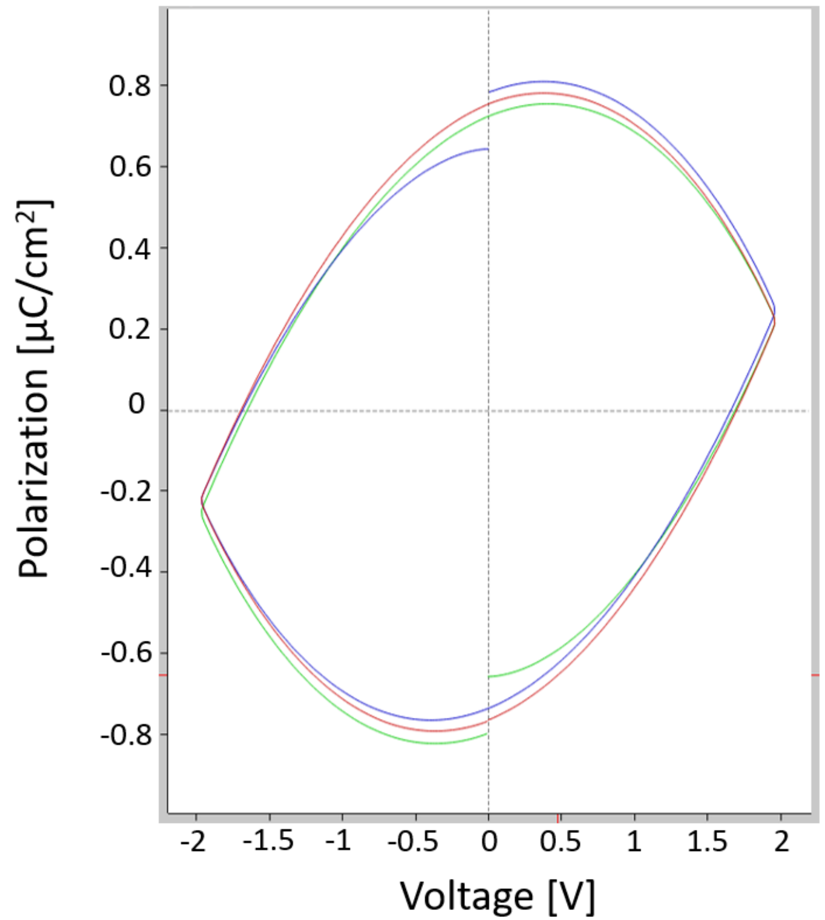
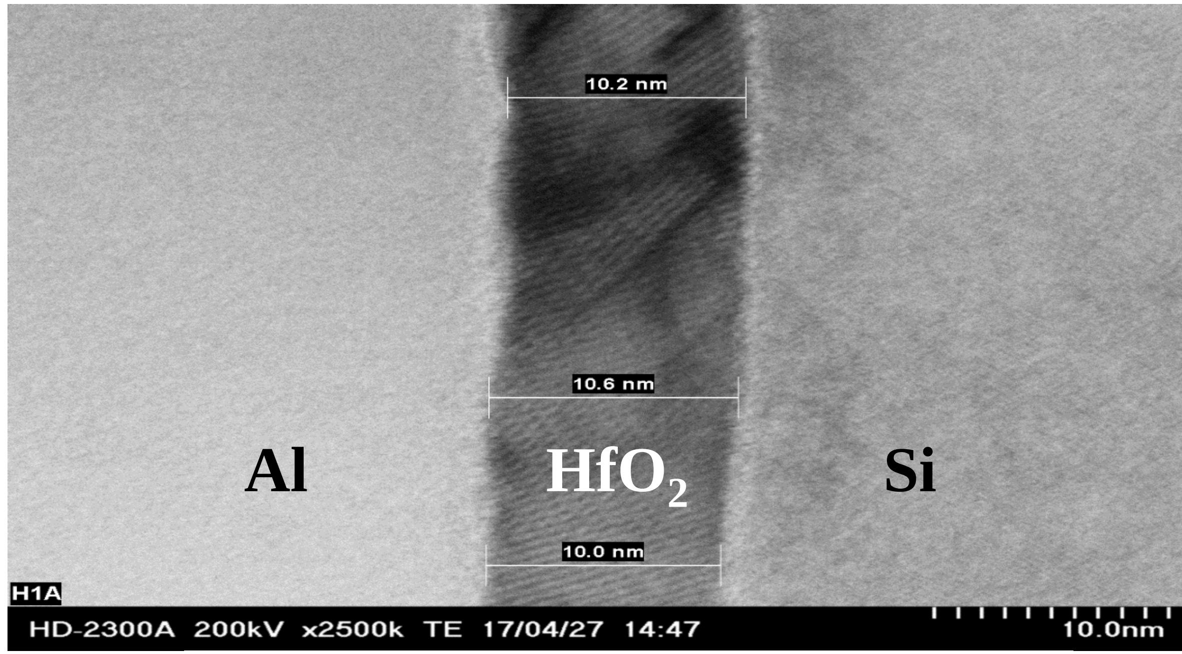
Polarization Measurements

