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Designing Suitable ALD Precursors for High-k Dielectrics, Barriers and Metals Applications

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Outline

- ALD Precursor Selection Criteria
- Metal Amidinates => Best Thermal Stability vis-à-vis Amides
- Zr Amidinate for ALD of ZrO_2
- Ru Amidinate for ALD of Ru
- La Formamidinate => Novel source for ALD of $LaAlO_3$
- Precursor Development for Improved Thermal Stability

ALD Precursor Selection Criteria

1) Adequate vapor pressure (> ~0.1 Torr at < 200 ^{o}C)
   - mononuclear metal complexes preferred
2) Acceptable Thermal stability during vaporization
3) Readily reacts with 2nd reactant at a low temperature
4) Exhibits low impurity incorporation in the films
5) Liquid sources are preferred for consistent vapor delivery

Precursor Design: Practical for commercial application, i.e. Safety, Stability, Shelf-life, Throughput, and Price.

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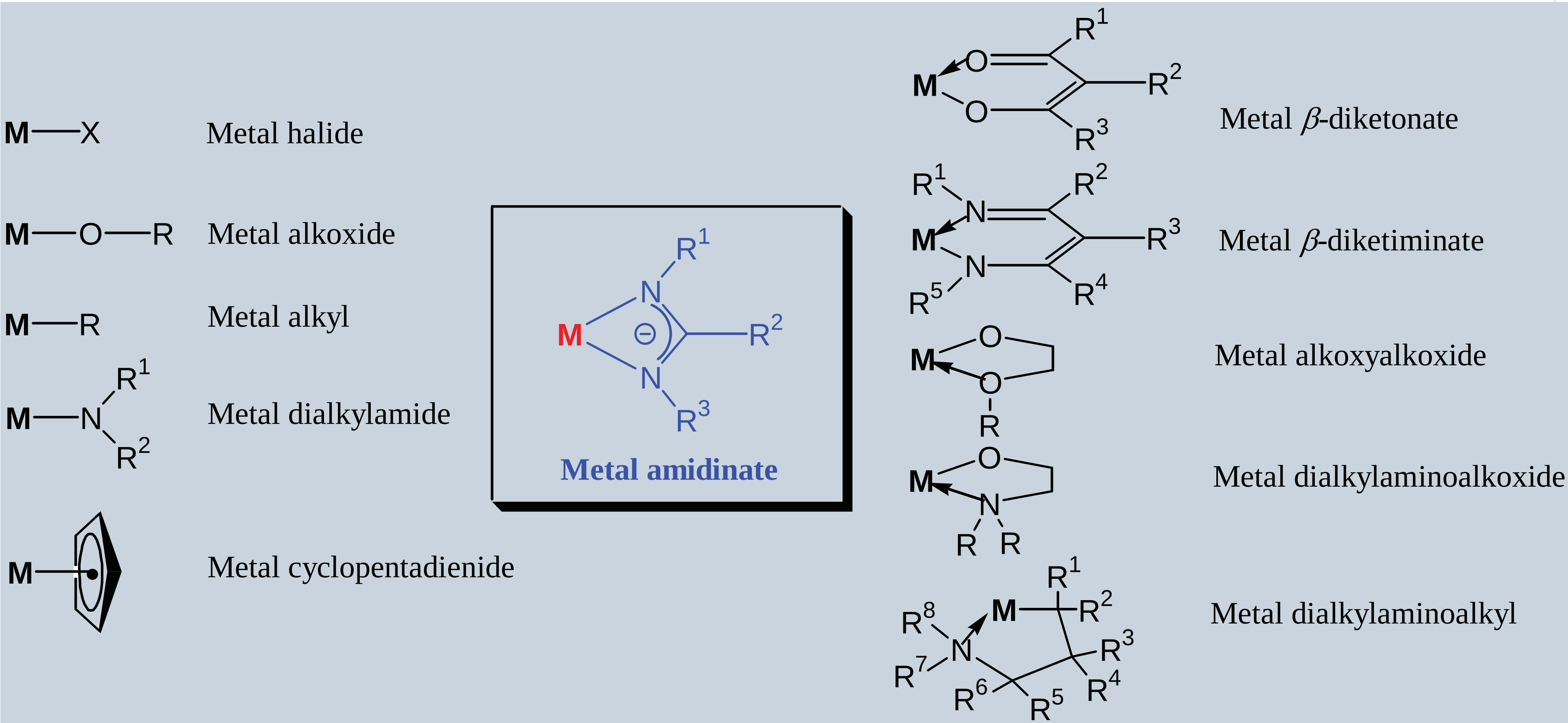
Selection of Suitable Precursors for ALD



***Metal Amidinates**: No direct M-C bonds, and exhibit significantly better thermal stability than amides, as a result of "chelating" amidinate ligand.*

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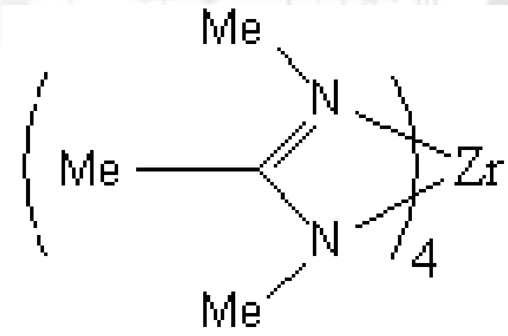
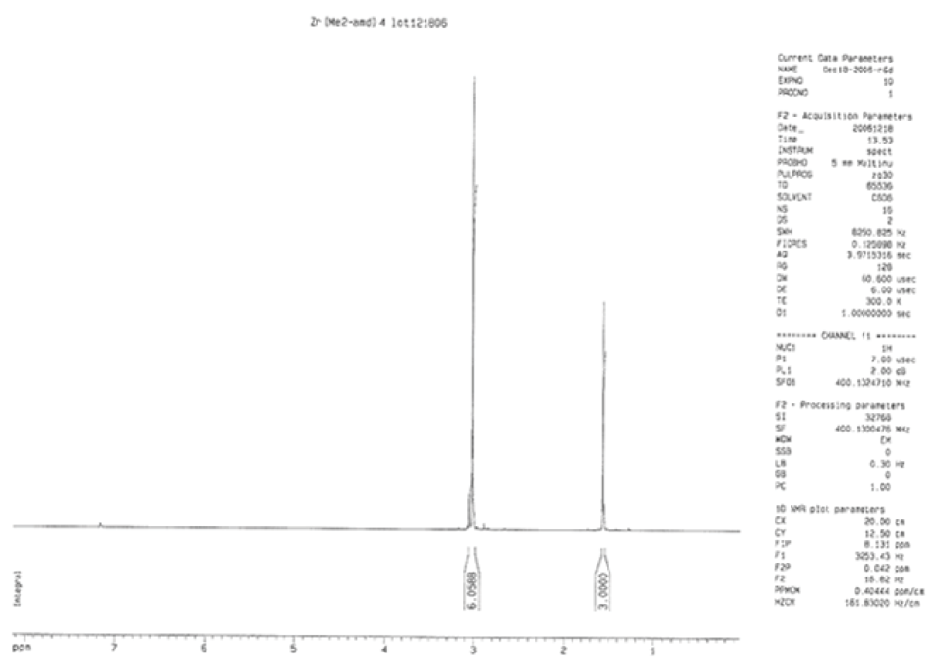
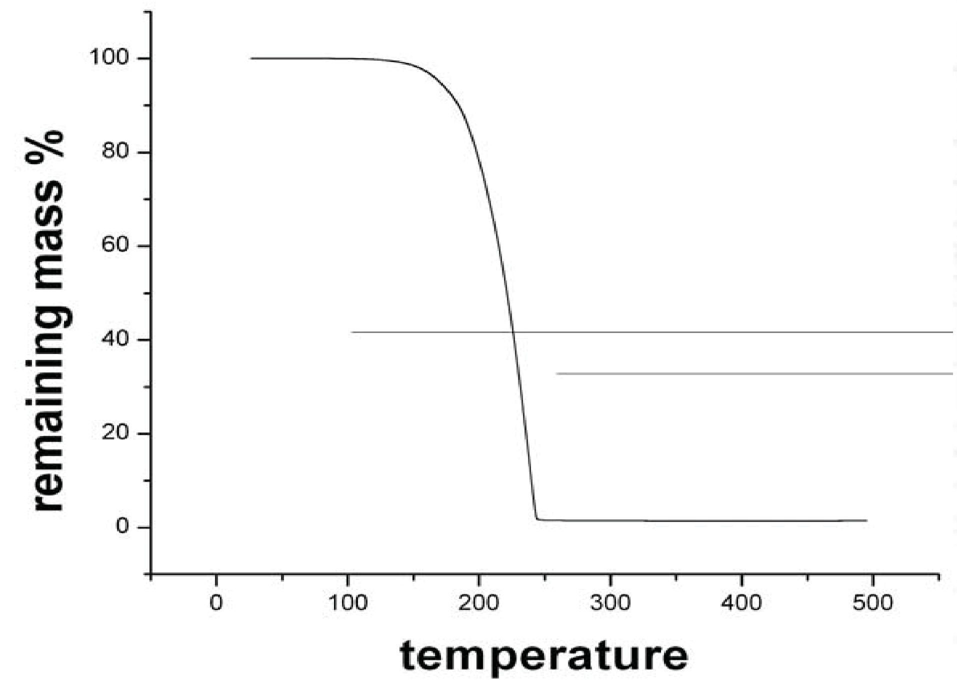
Zr(amidinate)$_4$ for High-k Application







