New Precursors for ALD of High-k Dielectrics

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Outline

ALD HfO_2 from stable Hf amidinate precursors

Stable, amorphous high-k dielectrics
=> $LaLuO_3$ has the best properties

Volatile Precursors for Lanthanum Oxide

ALD of La_2O_3 and $LaAlO_3$

Volatile Precursors for Lutetium Oxide

Why More Stable Hf and Zr Precursors?

High-k HfO_2 or ZrO_2 with very low electrical leakage needed

Carbon impurity in films increases leakage

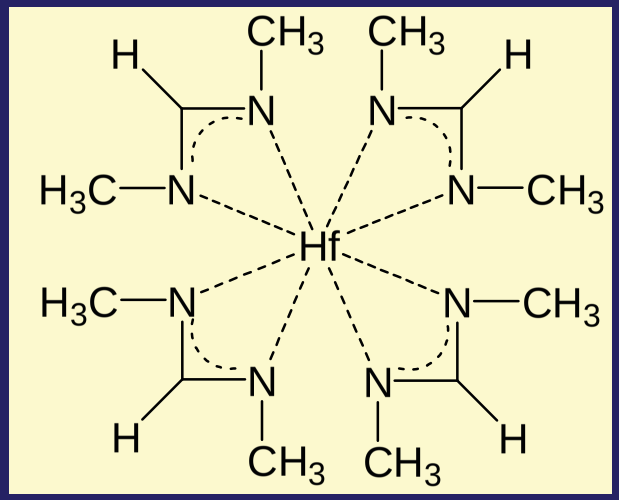
Thermal decomposition of organic precursors adds C to films

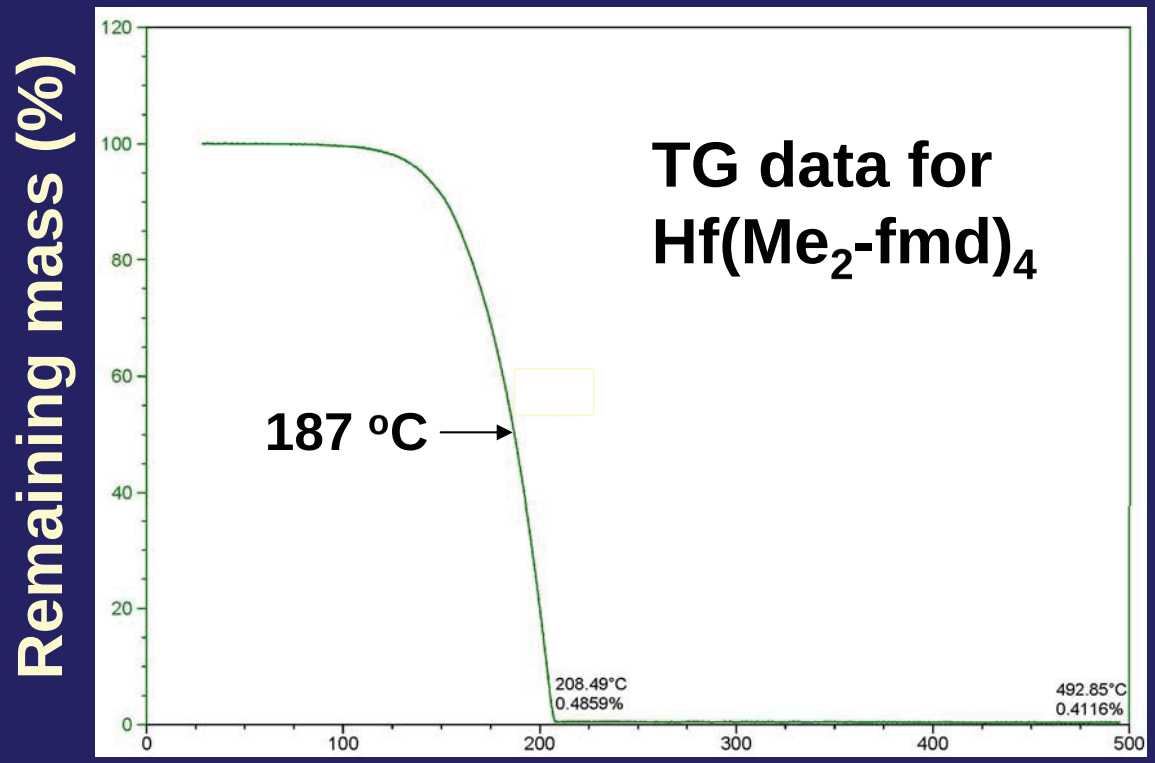
Thermal decomposition destroys uniformity and conformality

Deposition T ~ 350 ^oC needed for $HfAlO_x$ with ALD Al_2O_3

Hf alkylamide precursors decompose too quickly at 350 ^oC

Hafnium tetrakis(N,N'-dimethylformamidinate)

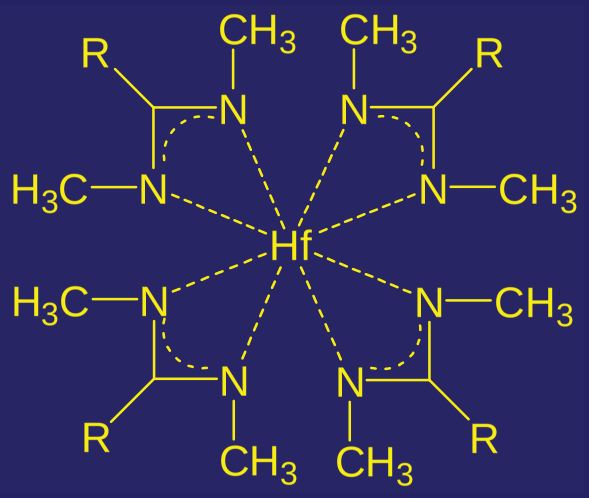




Negligible residue after TG

=> Sufficient volatility and thermal stability for ALD

Hafnium Amidinates



R		Melting Point, °C	TG $T_{½}$ °C
H	fmd	141	187
CH_3	amd	171	221
CH_2CH_3	pmd	80	251
$CH_2CH_2CH_3$	bmd	<20	246

