Growth of Y_2O_3 and HfO_2 as Single Compounds and as Nanolaminates on Si using Atomic Layer Deposition

Adam Kueltzo

Thornton Fractional North High School

July 31st, 2008

University of Illinois at Chicago

Advanced Materials Research Laboratory (AMReL)

Mentors: Dr. G. Jursich and Dr. C.G. Takoudis

Departments of Bioengineering and Chemical Engineering

Motivation for Research

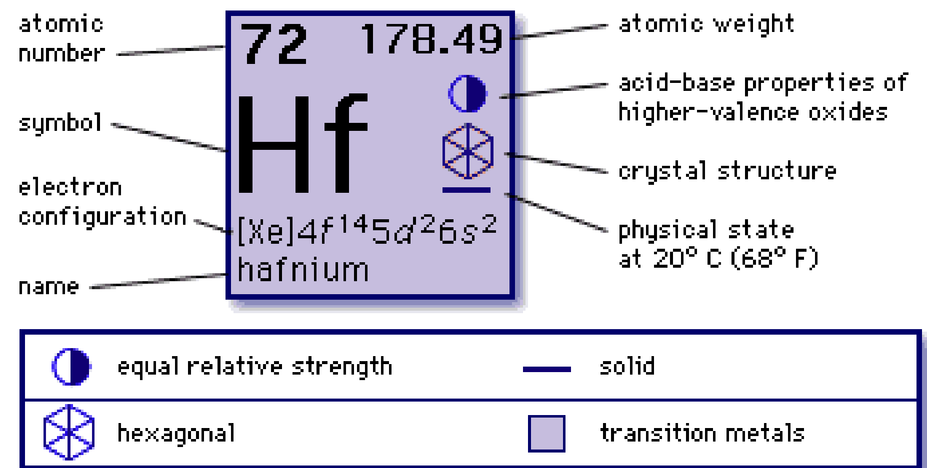
- To work with new high dielectric constant (k) materials such as and HfO_2 and Y_2O_3 to replace SiO_2 in micro- and nano-electronics
- To run experiments in the atomic layer deposition (ALD) reactor and to examine thin film growth rates
- To analyze the resulting thin films on silicon using spectral ellipsometry, Fourier Transform Infrared (FTIR) spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and Atomic Force Microscopy (AFM).

Hypotheses

- A self-limiting reaction between an yttrium precursor, a hafnium precursor, an oxidizer, and the silicon substrate
- Good film uniformity on the substrate (using a spectral ellipsometer)
- Absence of organic compounds in the resulting film structures (using FTIR spectroscopy)
- Stoichiometry of the high-k material and the bonding states of the elements (using XP Spectroscopy)

New High-k Dielectric Materials

- Last summer and through the following school year work was conducted with Hafnium and Yttrium



- Hafnium oxide has a k value of 20-25

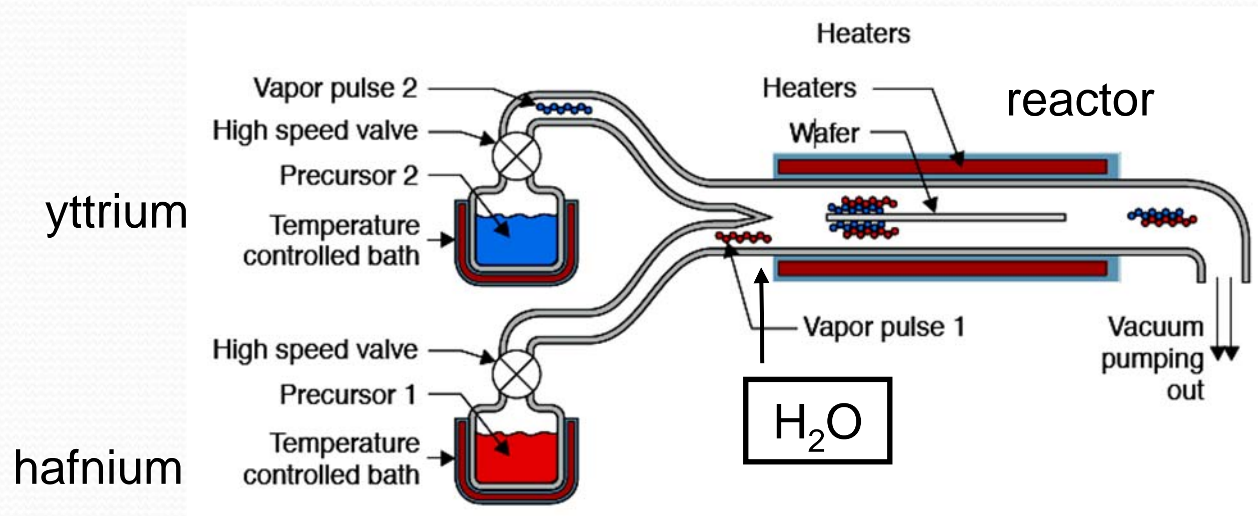
- Yttrium oxide has a k value of 15-18

Why co-deposition?

- Enhances dielectric constant
- Aids in the size minimization of semiconductor devices

Atomic Layer Deposition (ALD)