High thermal stability:

No residue after TG

No change in NMR after heating at 250 ºC for 1 week

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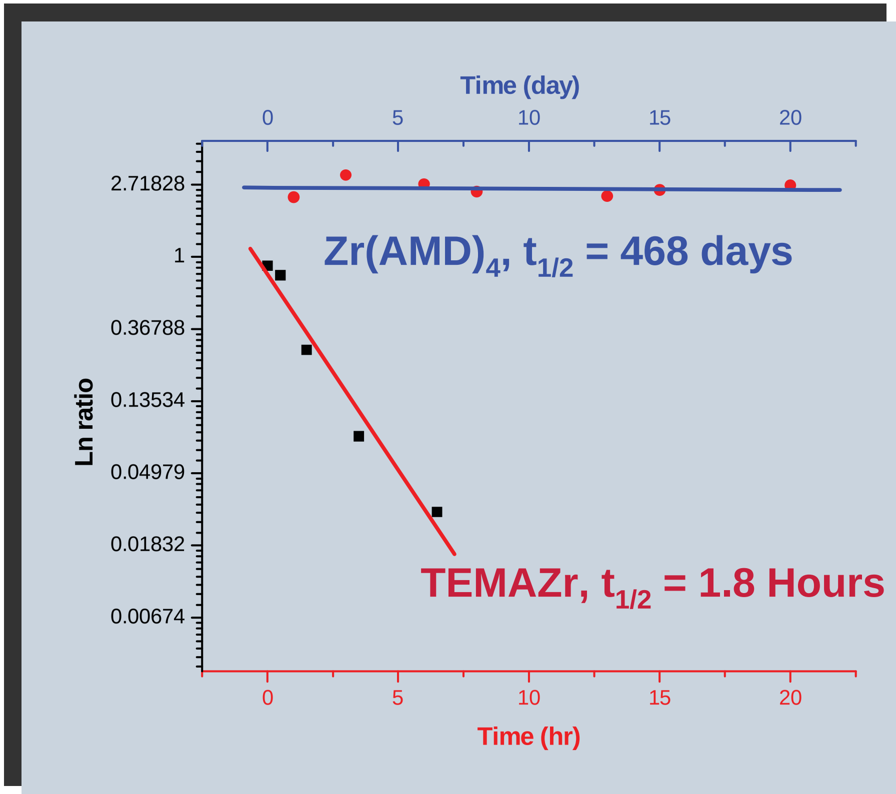
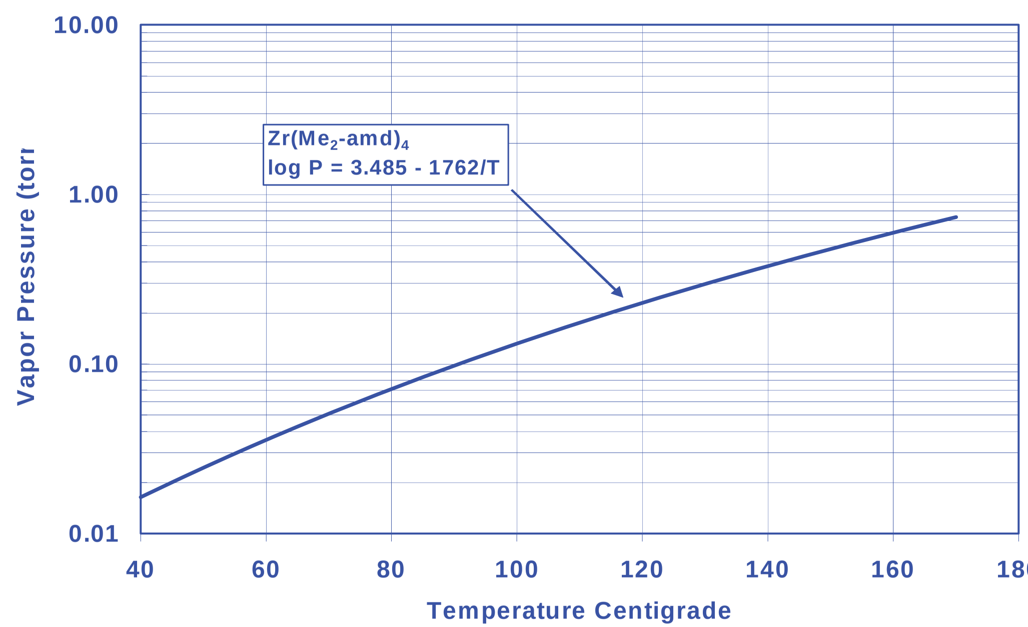
Decomposition Profiles for TEMAZr and Zr(amidinate)$_4$



Vapor Pressure Curve for Zr(amidinate)$_4$



No decomposition of Zr amidinates for > 1000 Hours at 200 ºC
Solid source with reasonable vapor pressure for ALD application
Best candidate for potential direct liquid injection delivery in ALD
Further DLI formulation work is ongoing, and will be presented in due course