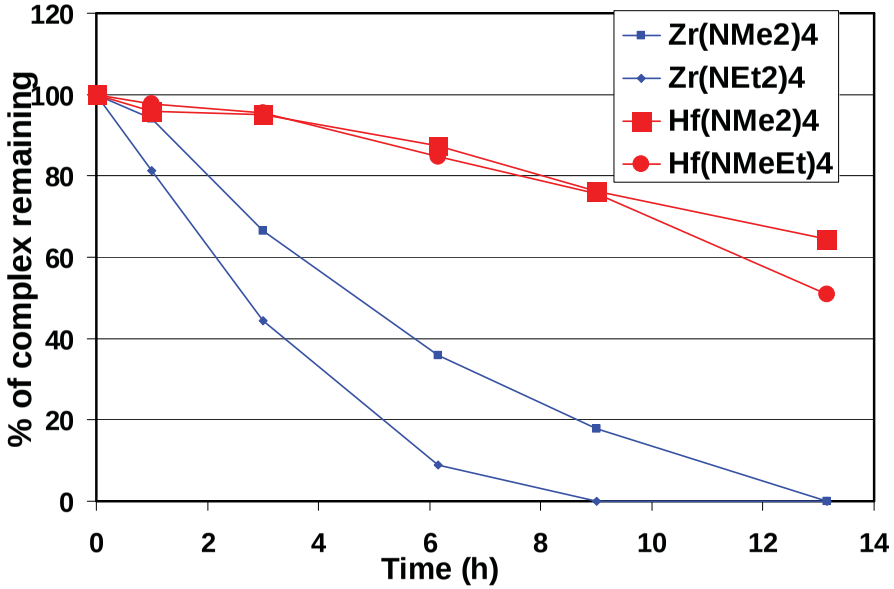
⇒ R = H is the most volatile; liquid in bubbler > 141 °C
Solid at 20 °C, soluble for use in direct liquid injection

⇒ R = $CH_2CH_2CH_3$ (propyl) is a liquid Hf precursor 20 °C

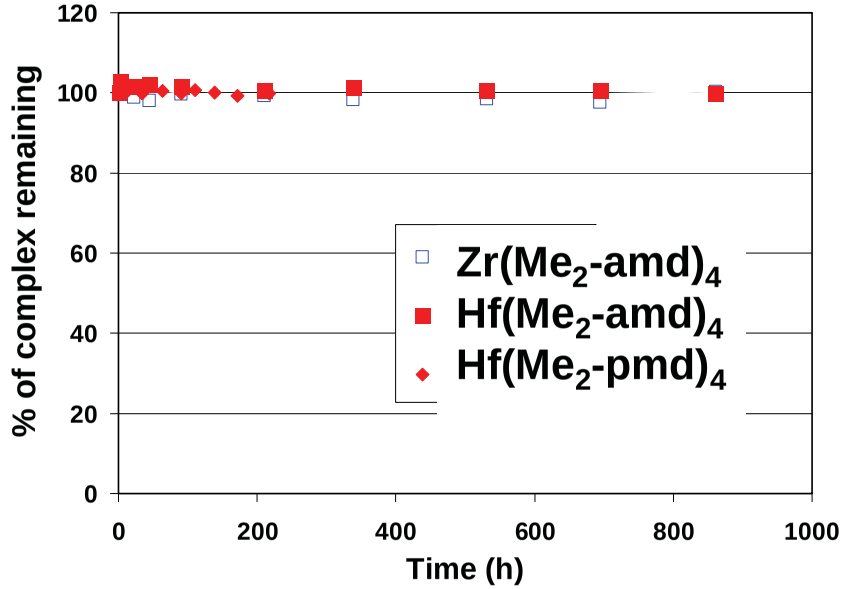
Thermal Stability of Hf and Zr Precursors

Precursors dissolved in mesitylene-*d*12, heated, and NMR spectra taken periodically

Hf and Zr amides completely decomposed in a few hours at 200 °C:

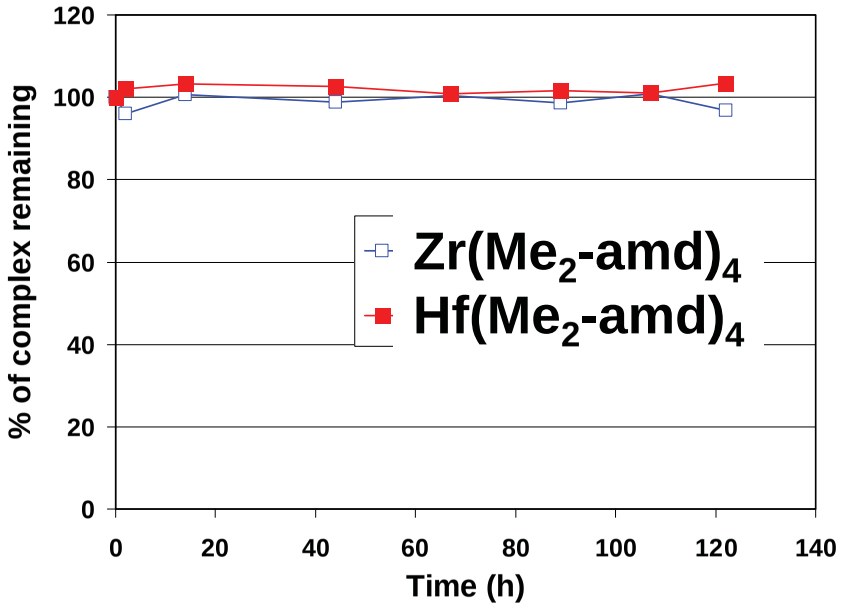


No decomposition of Hf or Zr amidinates during 1000 hours at 200 °C:

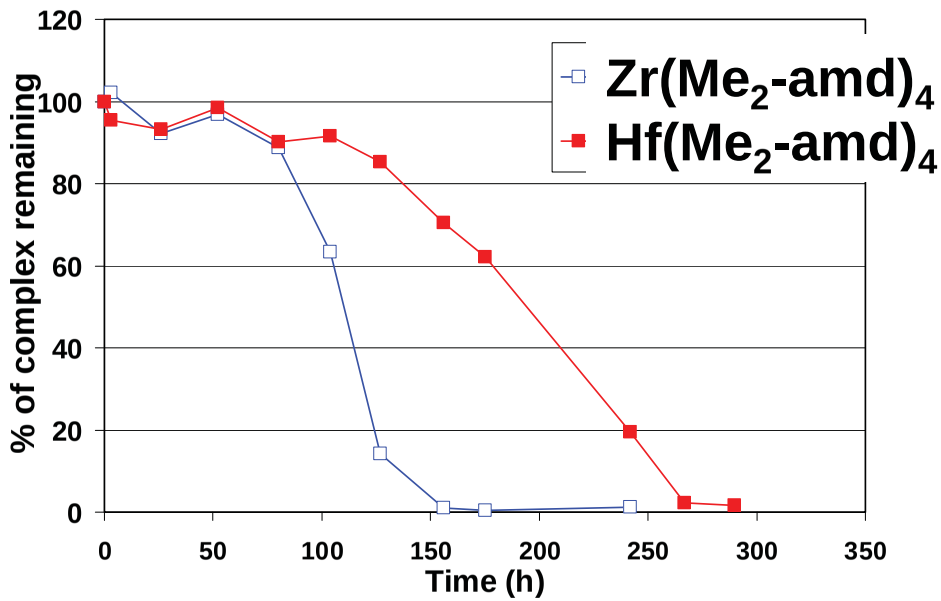


Thermal Stability of Hf and Zr Amidinates

No decomposition during 140 hours at 250 °C

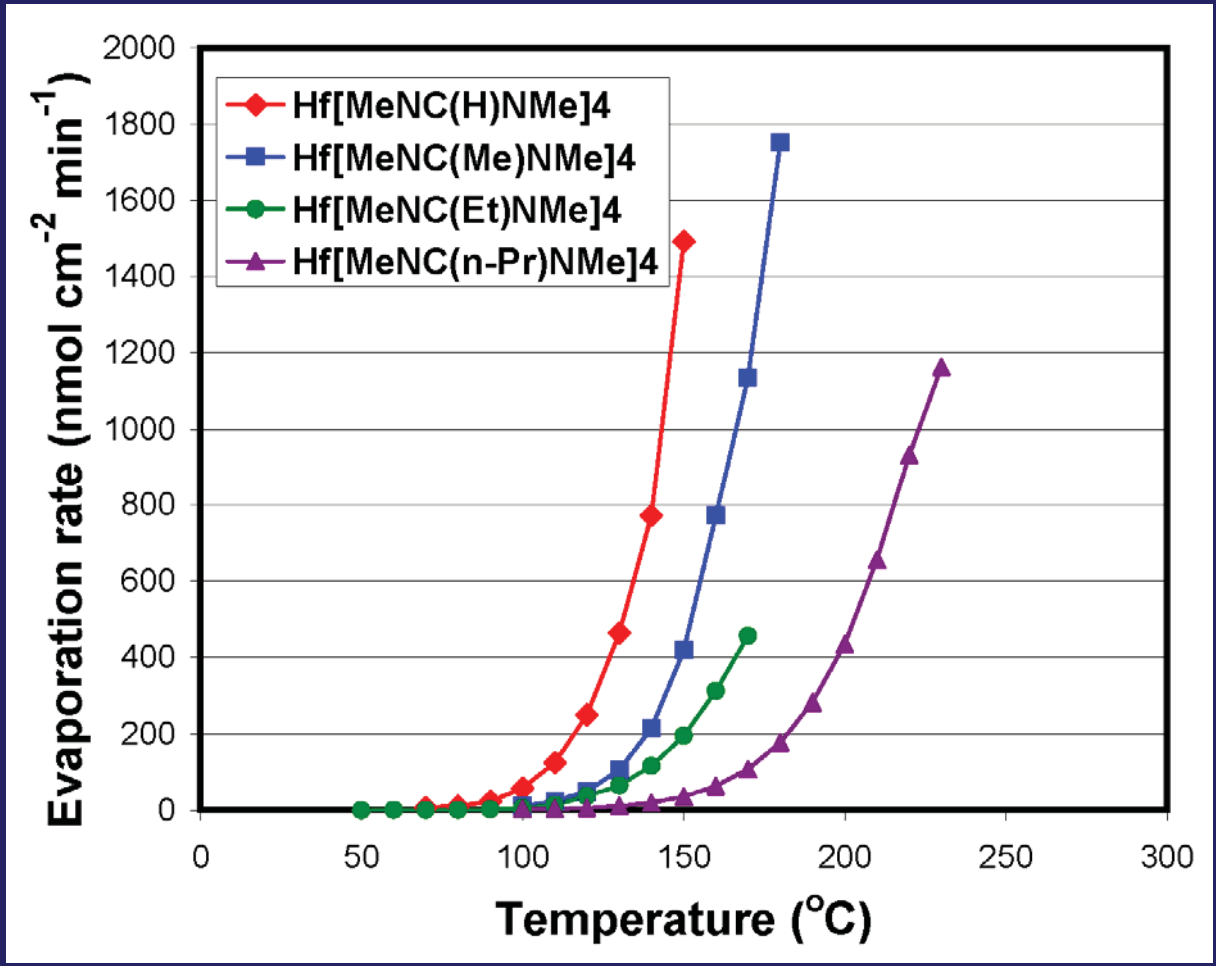


Decomposition after ~200 hours at 280 °C



=> Hf and Zr amidinates much more stable than amides

Vaporization Rates of Hafnium Amidinates



Highest rate with Hf tetrakis(N,N'-dimethylformamidinate)

=> High evaporation rates from thermally stable liquids

ALD of HfO_2 from Amidinate Precursors

ALD Conditions

- Typical bubbler temperatures 100-150 °C (mp 141 °C)
- ALD with H_2O self-limiting at ~0.1 nm per cycle
- ALD "window" ~150 to ~400 °C

Electrical Properties (non-optimized)

- Dielectric constant >16
- Breakdown field ~6 MV/cm

Stable Amorphous High-k Dielectrics

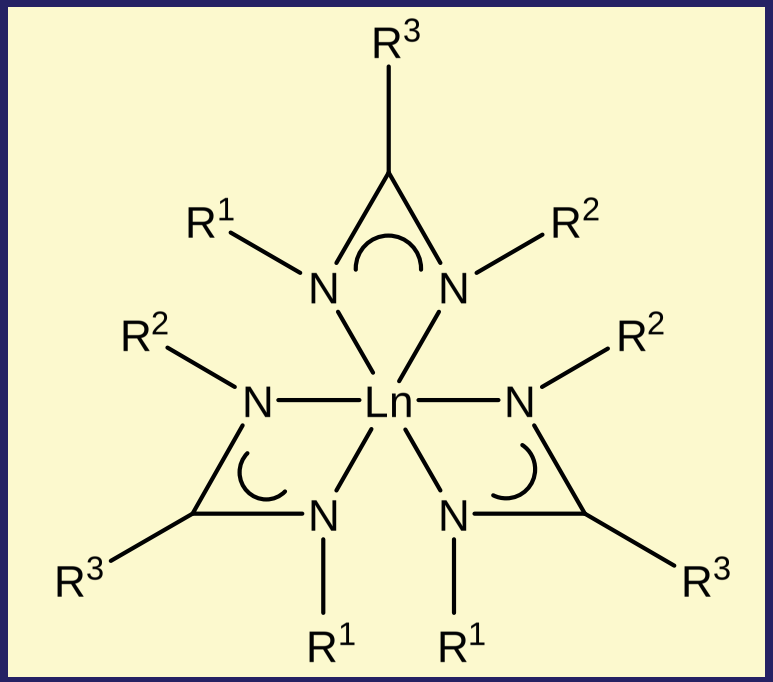
	k	Conduction band offset	Valence band offset
SiO_2	3.9	3.5	4.4
Al_2O_3	8	2.8	4.9
$HfSiO_4$	12	1.5	3.4
$LaAlO_3$	18	1.9	3.2
$La_2Hf_2O_7$	20	2.0	2.6
$GdScO_3$	22	2.0	2.5
$DyScO_3$	22	2.0	2.5
$LaLuO_3$	**32**	**2.1**	**2.1**

=> $LaLuO_3$ has the best properties!

