

Metal Nitride Films using Savannah ALD

Suhas Kumar and Adair Gerke
Mentors: J Provine
and Krishna Saraswat

Background and Motivation

Fall 2010 EE412 Savannah ALD Project Conclusions:

- Found extremely high oxygen concentration in TiN
- Identified source as air leaking into NH₃ line
- Fixed leak but could not characterize nitrides afterwards

Spring 2011 EE412 Goals:

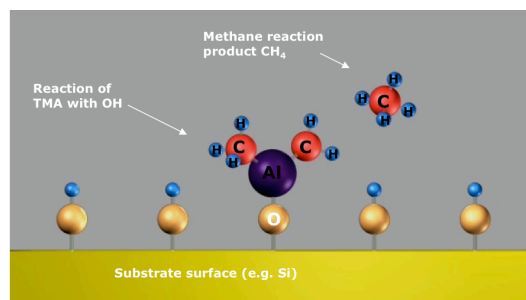
- Analyze chemical purity and electrical properties of metal nitrides grown by Savannah without NH₃ line leak
- Determine source of further impurities

Experiments and Goals

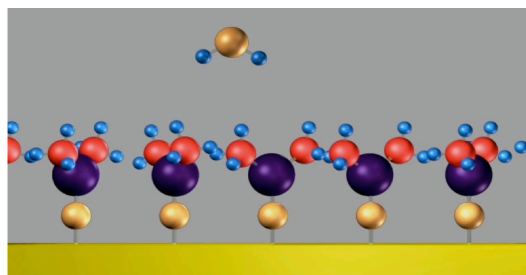
- ALD Control Experiments:
 - Run ALD cycle with one or more precursor missing
 - To identify source of unwanted oxide growth
- Leak test: characterize air leak in chamber
- Ellipsometry
- XPS and NanoSIMS
 - To directly determine chemical composition
- "MOS" Capacitors
 - C-V curves
 - To evaluate performance of Savannah's nitrides for this important application
 - To evaluate performance of oxides of Savannah
- Conductivity test on the films
- The precursor chemistry revisited

Overview of Atomic Layer Deposition (ALD)

- Sequential introduction of 2+ precursors
- Each forms monolayer on surface
- Advantages: conformal, monolayer/cycle growth
- In SNF Savannah:
 - TDMA(Metal) + H_2O = Oxide
 - TDMA(Metal) + NH_3 = Nitride

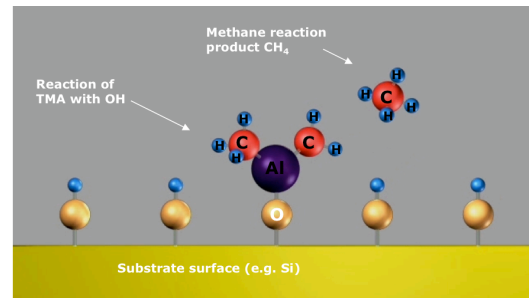


Precursors form monolayer

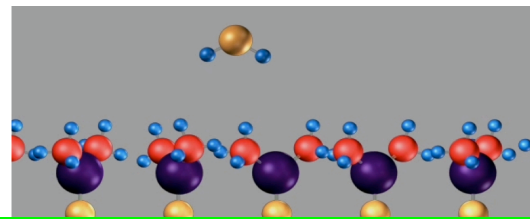


Overview of Atomic Layer Deposition (ALD)

- Sequential introduction of 2+ vapor precursors
- Each forms monolayer on surface
- Advantages: conformal, monolayer/cycle growth
- In SNF Savannah:
 - TDMA(Metal) + H_2O
= Oxide
 - TDMA(Metal) + NH_3
= Nitride



Precursors form monolayer



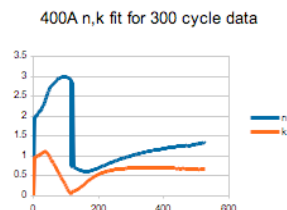
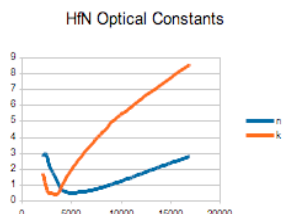
Weakness: If multiple precursors ever introduced simultaneously, controlled ALD is not happening