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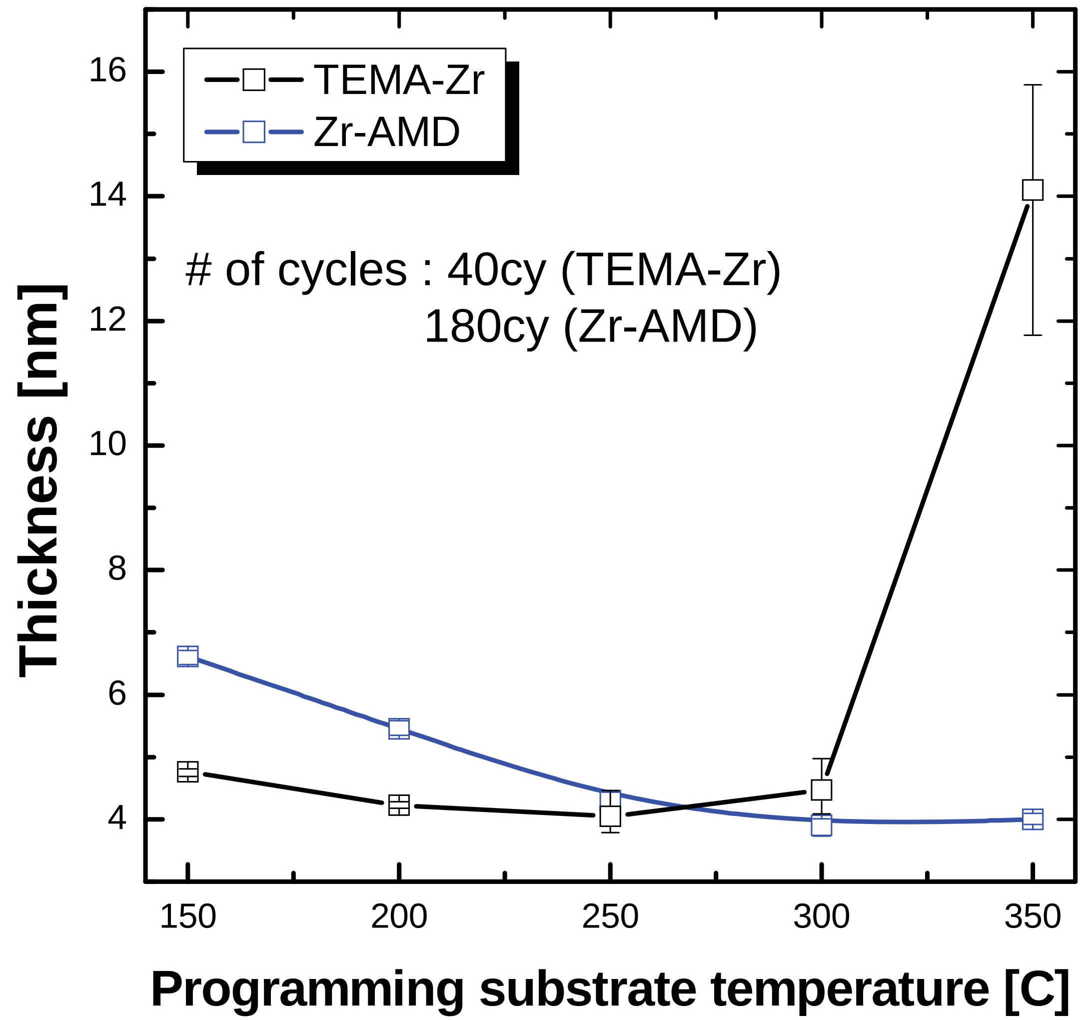
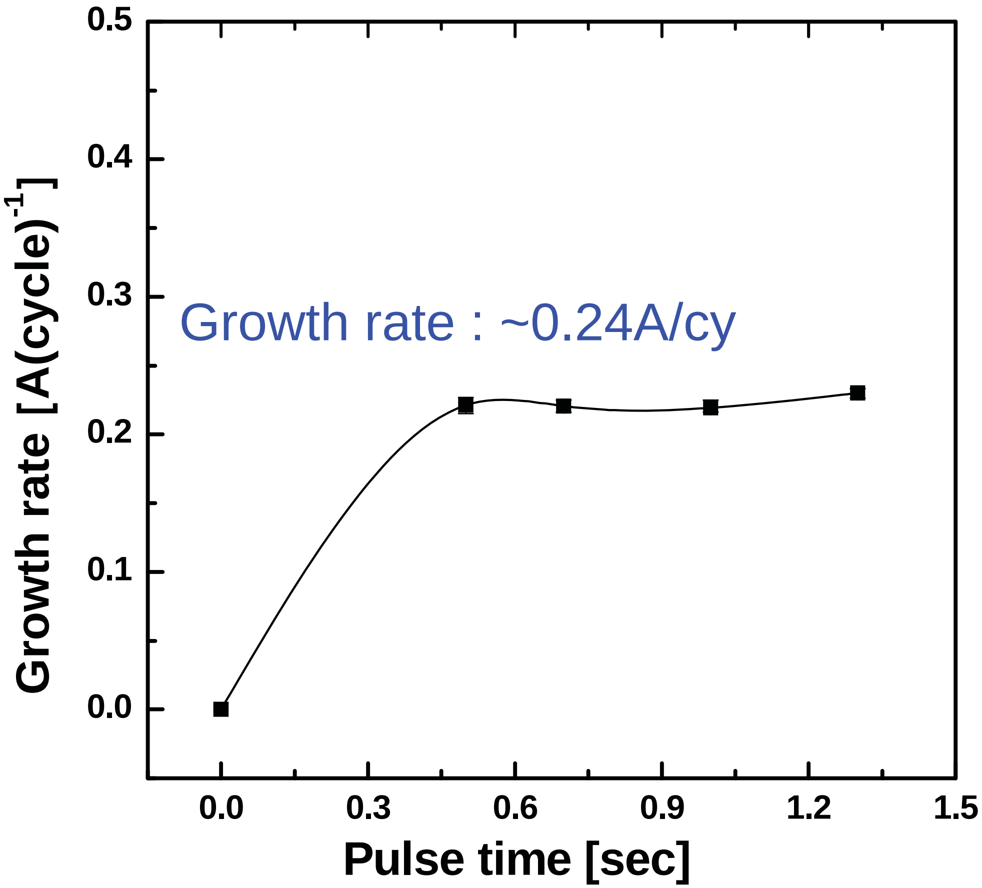
ALD of ZrO_2 Using $Zr(amidinate)_4$ & TEMAZr at UT Dallas