Advantages of $LaLuO_3$ as high-k dielectric

- High dielectric constant (*k~32*) for amorphous phase
- Sharp interface with Si, and no low-k interlayer
- Stays amorphous and doesn't form alloys with Si or Ge after respective S/D activation anneals
- Both band offsets w.r.t Si are large (2.1 eV), helping to achieve low leakage currents

Amidinate Precursors for Lanthanides

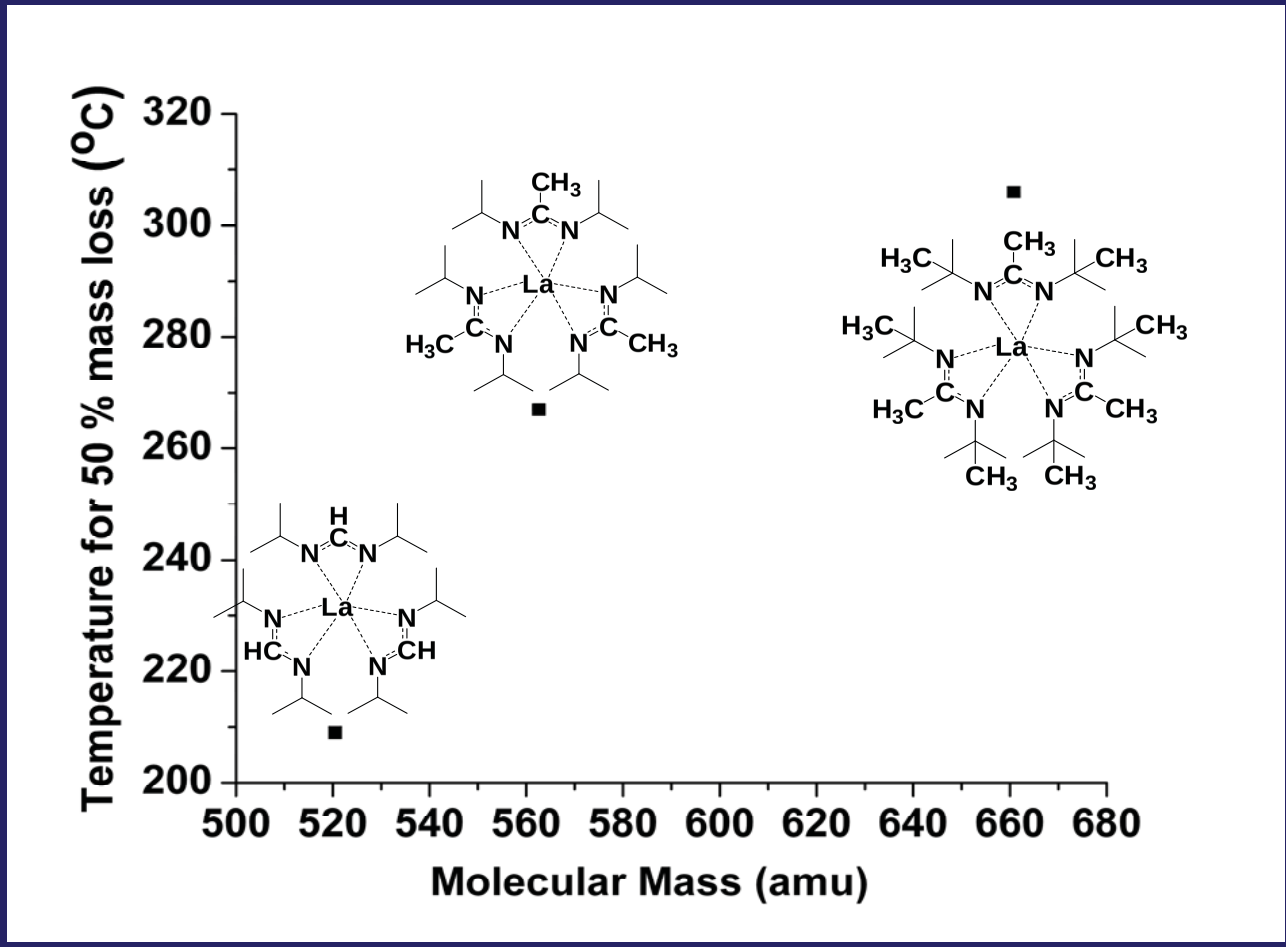


The R^1 and R^2 are alkyl groups: isopropyl, *tert*-butyl, ethyl, etc.

R^3 can be an alkyl group or hydrogen

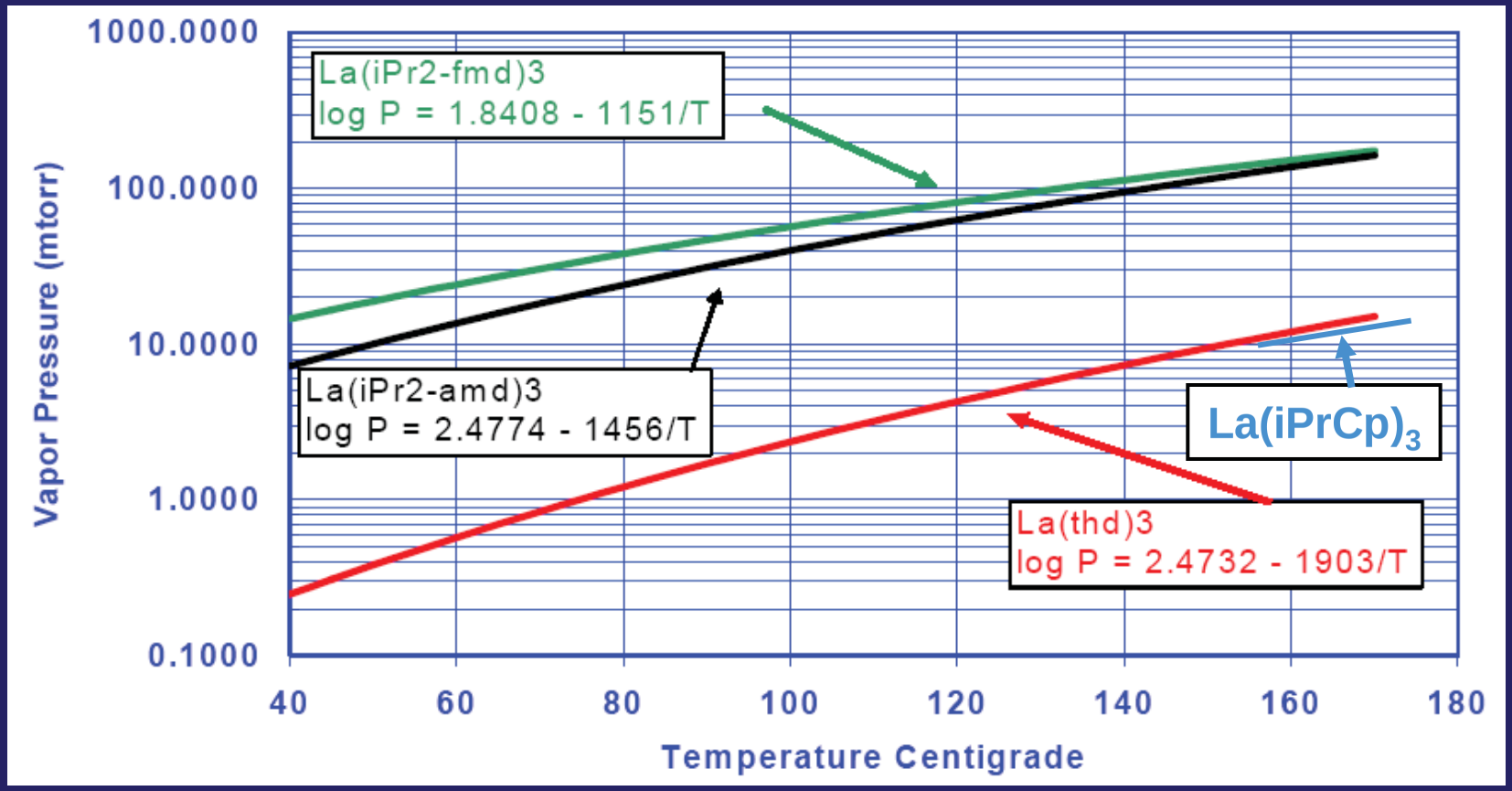
The choices of R^n affect the volatility, reactivity and stability.