Initial depositions

There was enough nitrogen to give colors to the films, a visible change from Fall 2010 ALD nitrides

Ellipsometry did not help -

- We did not know the films' composition;
- Effective Medium Approx. methods failed
 - Modeld HfN/HfO₂ mixture
 - n, k qualitatively wrong for any ratio



Film composition: XPS & NanoSims

Film	Sputtering	XPS Composition
HfN	0 sec	42% O, 19% Hf, 12% N, 6% C,
HfN ^{1,3}	22 sec	55% O, 20% Hf, 25% N
TiN	0 sec	43% O, 18% Ti, 13% N, 25% C
TiN ^{1,2}	30 sec	59% O, 25% Ti, 10% N, 6% C
TiO ₂	0 sec	61% O, 19% Ti, 20% C
TiO ₂	30 sec	76% O, 23% Ti
HfO ₂	0 sec	61.93% O, 22.04% C, 16.03% Hf
HfO ₂	30 sec	66% O, 34% Hf

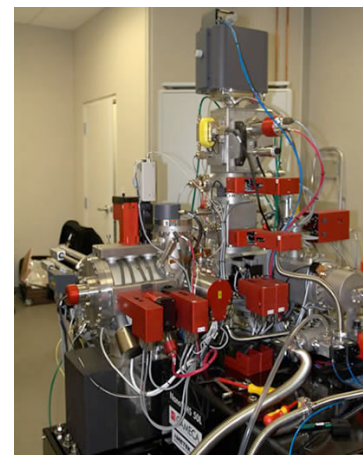
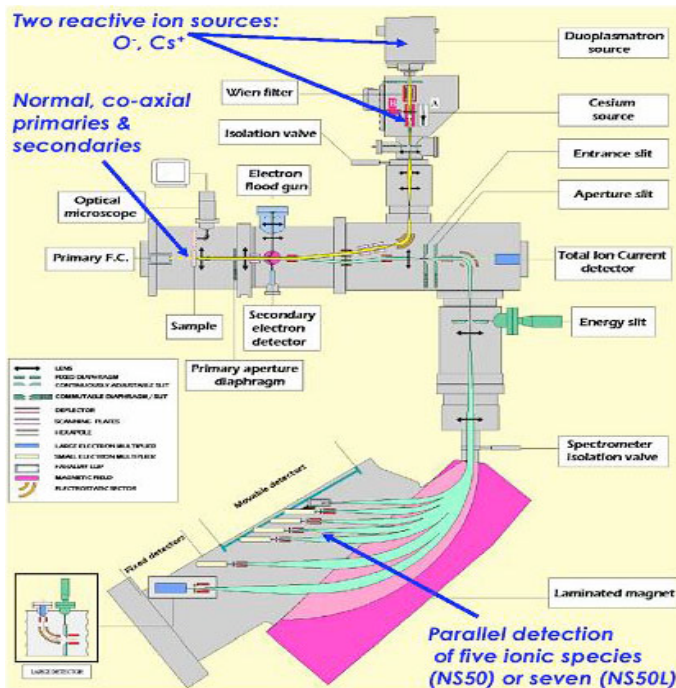
¹Oxygen content: very high, but lower than Fall 2010

²Carbon throughout film

³Fluorine found throughout



NanoSims: Tool Overview

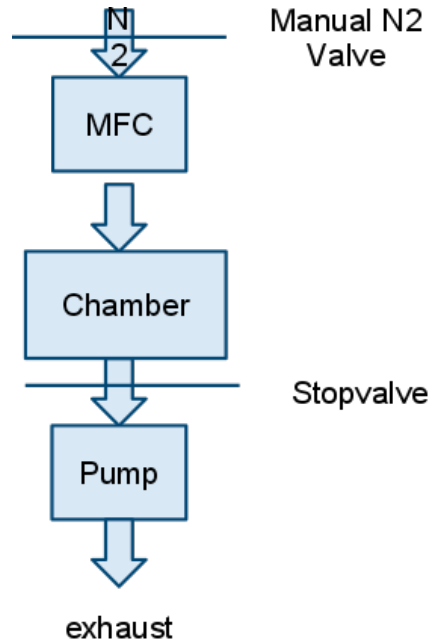


Leak Test

GOAL: determine amount of air introduced via o-ring leak

METHOD:

- Turn of input N₂ using manual N₂ valve
- Take baseline pressure with pump
- Close stop valve
- Record pressure vs time
- Open stop valve
- Check baseline returns
- Control: ran test with known 5 sccm N₂

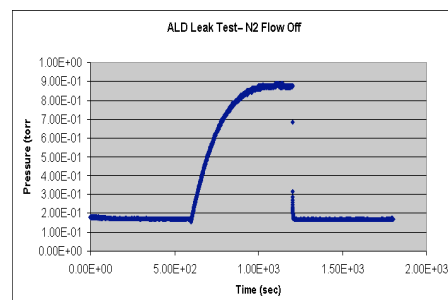
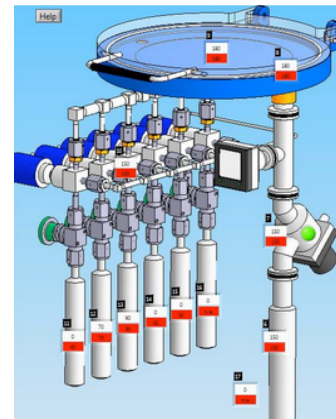


Leak Test: Results and Discussion

- Flow sensor reads 2sccm even when N₂ is turned off - needs zero calibration
- Results: with stopvalve open, pressure increases indicating atmospheric leak - 0.04 torr/sec
- Not primary source of H₂O

ALD repairs possible:

- Replace o-ring, re-test leakage
- Zero-calibrate the sensor



ALD Control Experiments

Goal: determine if environmentally introduced water/oxygen grows oxide

Precursors (400 cycles)	TDMA (Ti) Only	TDMA(Hf) Only	NH ₃ Only	None
Growth (A) measured Woollam	9	0	0	0

Conclusion: *Introduced air does not account for the full amount of oxygen incorporated into nitride films*

Electrical testing

4-point resistivity measurements on surface:
Using Micromanipulator, visually aligning two/four probes

HfN ~ 10 ohm-cm
TiN ~ 10m ohm-cm

Prometrix seemed to punch thru the films

We might be getting the precursor chemistry wrong and getting to Hf₃N₄ (insulating) instead of Hf₃N₃ (conductive).

In literature, PEALD typically gives Hf₃N₃.

*Chemical vapour deposition: precursors, processes and applications - Anthony C. Jones, Michael L. Hitchman - 2009 - Technology & Engineering

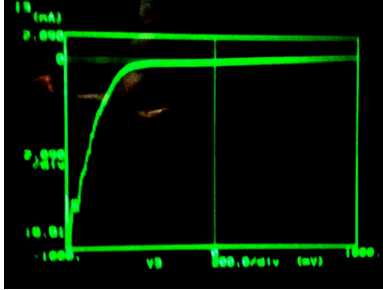
Hf₃N₄ can be converted to metallic HfN at 1000C

*Gordon, R. Precursors with Metal-Nitrogen Bonds of ALD of Metals, Nitrides and Oxides. San Jose, CA: American Vacuum Society, 2005

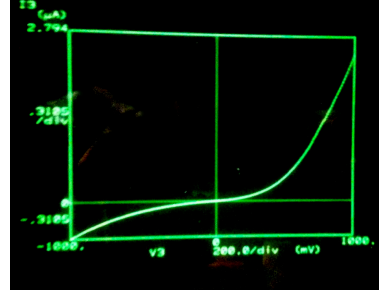
Evaluation of contact I-V

IV thru the thickness to evaluate contacts and resistivity
 Aluminum (1 μ m) - TiN (20nm) - (p/n)Si
 cross section 50 μ m*50 μ m (cut out using FIB)