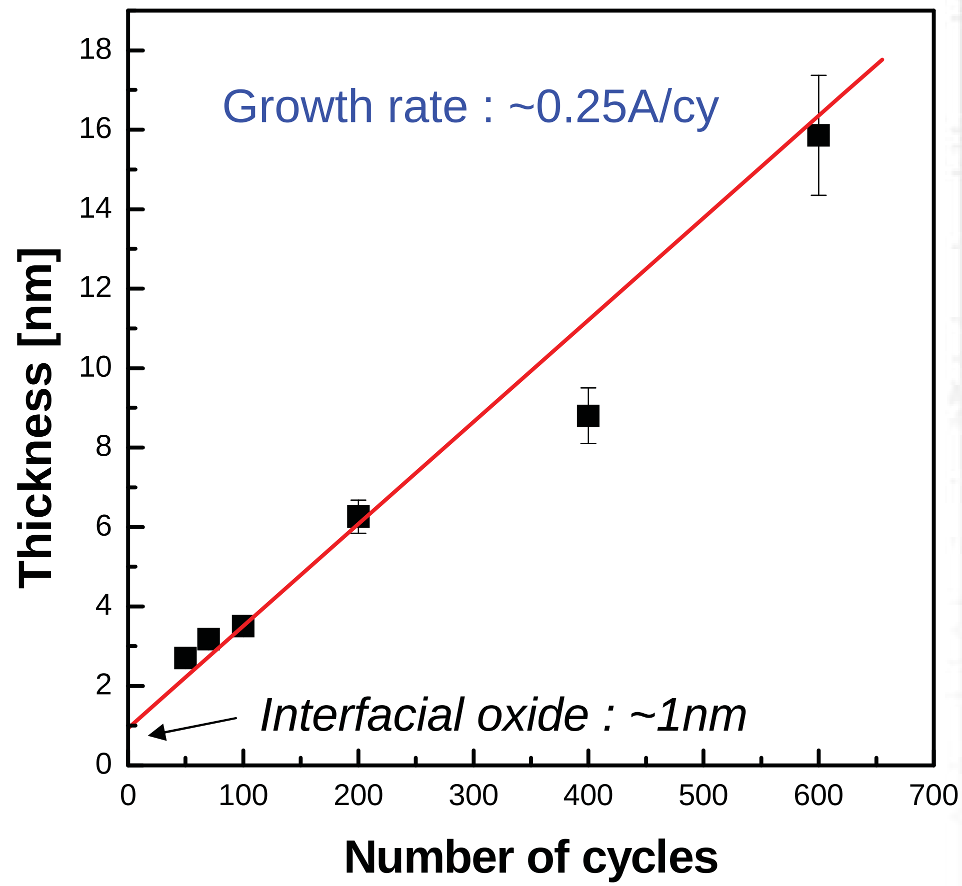


- *For **TEMA-Zr**, the growth rate increased rapidly above 300C and poor uniformity was observed.*
- *For **Zr-AMD**, the growth rate does not vary significantly even at a deposition temperature of higher than 300C and a good uniformity was observed as well.*

Saturation Curve : ZrO_2 Using $Zr(amidinate)_4$ at UT Dallas

- Substrate : HF-treated Si
- Programming substrate temp :300C

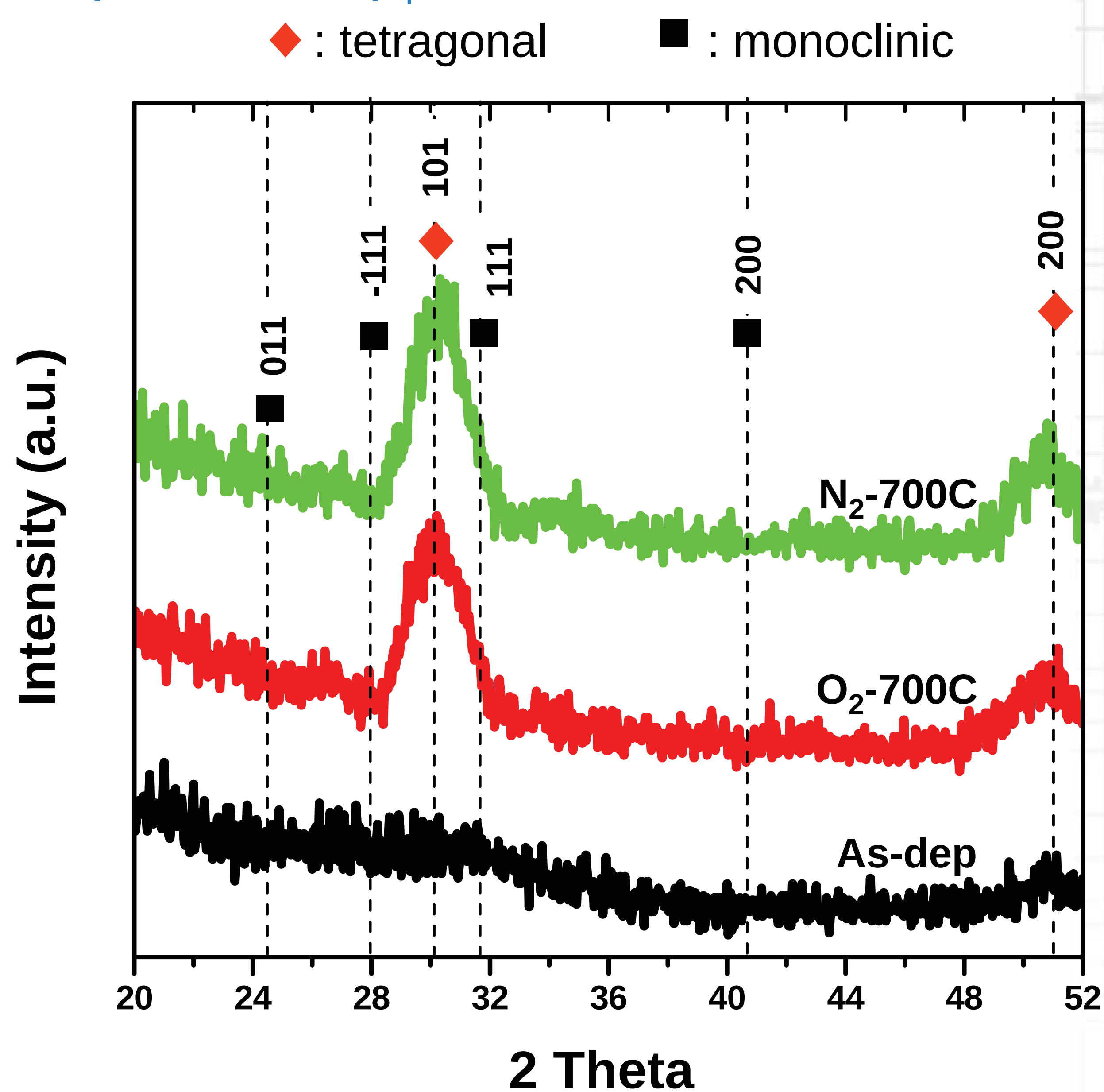




- *The self-limiting growth was verified for the ZrO_2 deposition process using the Zr-AMD precursor by increasing the pulse time at 300C.*
- *A linear deposition rate, characteristics of ALD, was also observed with Zr-AMD and H_2O.*

XRD: ZrO_2 ALD Using Zr(amidinate)$_4$ at UT Dallas

- ✓ Sample : ZrO_2 film (3.7nm)
- ✓ Substrate : SiO_2(1nm)/p-Si
- ✓ Annealing : RTA 700ºC for 30s
- ✓ Glancing Angle : 0.5º



- ✓ As-deposited one
  → *amorphous phase*
- ✓ As-annealed one in N_2/O_2
  → *tetragonal phase*

Summary: ZrO_2 ALD using $Zr(amidinate)_4$ and Ozone at ASM

- Reactors : **F-120** and **F-450** from ASM

  Si Substrate and Reaction temperature 200-350 °C
- The higher thermal stability of $Zr(amidinate)_4$ is demonstrated, and no thermal decompostion is found to occur during the precursor delivery at 100-120 °C using F-120 reactor.
- ALD mode thin film growth is demonstrated between 200-250C.
- At 200-250 °C, the film growth rate was found to be ca. 0.23 A/cycle under unoptimized conditions, and can be expected to be greater with further process optimization, as high as **1.4 A/cycle** based on preliminary customer evaluation results.