Thermogravimetric Analysis of Lanthanum Amidinates

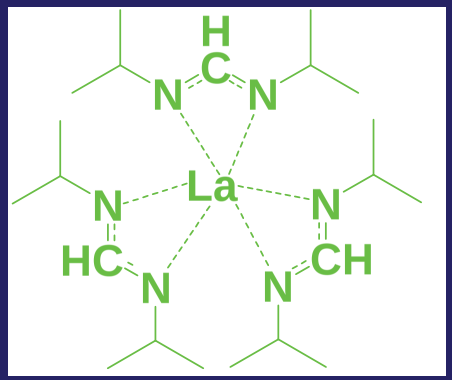


=> Vaporization temperature increases with molecular mass

Vapor Pressures of Lanthanum Precursors



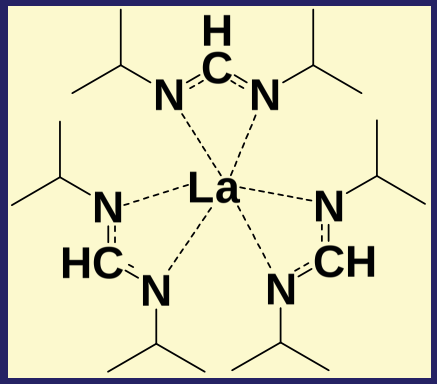
=> $La(iPr_2\text{-}fmd)_3$ is most volatile La compound known, 60 mTorr at 100 °C