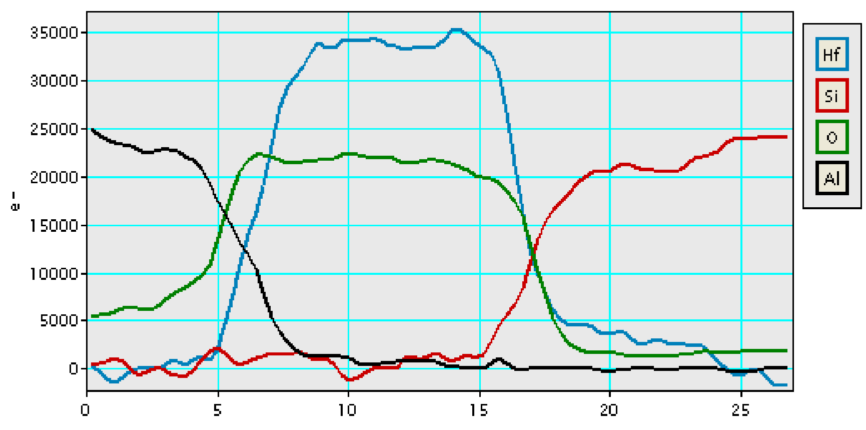




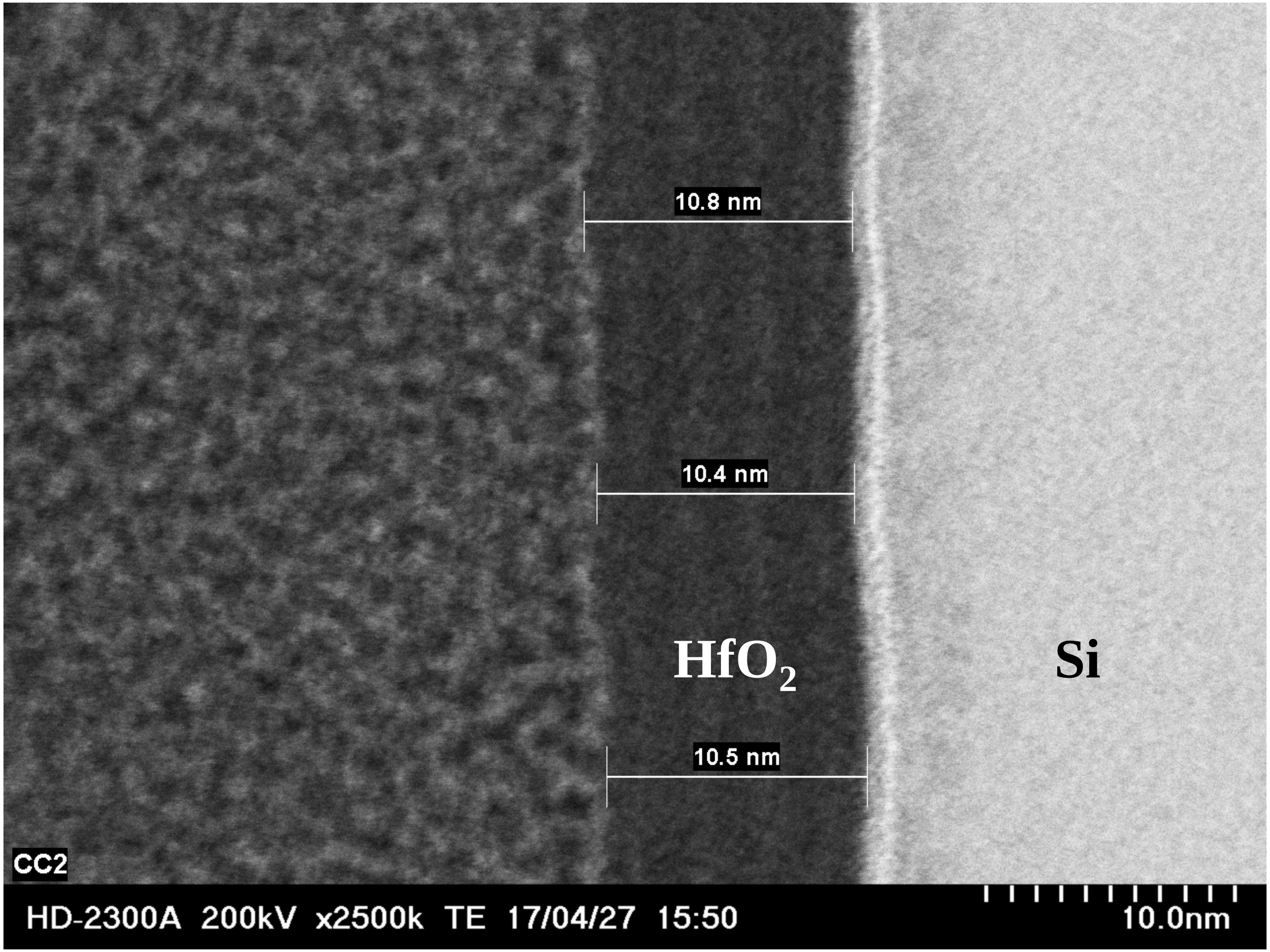
TEM and EELS

- **TEM and EELS of HfO_2 samples demonstrated that the new Savannah ALD system at RIT is capable of depositing the desired material as well as the desired thickness (target 10nm)**