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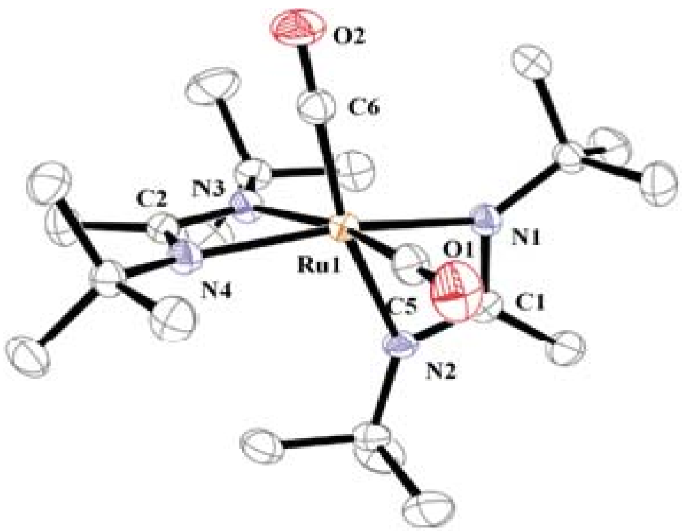
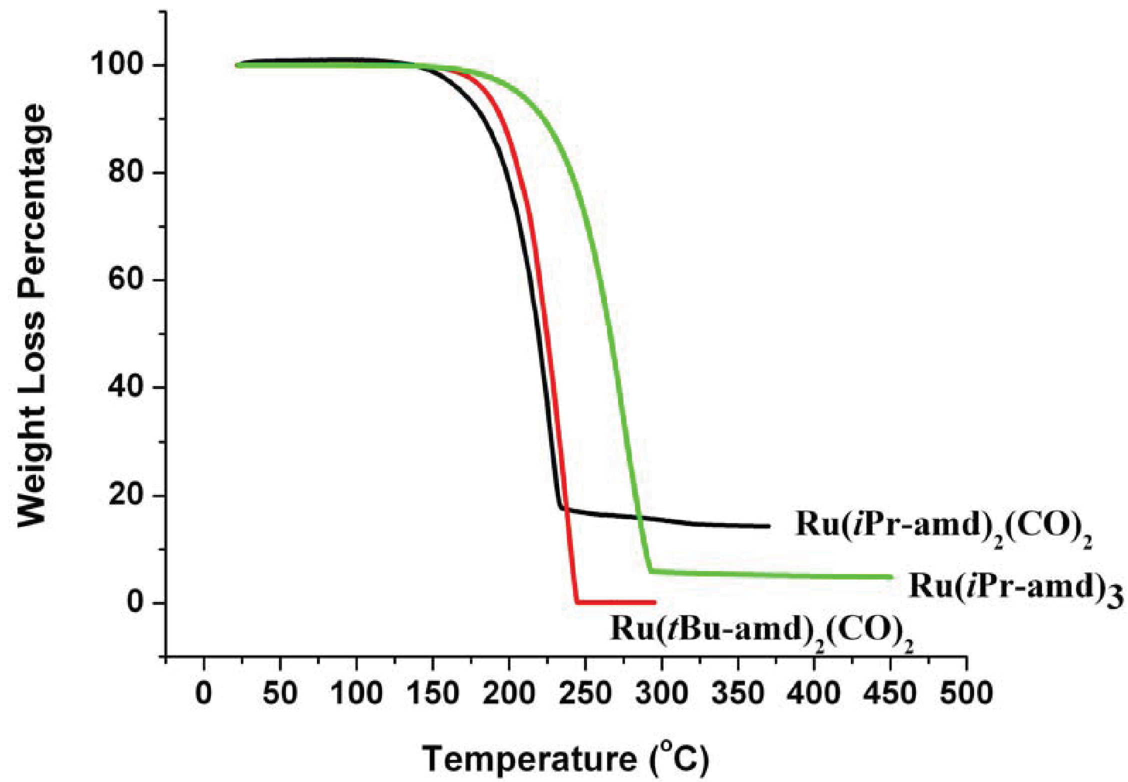
Ruthenium (Carbonyl) Amidinates for ALD Application

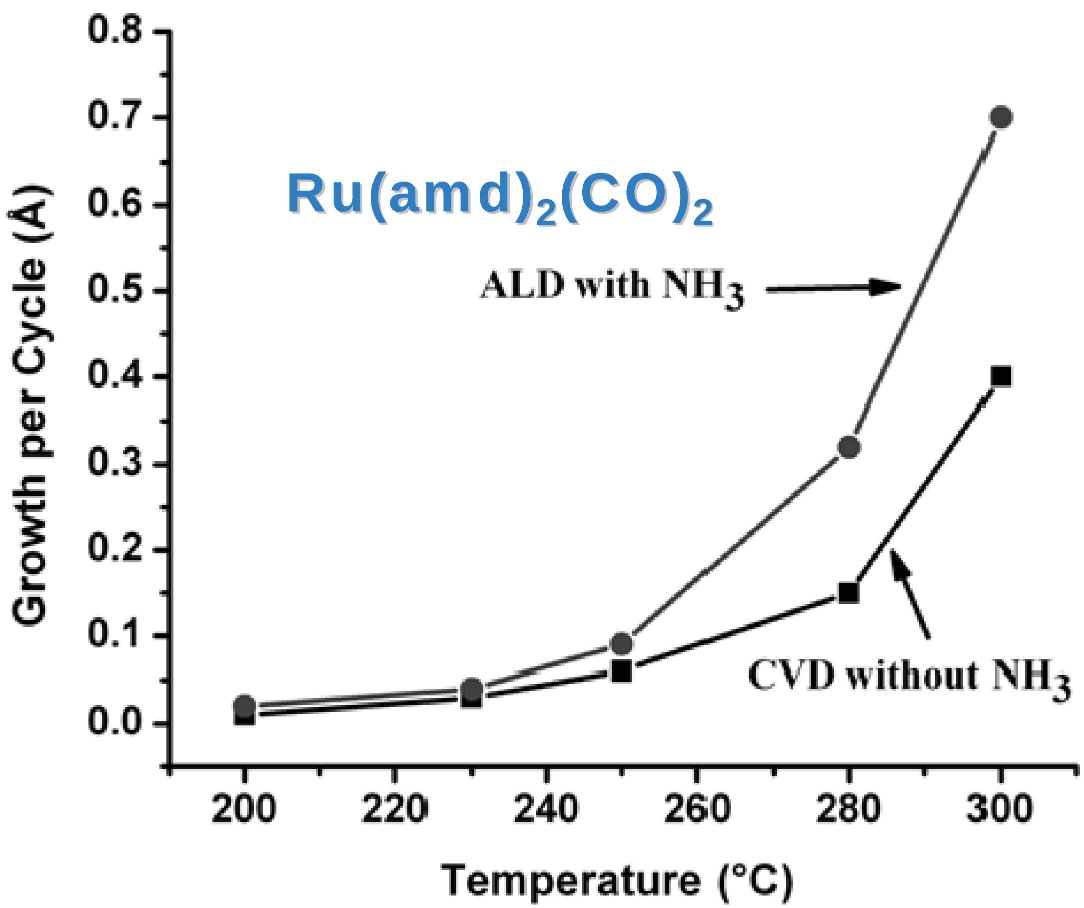


Ru(amd)$_2$(CO)$_2$



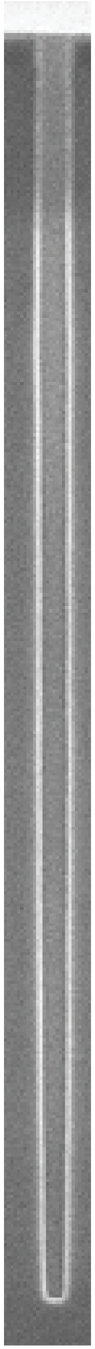
Ru(tBu$_2$-AMD)$_2$(CO)$_2$ is an air & moisture stable solid
Vapor pressure>0.05 Torr @130°C
Low evaporation residue 0.14% by TGA

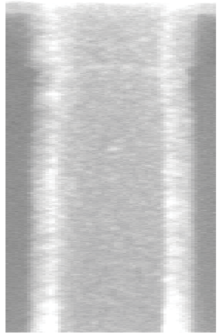
$Ru(CO)_2(amidinate)_2$: ALD and CVD Growth Rates



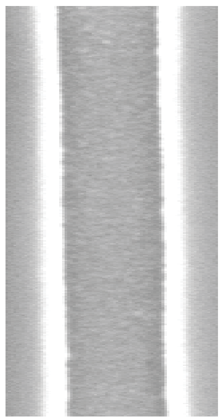
Advantage: Oxygen-free ALD Process !!