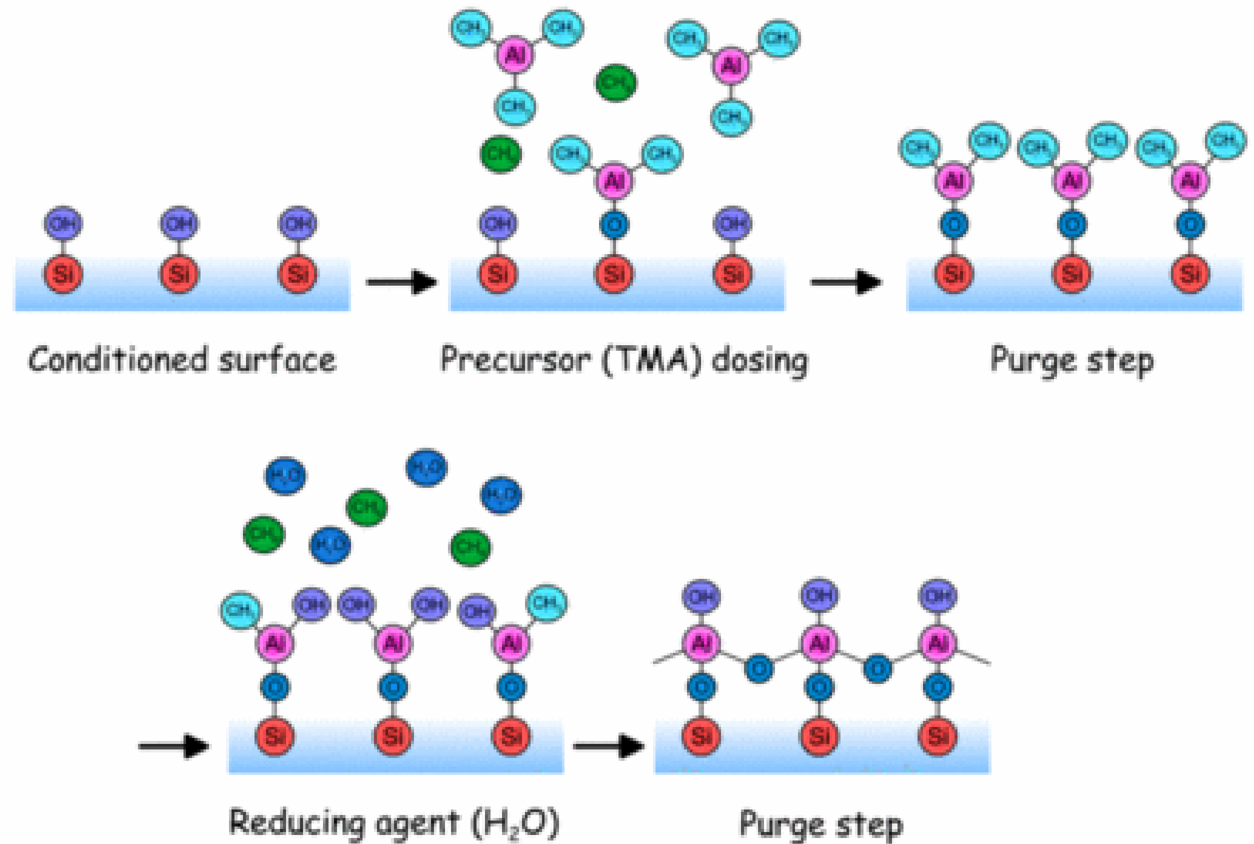
- Uses pulses of gaseous reactants (precursor and oxidizer) alternately fed into the reactor
- Produces atomic control
- Film thickness depends on number of deposition cycles



www.icknowledge.com/misc_technology/Atomic%20Layer%20Deposition%20Briefing.pdf

ALD Process

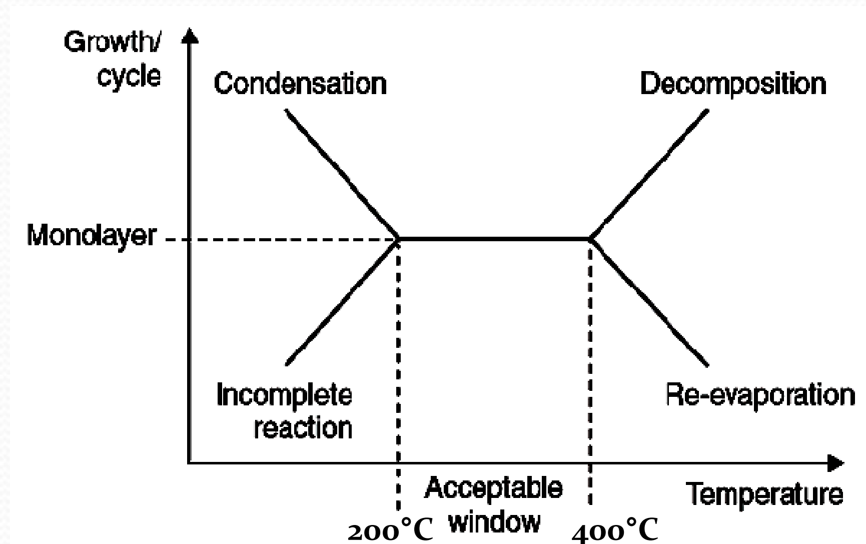
- "One Cycle"
- Precursor
- Purge (N_2)
- Oxidizer (H_2O)
- Purge (N_2)



http://www.cambridgenanotech.com/

Acceptable Temperature Window

- ALD reactions usually occur between 200-400 °C in the reactor
- Above 400 °C, the chemical bonds are not stable and the precursor may decompose
- Below 200 °C, the reaction rate may be reduced

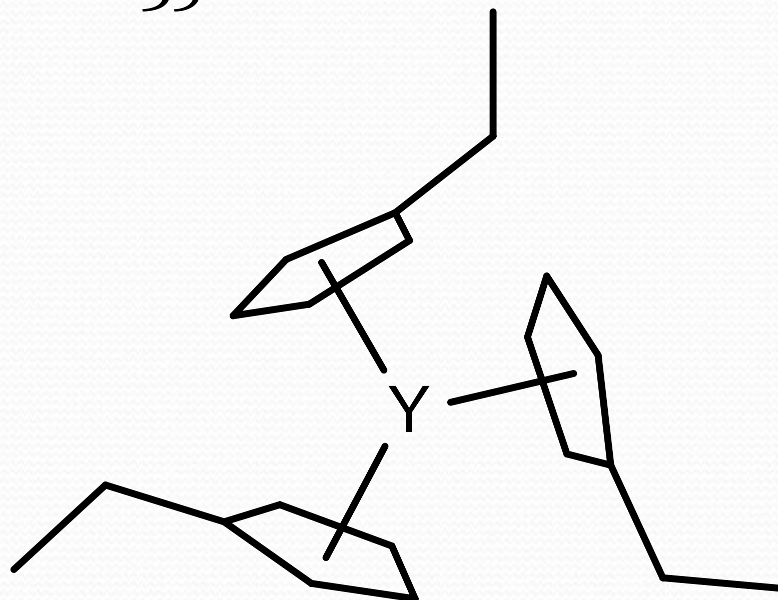


www.icknowledge.com/misc_technology/Atomic%20Layer%20Deposition%20Briefing.pdf

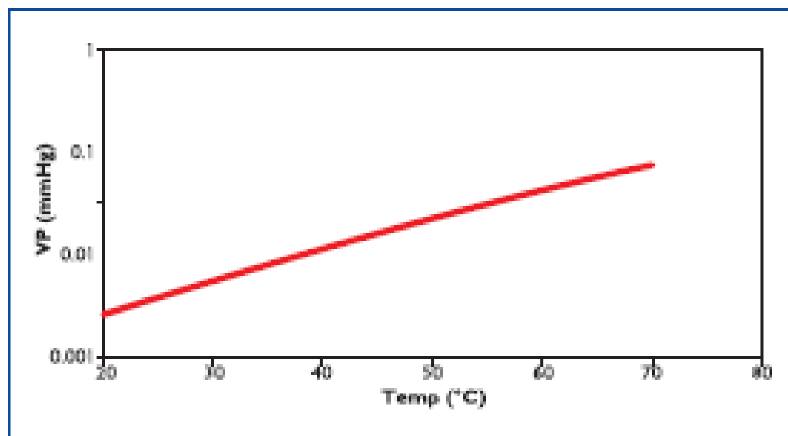
Properties of the Precursors

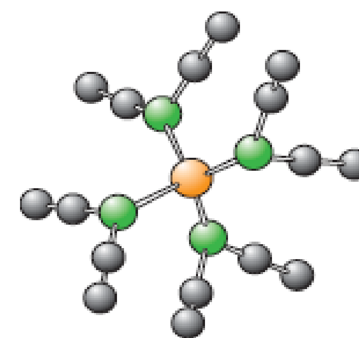
- $Y(CpCH_2CH_3)_3$ -- tris(ethylcyclopentadienyl) yttrium