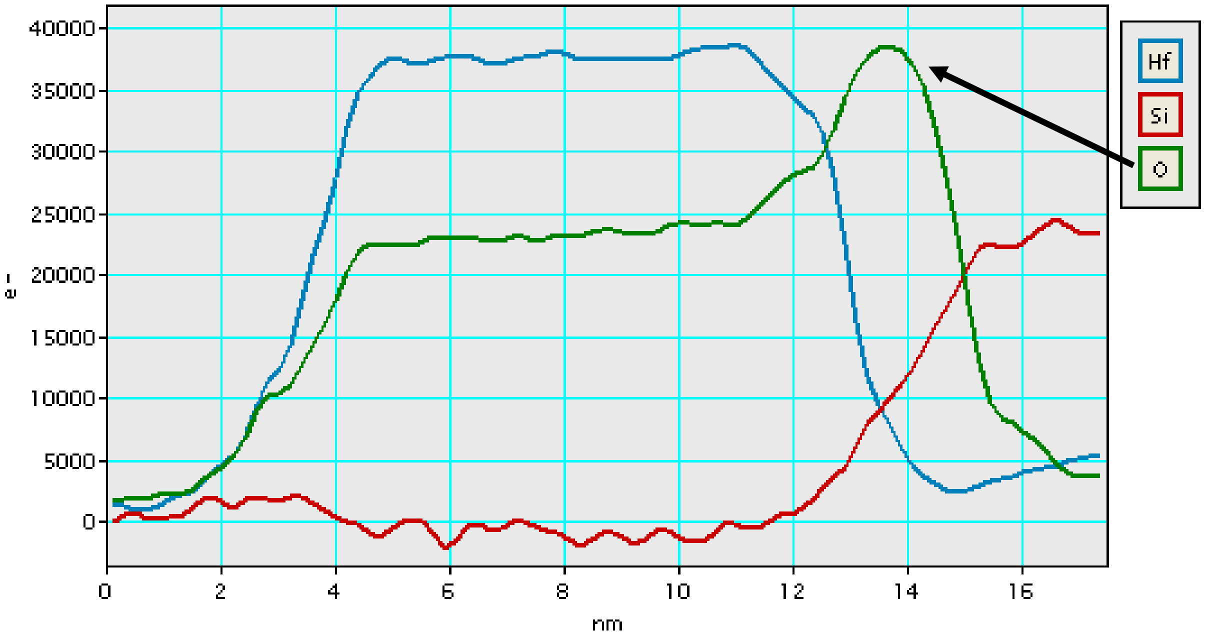


TEM and EELS


10.8 nm
10.4 nm
10.5 nm
HfO2
Si
CC2
HD-2300A 200kV x2500k TE 17/04/27 15:50
10.0nm

TEM and EELS

- **Approximately 2 nm of interfacial oxide was present in Al doped samples**
- **Two capacitors in series**



CV Measurements

- **Modeling both capacitors in series with measured total capacitance:**

$C_{tot} \approx 190 \text{ pF}$

$A \approx 2 \text{ x } 10^{-4}\ cm^2$

$t_{SiO_2} \approx 2 \text{ x } 10^{-7}\ cm$

$t_{Al:HfO_2} \approx 1 \text{ x } 10^{-6}\ cm$

$\epsilon_0 = 8.854 \text{ x } 10^{-14}\ F/cm$

$$C_{ox} = \frac{\epsilon A}{t} = \frac{\epsilon_0 \epsilon_r A}{t}$$

$$C_{tot} = \frac{1}{\frac{1}{C_{SiO_2}} + \frac{1}{C_{Al:HfO_2}}}$$

$$\therefore \epsilon_{rAl:HfO_2} \approx 23.9$$

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Conclusions

- **HfO_2 and Al:HfO_2 have both been successfully deposited by ALD at RIT**
- **Capacitors with the deposited materials were fabricated and tested**
  - **Low breakdown voltage as well as high leakage current was observed**
- **The dielectrics have been verified to be high k (≈25)**

Future Work

- Fabrication variations will be considered to limit interfacial oxide
- A study of annealing conditions will be done to achieve the proper orthorhombic crystal phase
- XRD will be done to calculate crystal structure of film

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FeDR@RIT namlab nanoelectronic materials laboratory NSF R·I·T Semiconductor & Microsystems Fabrication Laboratory

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THANK YOU!