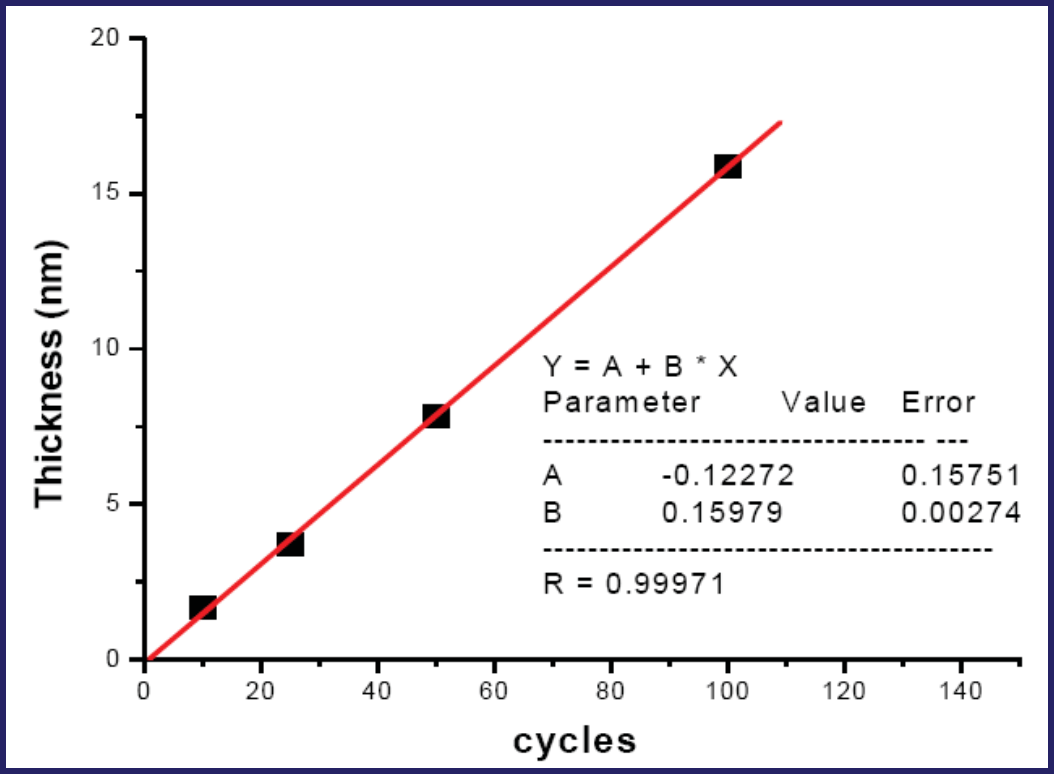


ALD of La_2O_3

Precursors:
H_2O and

tris(N,N'-diisopropyl-formamidinato)lanthanum
$(^iPr_2\text{-fmd})_3La$



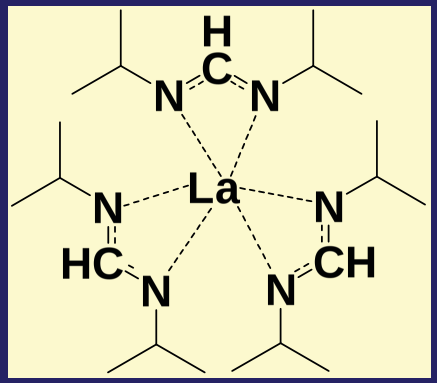


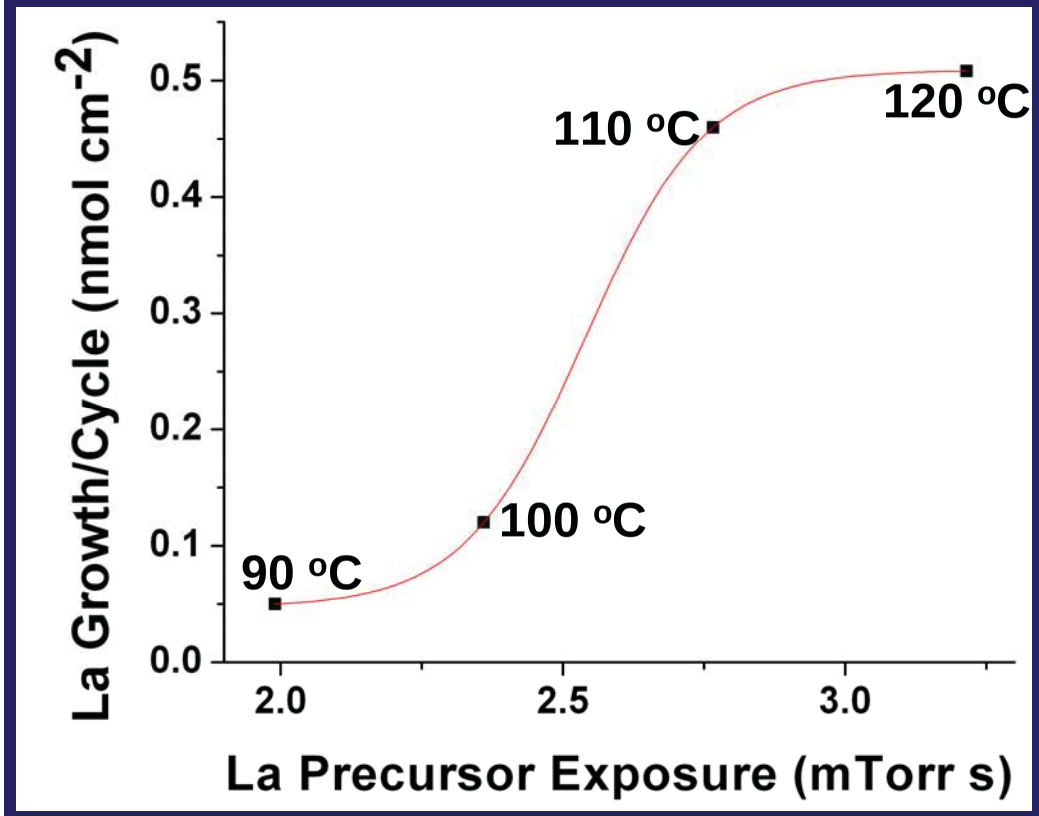
=> 0.16 nm per cycle

=> negligible delay in nucleation on SiH

Growth per La Cycle for ALD $LaAlO_3$

Precursors: Me_3Al, H_2O and tris(N,N'-diisopropyl-formamidinato)lanthanum $(^iPr_2\text{-fmd})_3La$





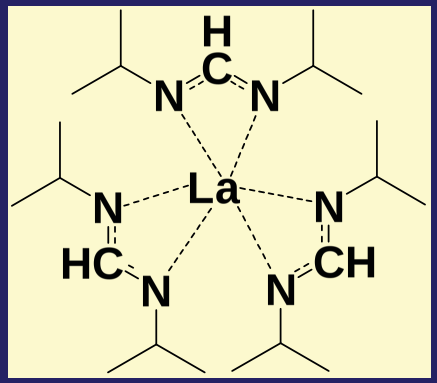
Bubbler temperature 90 to 120 °C
Substrate temperature 300 °C

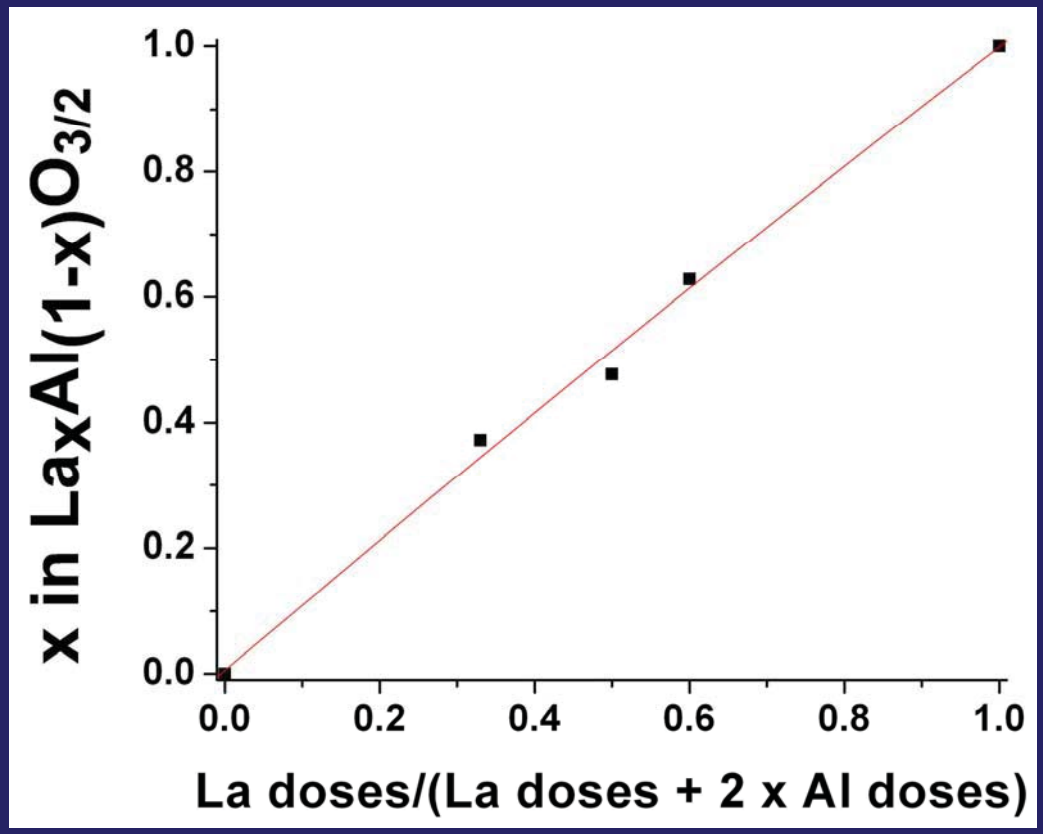
=> ALD saturation at 0.08 nm per La cycle

Growth even at bubbler temperature <100 °C

Composition of ALD $La_xAl_{1-x}O_{3/2}$

Precursors:
Me_3Al, H_2O and
tris(N,N'-diisopropyl-formamidinato)lanthanum
$(^iPr_2\text{-fmd})_3La$