- Vapor pressure: ~ 60 mTorr @ 100 °C
- Decomposition temperature: > 350 °C
- Melting point: 38 °C



- $Hf[N(C_2H_5)_2]_4$ -- tetrakis(diethylamino)hafnium
  - Boiling point: 130°C
  - Density: 1.22g/ml
  - Appearance: dark yellow liquid

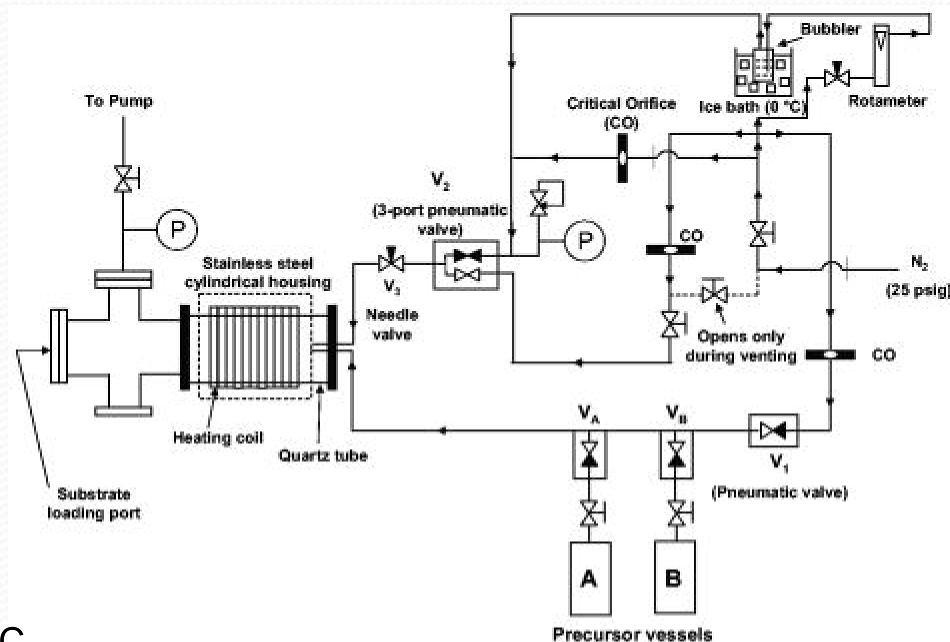




https://www.sigmaaldrich.com/sigma-aldrich/general_information/epichem-hafnium.pdf

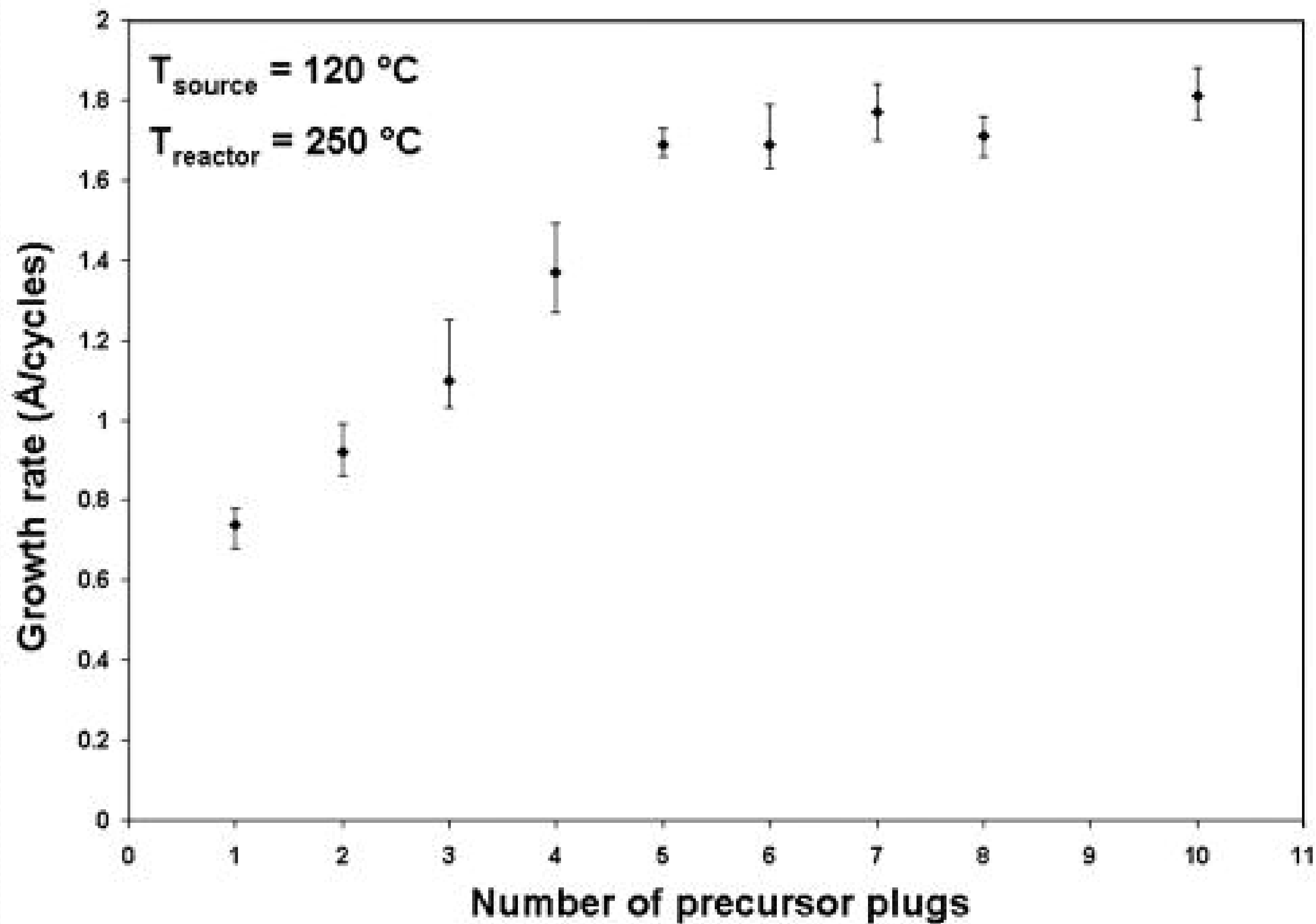
Experimental Conditions

- ALD Reactor
- Precursor A(Hafnium): 65 ºC
- Precursor B(Yttrium): 120 ºC
- Reactor: 250 °C