Step coverage: Ru film using $Ru(CO)_2(amidinate)_2$

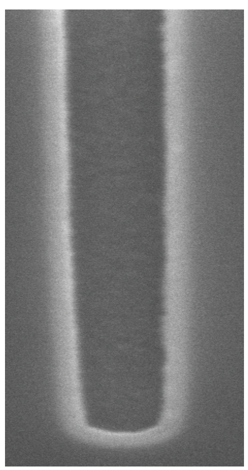




Top of trench
45 nm



Middle of trench
40 nm



Bottom of trench
40 nm

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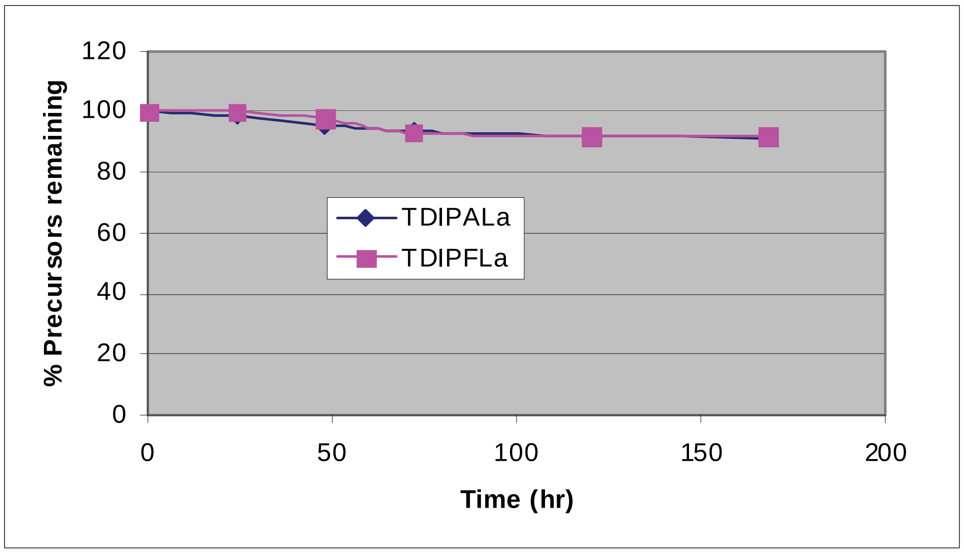
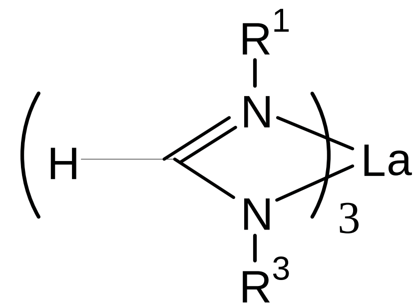
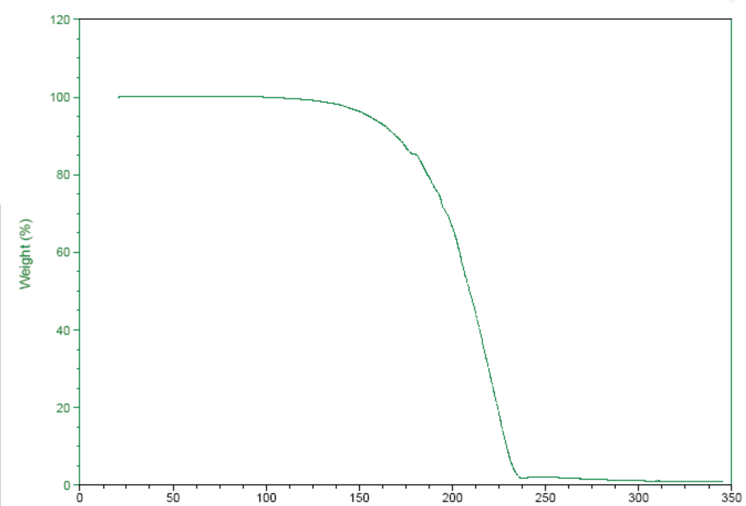
New La Source from Rohm and Haas Company: **Lanthanum Formamidinate, $La(FAMD)_3$**

Thermal Stability at 200 °C





Lanthanum Formamidinate



TGA of $La(FAMD)_3$

- ***Excellent Thermal Stability***
- ***TGA: $t_{1/2}$ = 209°C with negligible residue***
- ***Most Volatile La Source so far***
- ***Higher Vapor Pressure than $La(Cp)_3$ and $La(thd)_3$***

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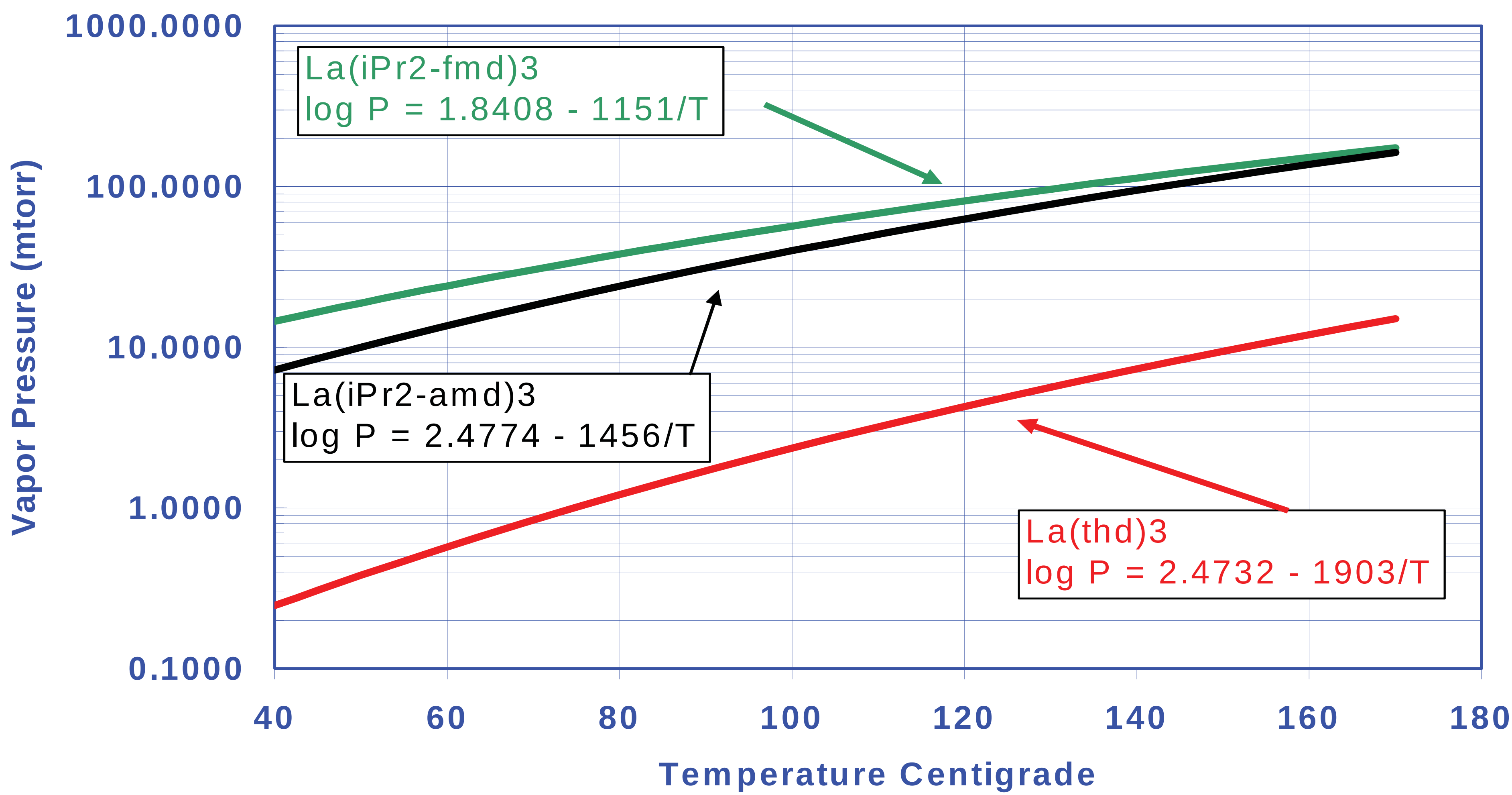
Vapor Pressures for La(amd)$_3$ and La(formamidinate)$_3$