Growth conditions:
Bubbler temperature 120 °C
Substrate temperature 300 °C

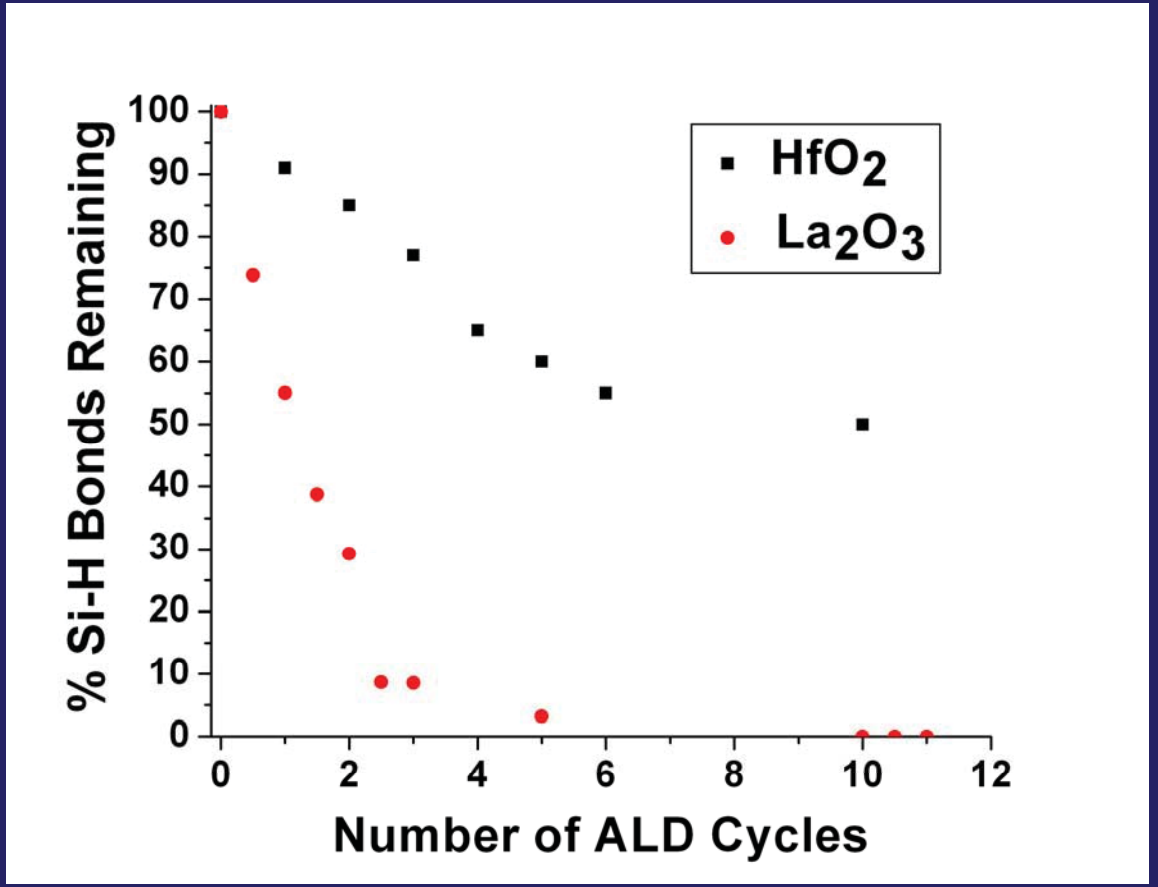
=> Composition control by changing ratio of precursor doses

=> 2 x as many Al atoms as La atoms per dose

Precursor Reactivity with SiH Surface by IR

Hf alkylamide only reacts with half of the Si-H bonds on the surface even after many cycles

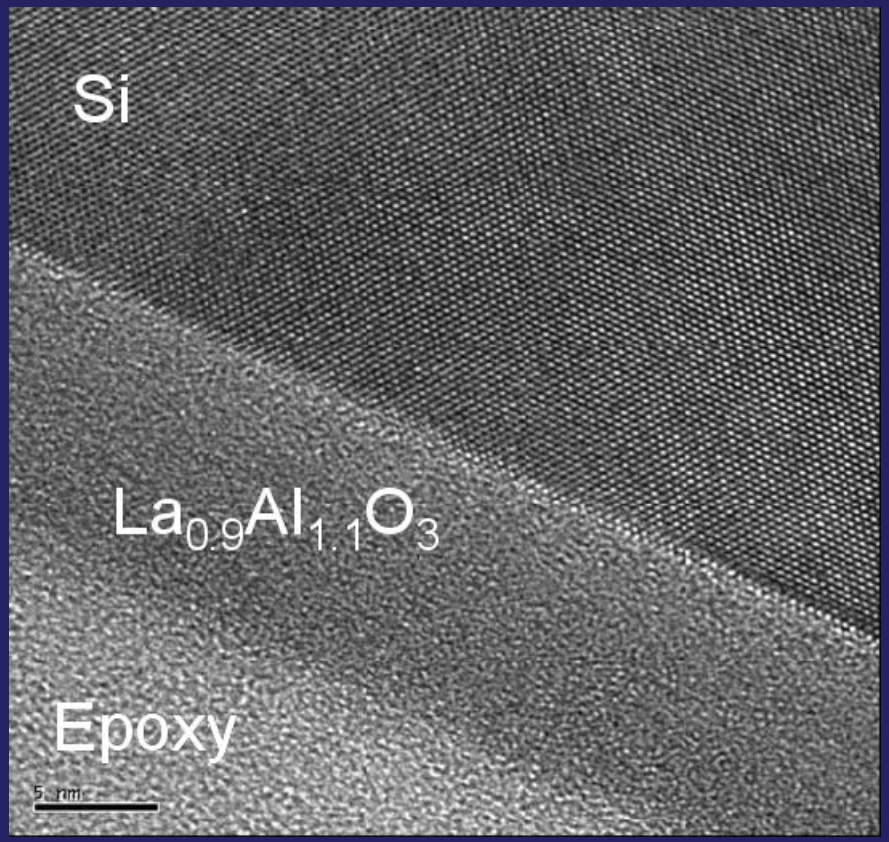
La amidinate reacts with nearly all the Si-H bonds in only 3 cycles