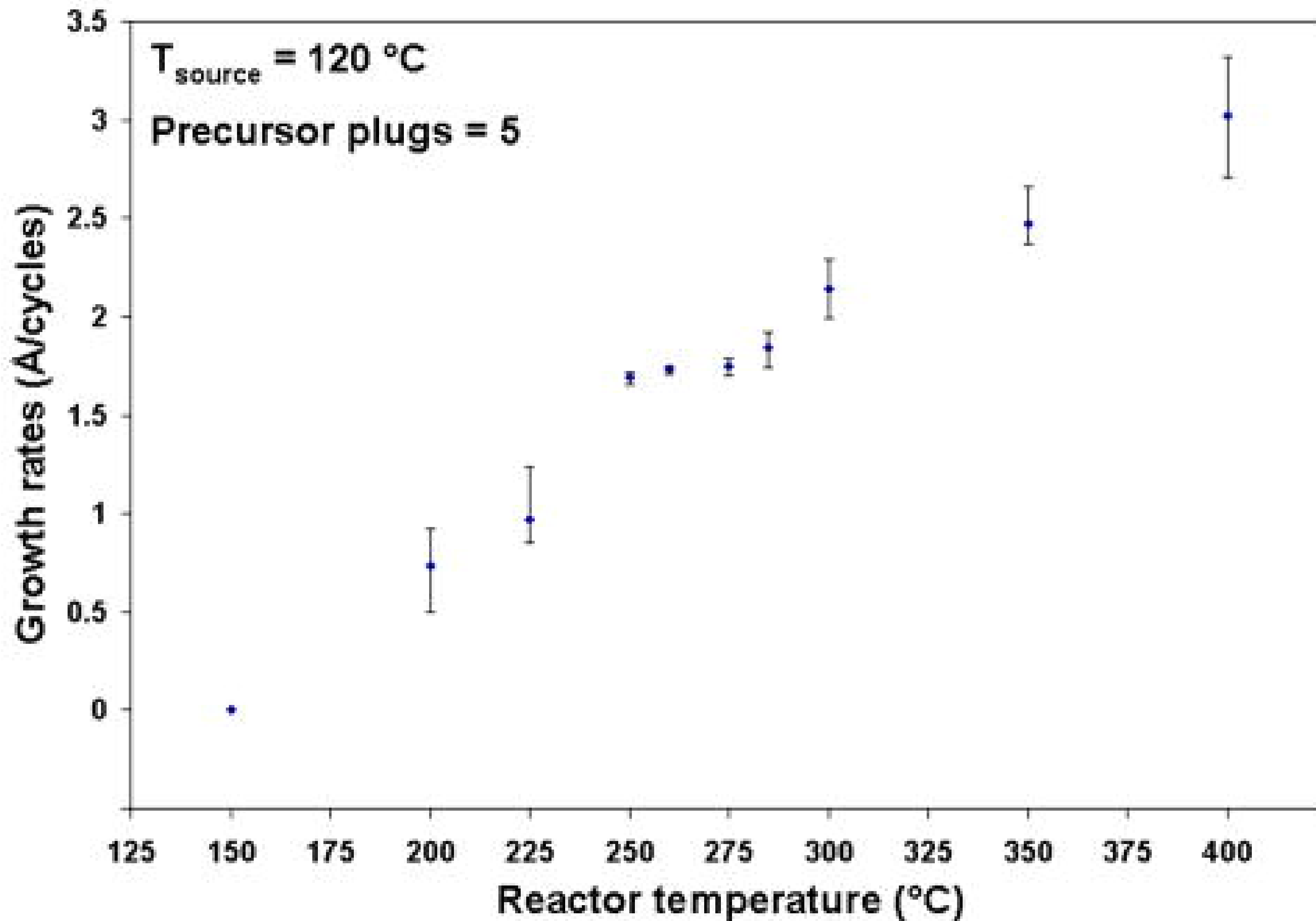
Majumder,P., Jursich, G., Kueltzo, A., Takoudis, C.
Journ.Electrochem. Soc. **155** (8), G152-G158 (2008)

Y_2O_3 Growth Rate vs. Precursor Dosage



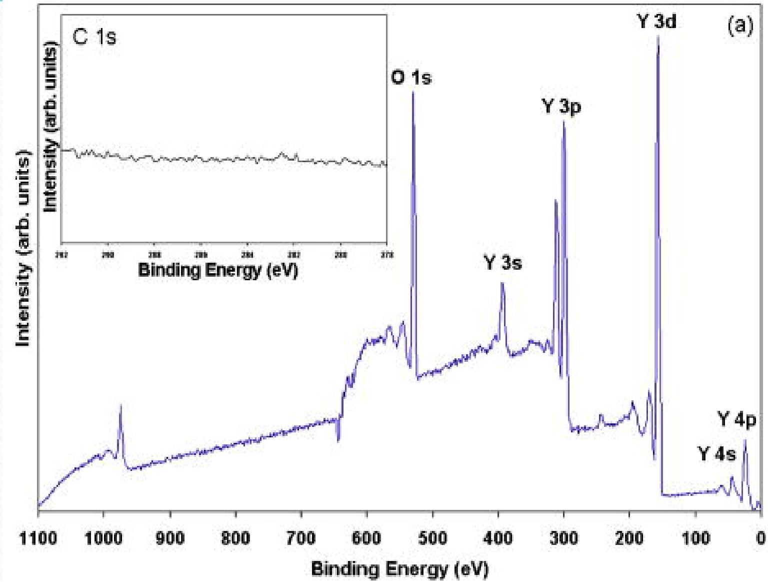
Majumder,P., Jursich, G., Kueltzo, A., Takoudis, C. *Journ.Electrochem. Soc.* **155** (8), G152-G158 (2008)

Y_2O_3 Growth Rate vs. Reactor Temperature

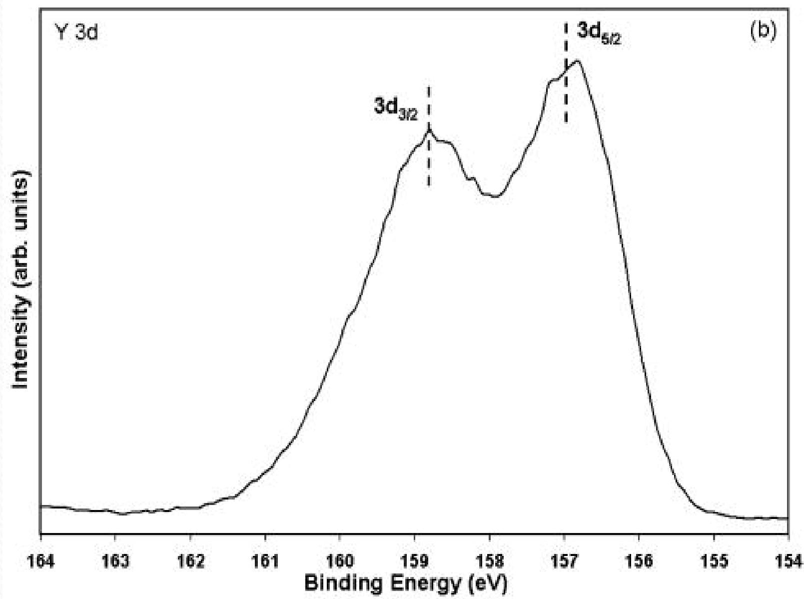


Majumder,P., Jursich, G., Kueltzo, A., Takoudis, C. *Journ.Electrochem. Soc.* **155** (8), G152-G158 (2008)