Highly Schottky type IV curves-- indicates band offset



p Si Substrate = GND



n Si Substrate = GND

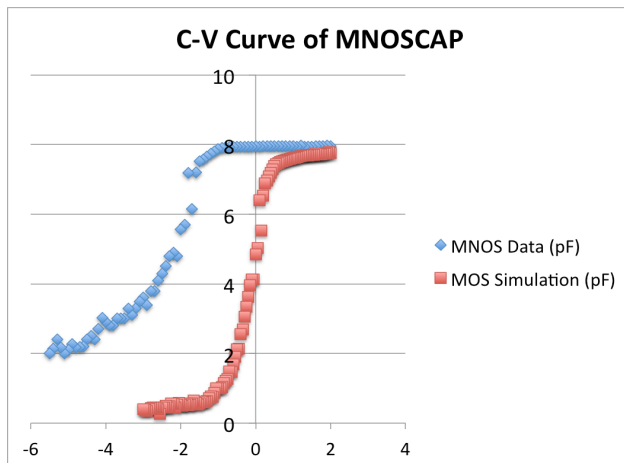
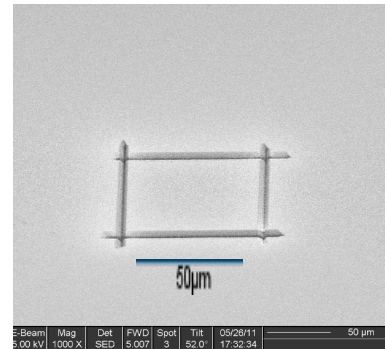
Dependence of rectification direction on doping indicates Schottky is between TiN and Si

next: grow TiN sandwiched between metals, see if ohmic

MNOSCAPS

Structure:

Al(1 μ m)-TiN(20nm)-SiO₂ (110nm)- B-test
 Si (Defined by FIB)



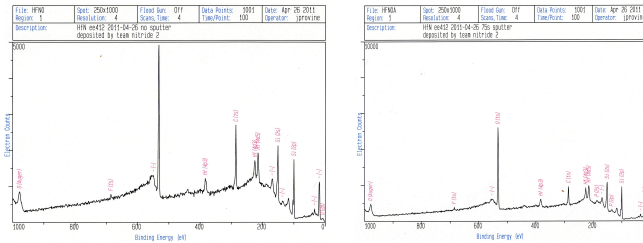
C_{ox} gives EOT~110nm, so nitride acts as metal with $\Phi < \Phi_{Al}$

Revisiting Carbon contamination

Carbon contamination was found thru the film in the nitride films (from nanoSIMS), but lesser in the HfN than in TiN (from XPS). TiO₂ had no bulk carbon contamination (from XPS).

Is this related to the precursor chemistry we just spoke of?

TiN data - Carbon thru the bulk of film



*Chemical vapour deposition: precursors, processes and applications - Anthony C. Jones, Michael L. Hitchman - 2009 - Technology & Engineering

Conclusion: Current State of Savannah Nitrides

Current State of ALD Nitrides:

- TiN:
 - Composition by XPS: 59% O, 25% Ti, 10% N, 6% C
 - MNOSCAP Performance: Nitride acts as metal
- HfN:
 - Composition by XPS: 55%O, 25%N, 20%Hf
 - Without plasma, removing O will not create conductive film

Cause of Oxidation: H₂O in as-purchased NH₃ precursor

Proposal: Improved nitrides possible with H₂O filter or Fiji

Acknowledgements

We gratefully thank J Provine and Krishna Saraswat for mentoring us.

Thanks to Professors Howe and Solgaard and Mary Tang for running the course

Lots more to the amazing SNF staff for patiently training us!

Savannah, Xactix, XPS- J

Woollam- Ed

Thermco2, prometrix, Gryphon- Maurice

Wbdiff, all litho, svgcoat - Uli

Evalign- Mahnaz

NanoSims, XPS- Chuck Hitzman