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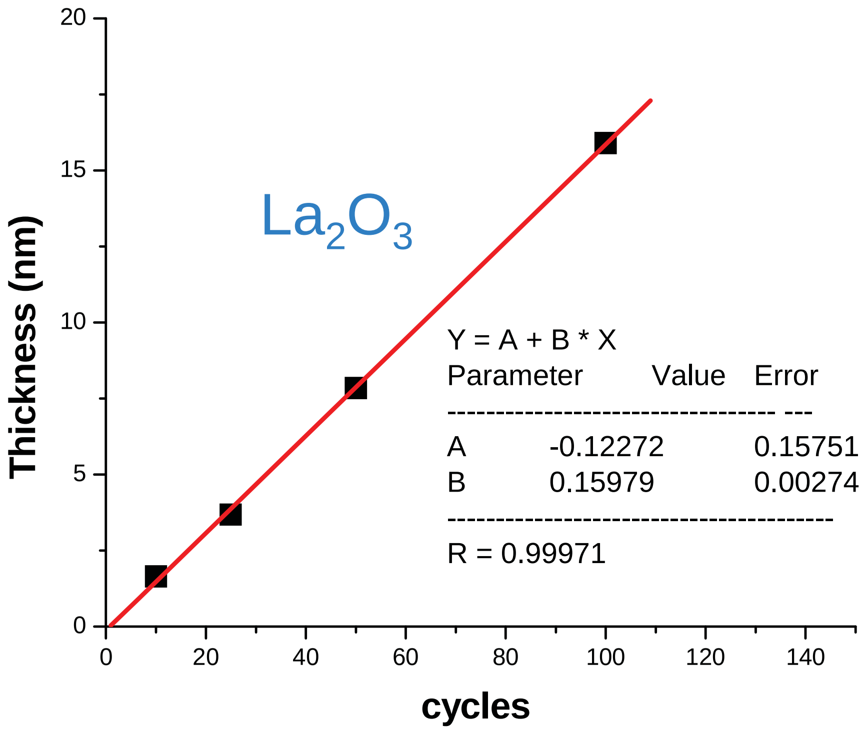
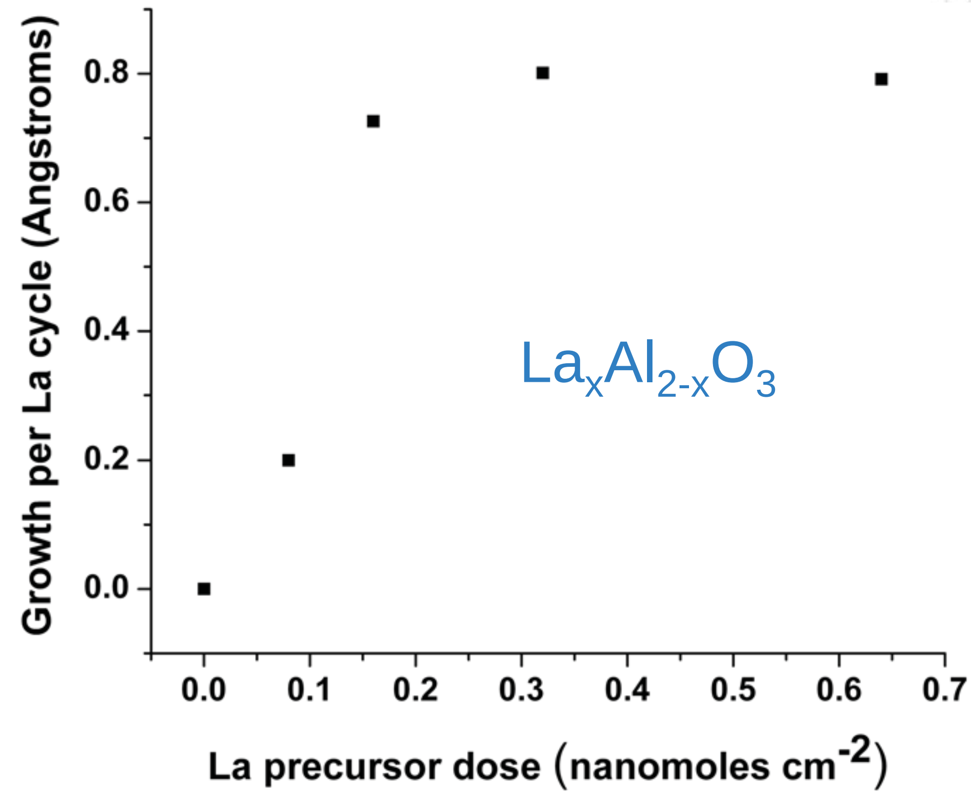
ALD of La_2O_3 and $La_xAl_{2-x}O_3$ Using $La(FMD)_3$ at Harvard University





Co-reactants: Trimethylaluminum (Me_3Al) and H_2O
Substrate Temperature: 300 ºC, Bubbler Temperature: 120 ºC
Reference: Results presented by Gordon et al. at this Conference