XP Spectra of Y_2O_3 on Si



(a)



(b)

Majumder,P., Jursich, G., Kueltzo, A., Takoudis, C. *Journ.Electrochem. Soc.* **155** (8), G152-G158 (2008)

Quantification Results

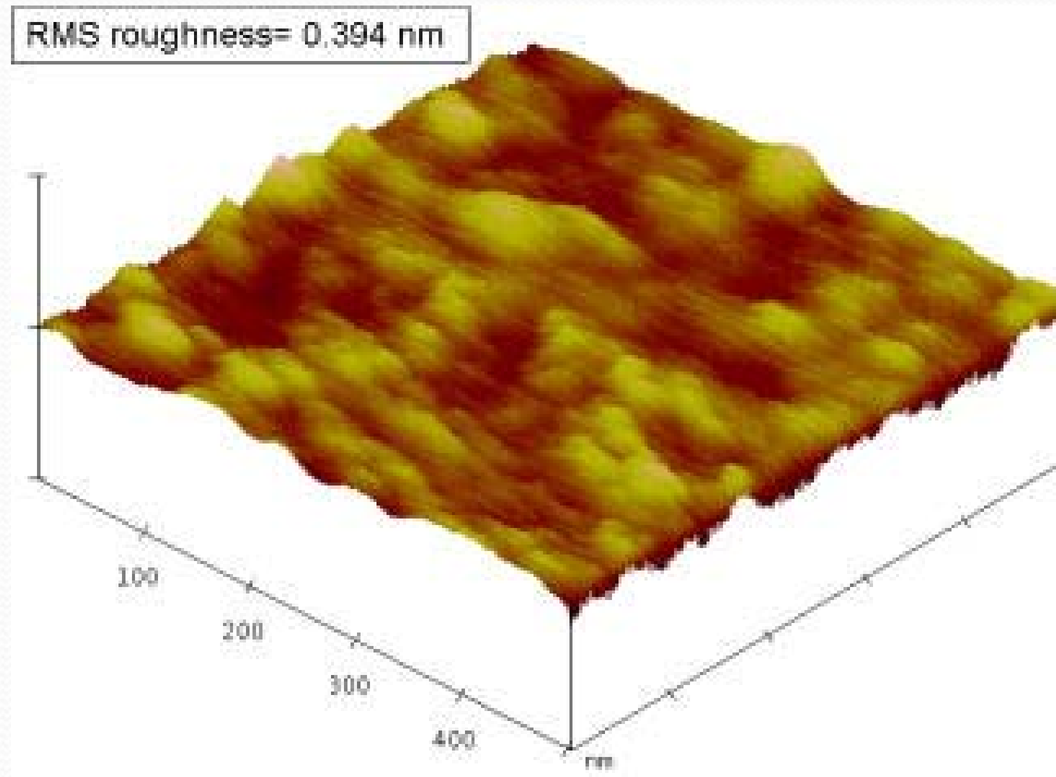
Y Atomic Concentration %: 39.2

O Atomic Concentration %: 60.8

O:Y = 60.8/39.2 = 1.5

Therefore Y_2O_3 was produced on the substrate.

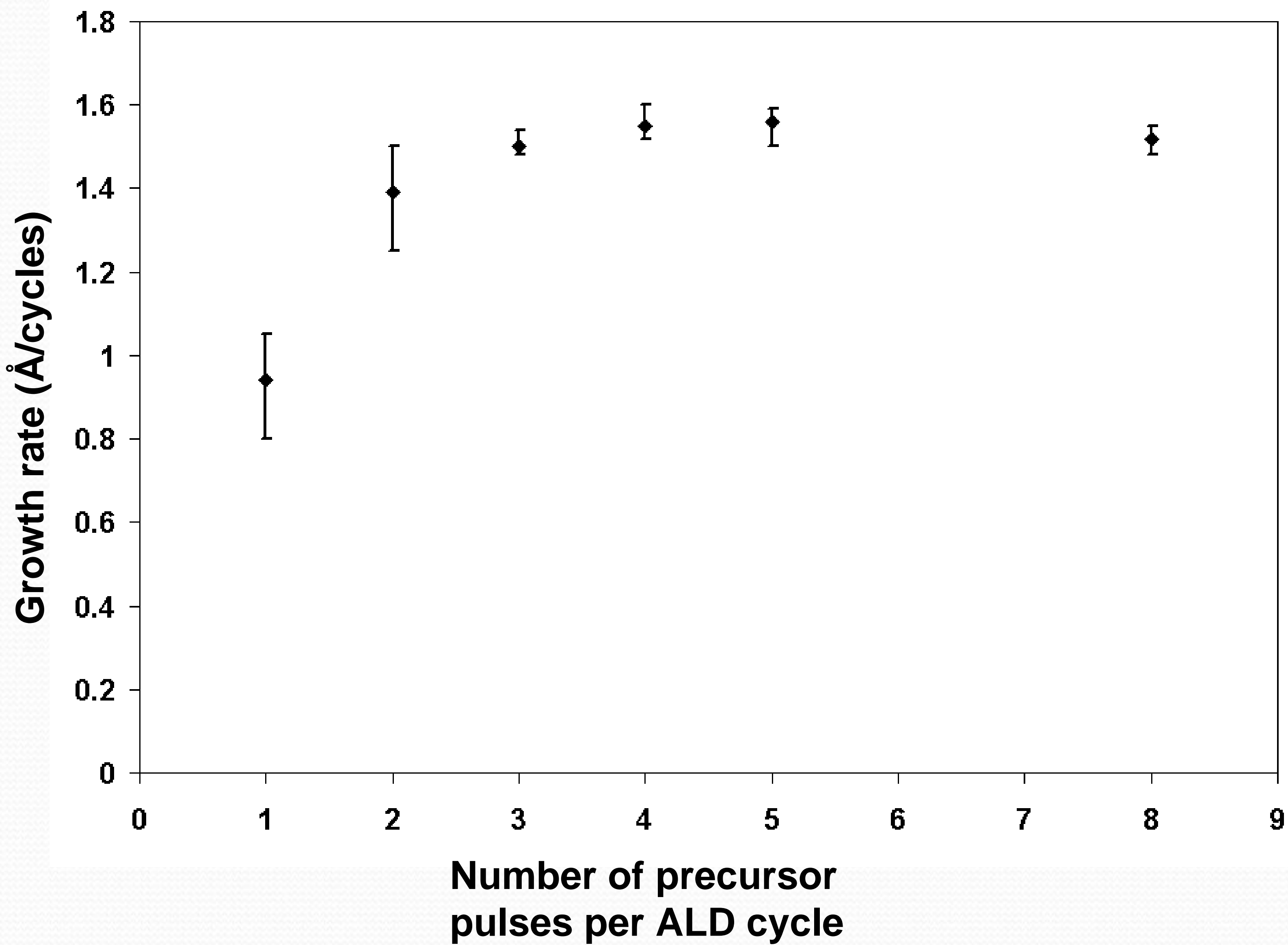
Surface Morphology (AFM)



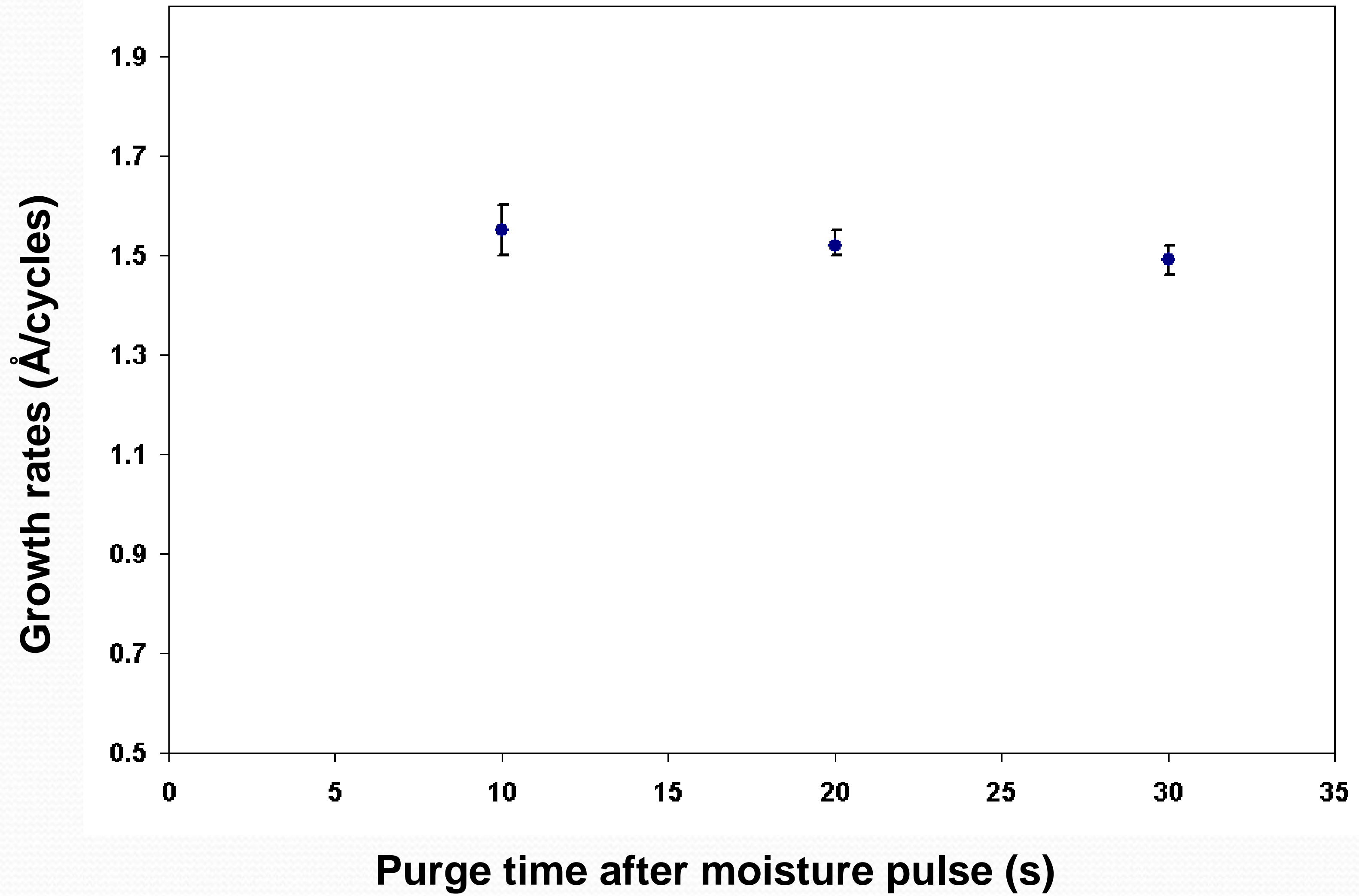
rms roughness ~.4 nm which is below 1% film thickness

Majumder,P., Jursich, G., Kueltzo, A., Takoudis, C. *Journ.Electrochem. Soc.* **155** (8), G152-G158 (2008)