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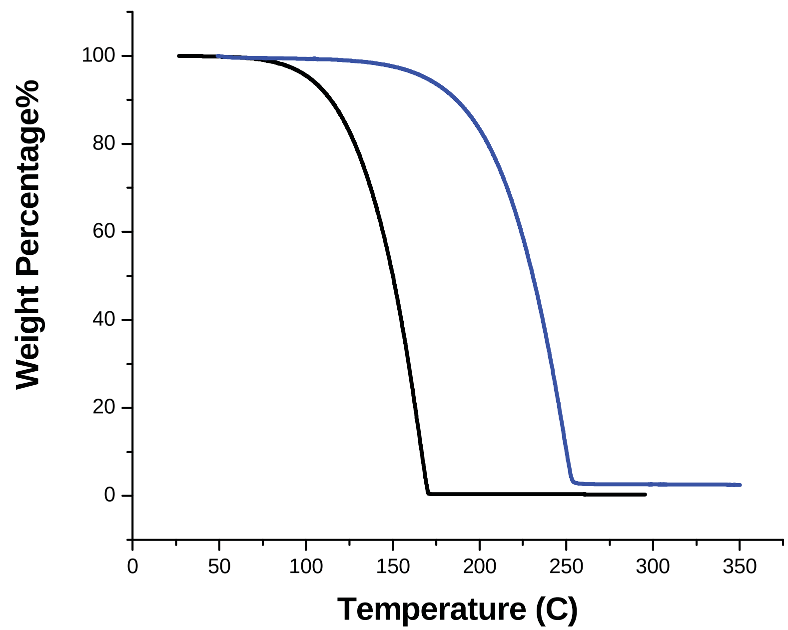
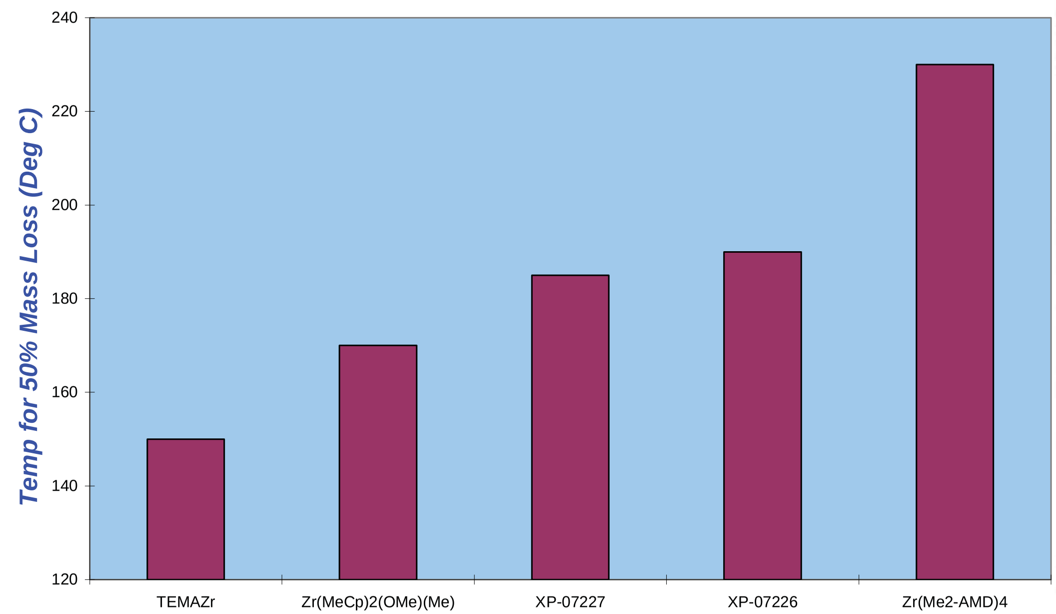
$Zr(Me_2\text{-}AMD)_4$, XP-07226 and XP-07227
New Zr Sources with Improved Thermal Stability From Rohm and Haas Company

TGA of TEMAZr and $Zr(Me_2\text{-}AMD)_4$



TGA Data for Zr Sources



- *Motivation: Greater Thermal Stability than conventional precursors.*
- *Desirable: Acceptable volatility (ca 0.1 Torr at < 200 ℃) and preferably a liquid precursor.*
- *$Zr(AMD)_4$, XP-07226 and XP-07227 exhibit better thermal stability vis-à-vis TEMAZr.*
- *XP-07227 is a liquid with higher vapor pressure than TEMAZr (160 mTorr and 28 mTorr at 40 ℃ resp) that is desirable for higher throughput in ALD.*

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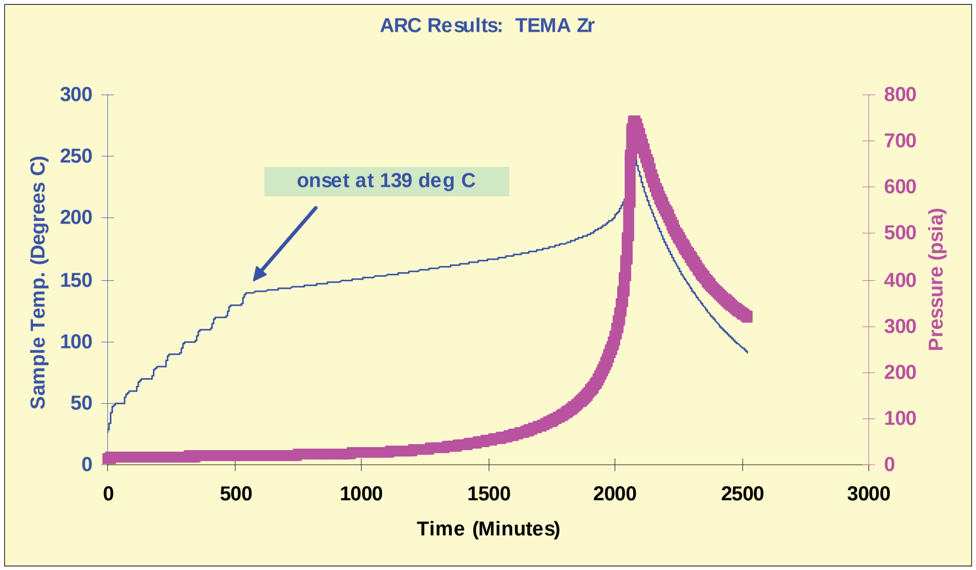
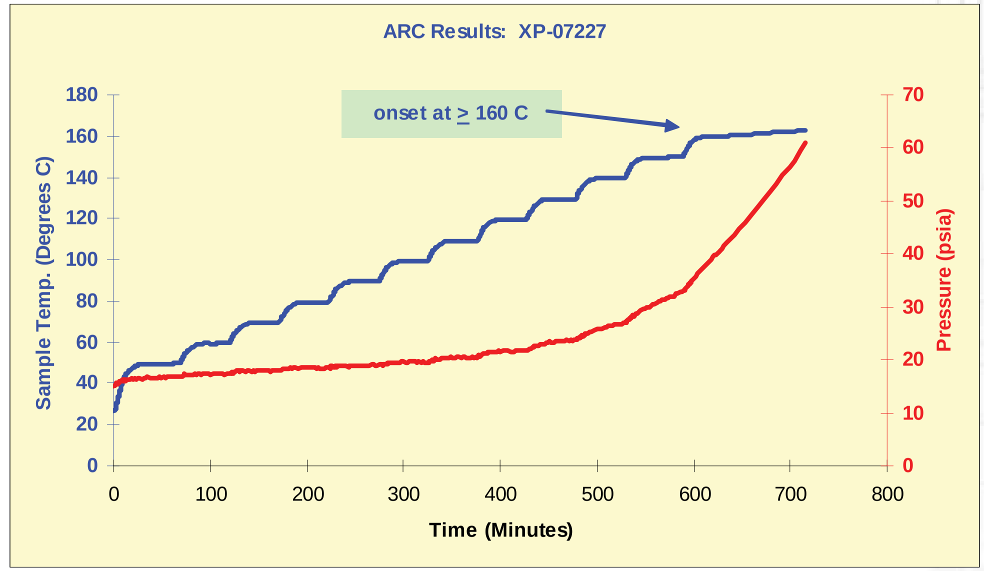
Accelerated Rate Calorimetry (ARC) and Improved Thermal Stability





- *Comparative ARC benchmarking of XP-07227 and TEMAZr confirms improvement in thermal stability.*
- *Zr(Me_2-AMD)$_4$ and La(FMD)$_3$ show no decomposition upto 250 ℃ (experiment termination point).*
- *More results on ALD and film characterization using new precursors will be reported in future.*

Summary

- Metal Amidinates are found to be more stable than conventional Metal Amides as precursors for ALD applications.
- Amidinates of Zr, Ru and La are demonstrated as suitable precursors for ALD of ZrO_2, Ru, La_2O_3 and $La_xAl_{2-x}O_3$
- La Formamidinate => a novel volatile La source from Rohm and Haas Company for ALD of La_2O_3 and $La_xAl_{2-x}O_3$.
- Ongoing development of new sources for ALD application at Rohm and Haas Company and in collaboration with Gordon Group at Harvard University.

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