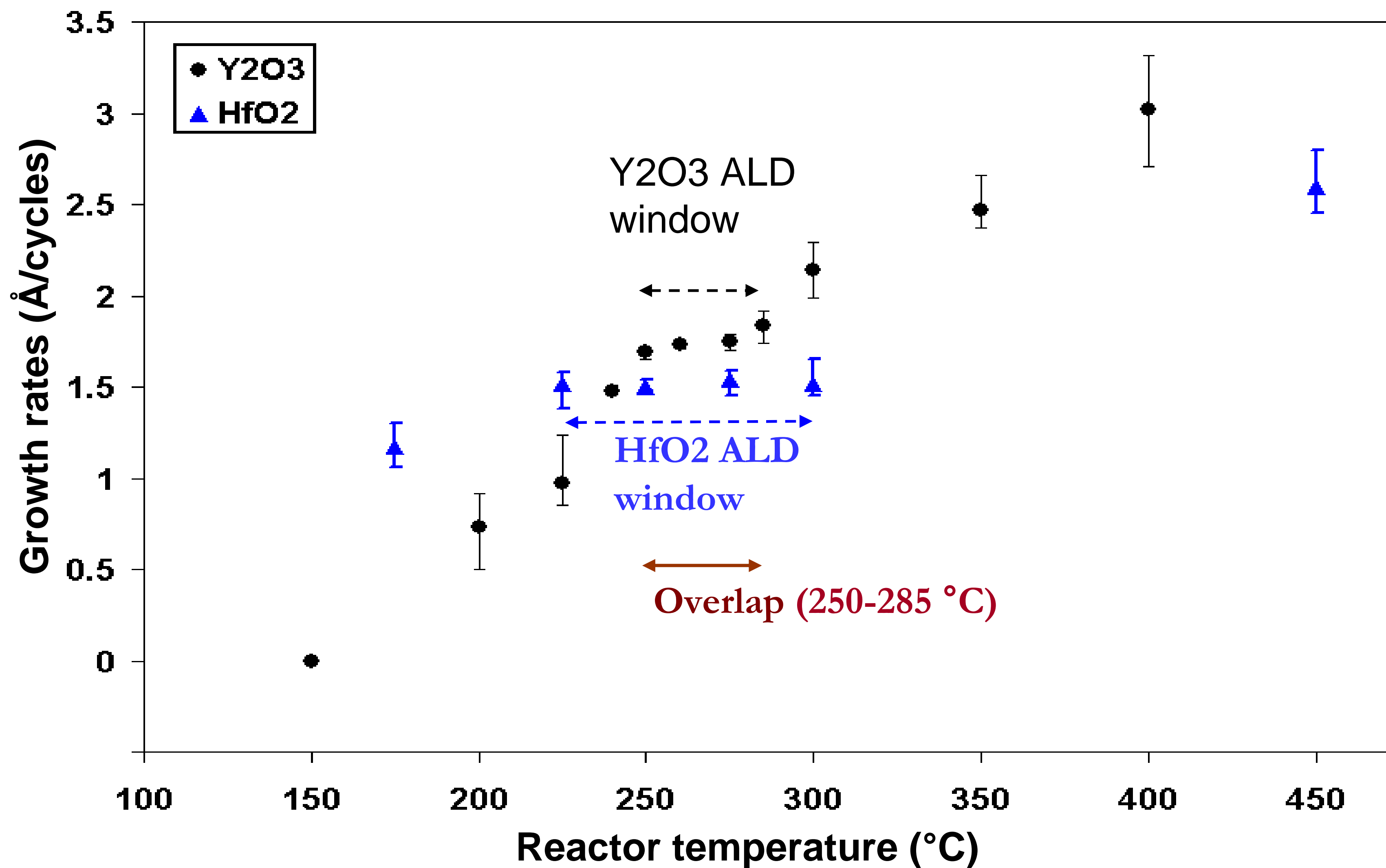
HfO_2 Growth Rate vs. Precursor Dosage



HfO_2 Growth Rate vs. Purge Time



HfO_2 and Y_2O_3 Growth Rate vs. Reactor Temperature

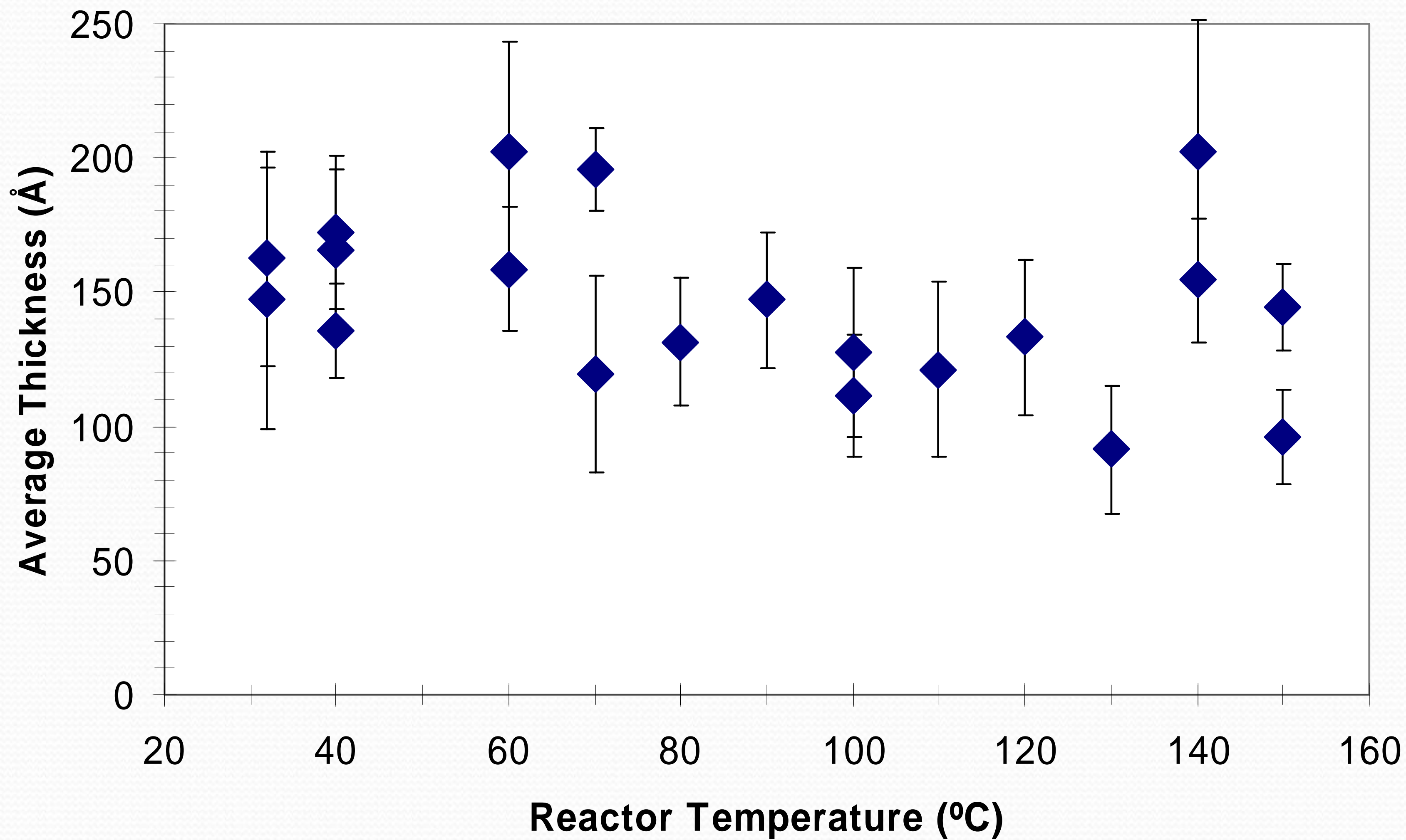


Low Temperature Deposition of HfO_2

- Joint effort to deposit Hafnium Oxide onto polymer nanofibers
  - Nanotubes
  - Physical properties ...compression
  - Electrochemical properties

- Low temperature needed to prevent vaporization

  - below 60 °C



HfO2 Average Thickness
After 50 cycles
Average Thickness (Å)
250
200
150
100
50
0
20
40
60
80
100
120
140
160
Reactor Temperature (ºC)

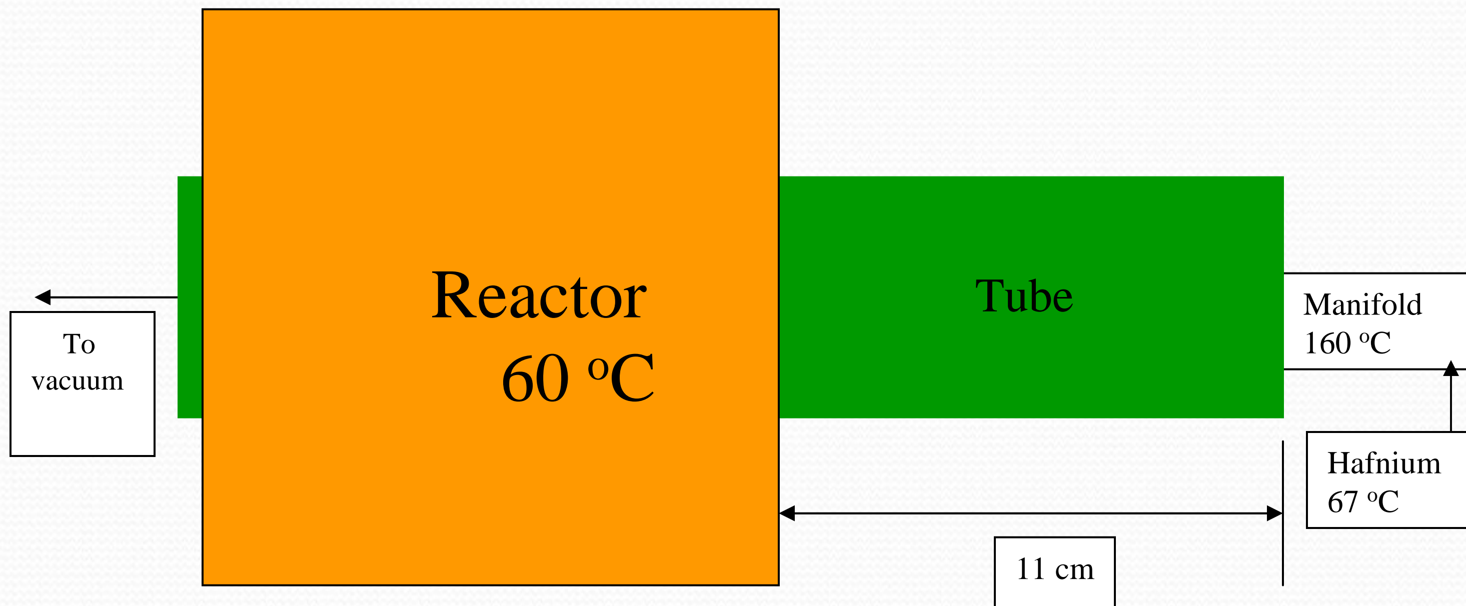
Hurdles

- Lower temperature needed to prevent vaporization
  - Room temperature not controllable
- Try 30 ^{o}C
- Fibers getting broken apart - substrate placement in the reactor

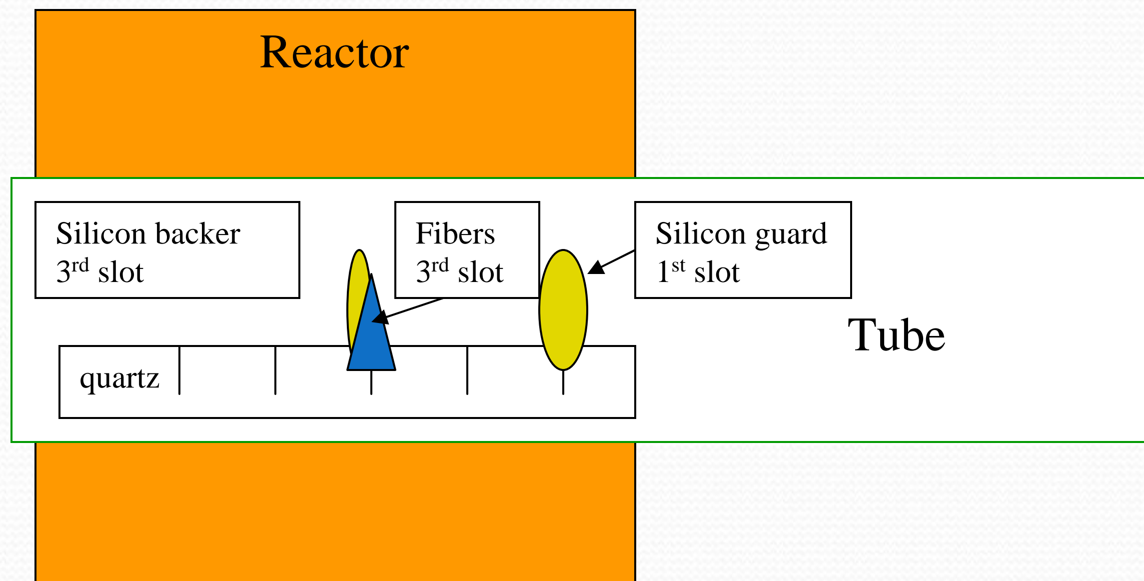
  -slow change in air pressure and purging reduces fiber movement

  - substrate holder moved away from reactor feed to reduce purge pressure coming from manifold

Fiber Deposition Arrangement



Cross Section of Reactor



All measurements and temperatures are the same as in previous slide

Findings

- Placement of fibers in the back of the vacuum chamber did not produce any encouraging results
- Fluid dynamics were changed
- Grated metal sheets were tried
- Ended up with steel envelope

- Analysis of samples using FT-IR to determine composition of deposition
- Teaching module / all school lab
  different classes have different inquiries

References

Anthony, J.M., Wallace, R.M., & Wilk, G.D. (2001). High-k Gate Dielectrics: Current Status and Materials Properties Considerations. Applied Physics Review, 89 , 5243-5275.

Brain, Marshall. (n.d.). How Semiconductors Work. [WWW page]. http://computer.howstuffworks.com/diode.htm.

Cambridge NanoTech, Inc. (2003-2007). Cambridge NanoTech: Atomic Layer Deposition Systems. [WWWpage]. http://www.cambridgenanotech.com/.

IC Knowledge LLC. (2004). Technology Backgrounder: Atomic Layer Deposition. [WWWpage]. http://www.icknowledge.com/misc_technology/Atomic%20Layer%20Deposition%20Briefing.pdf.

Intel® Education. (n.d.) Inside The Intel® Manufacturing Process: How Transistors Work. [WWWpage]. http://www.intel.com/education/transworks/index.htm.

Majumder, P., Jursich, G., Kueltzo, A., & Takoudis, C. (2008). Atomic Layer Deposition of Y_2O_3 Films on Silicon Using Tris(ethylcyclopentadienyl) Yttrium Precursor and Water Vapor. *Journal of The Electrochemical Society*. **155**(8), G152-G158.

Mutschler, Ann Steffora. (2007). Intel, IBM Embrace High-k Gates for 45nm. *Electronic News.*

Peters, Laura. (2007). Behind the Breakdown of High-k Dielectrics.*Semiconductor International*. p. 30.

Sigma-Aldrich Co. (2008) https://www.sigmaaldrich.com/sigma-aldrich/general_information/epichem-hafnium.pdf.

Zant, P. V. (2000). Microchip Fabrication (4th ed.). New York: McGraw Hill.

Acknowledgements

- DOD and NSF-EEC 0755115 and NSF-EEC 0839043
- Mentors: Dr. Greg Jursich and Dr. Christos Takoudis
- Doctoral students: Prodyut Majumder and Manish Singh
- Dr. Alex Yarin and Suman Sinharay
- Qian Tao
- K.C. Kragh