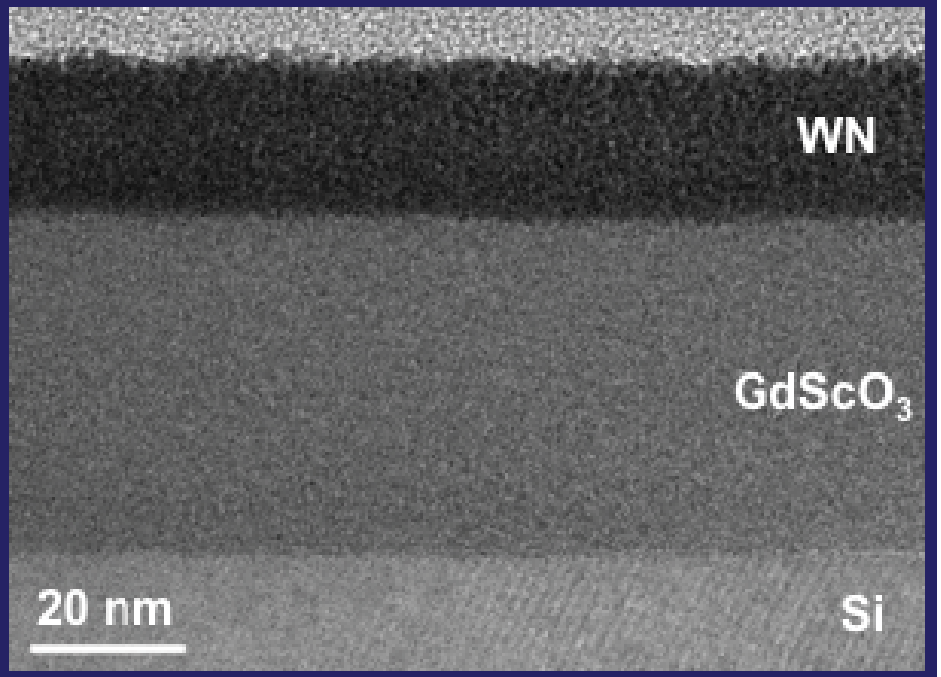


=> Completely uniform surface coverage by La amidinate

Details of the infrared spectra were given in a paper this morning by J. Kwon, M. Dai, E. Langereis, Y. Chabal, K.-H. Kim and R. G. Gordon.

TEMs of ALD $LaAlO_3$ and $GdScO_3$



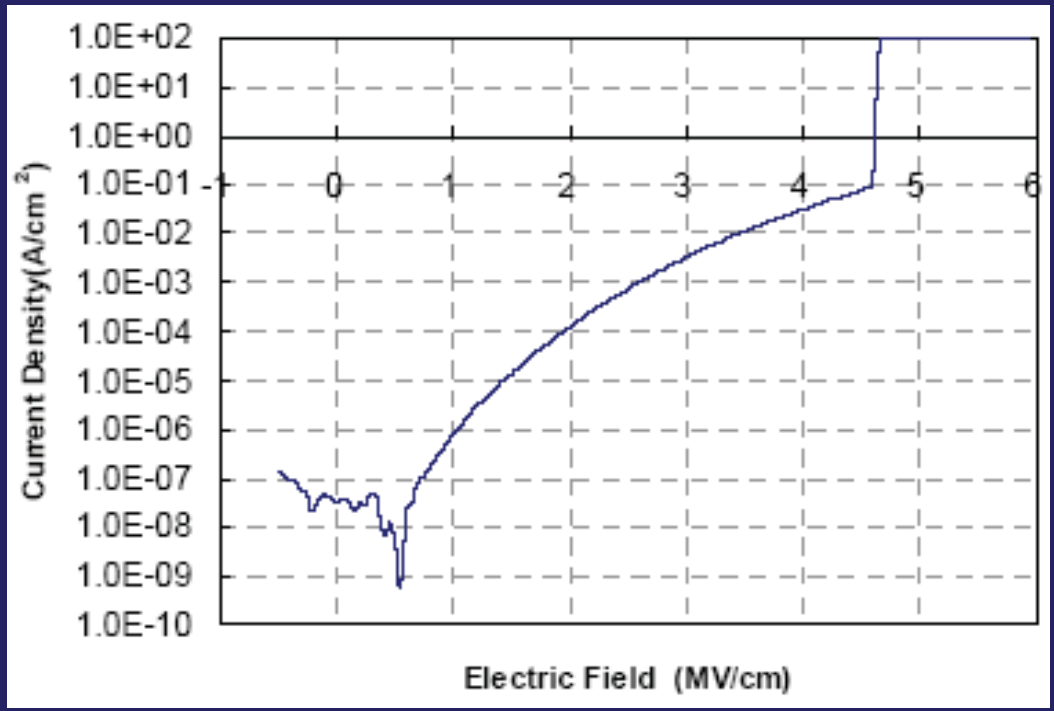


=> Sharp interfaces with silicon without interlayers

=> Uniform nucleation and thickness

Leakage Current through ALD La_2O_3

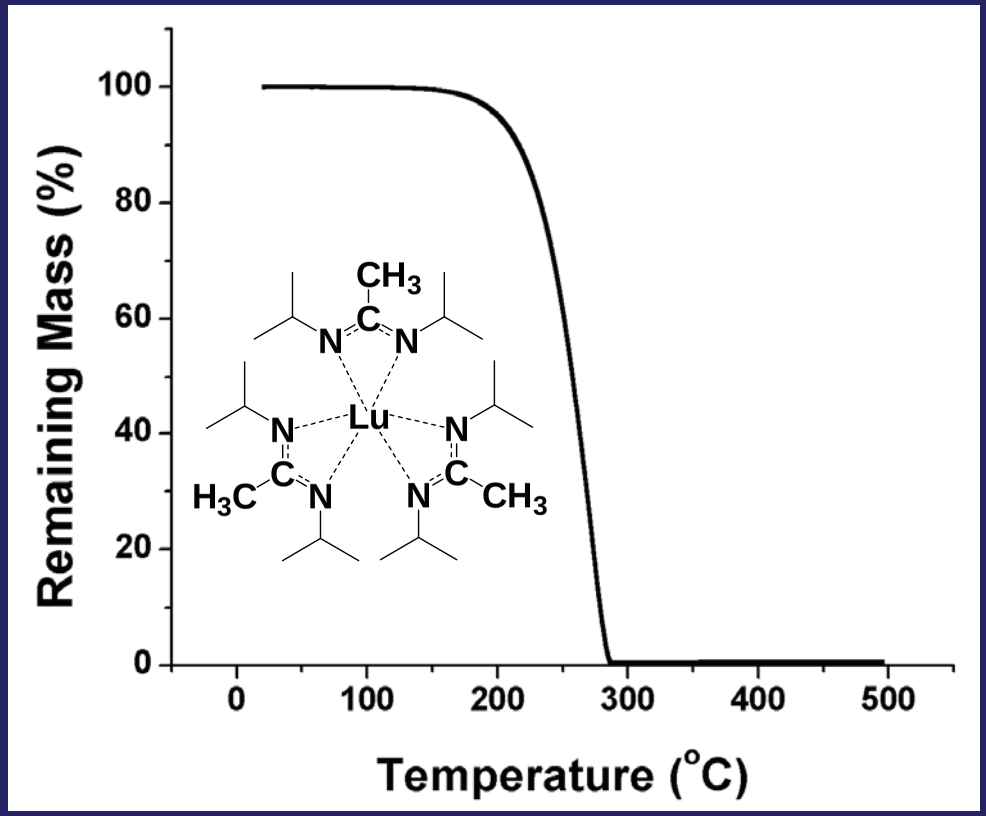
Vapor source: a solution of the La precursor (mp 194 °C) vaporized with an MKS MDD system



Low leakage current similar to films made from a bubbler.

=> negligible carbon contamination from solvent

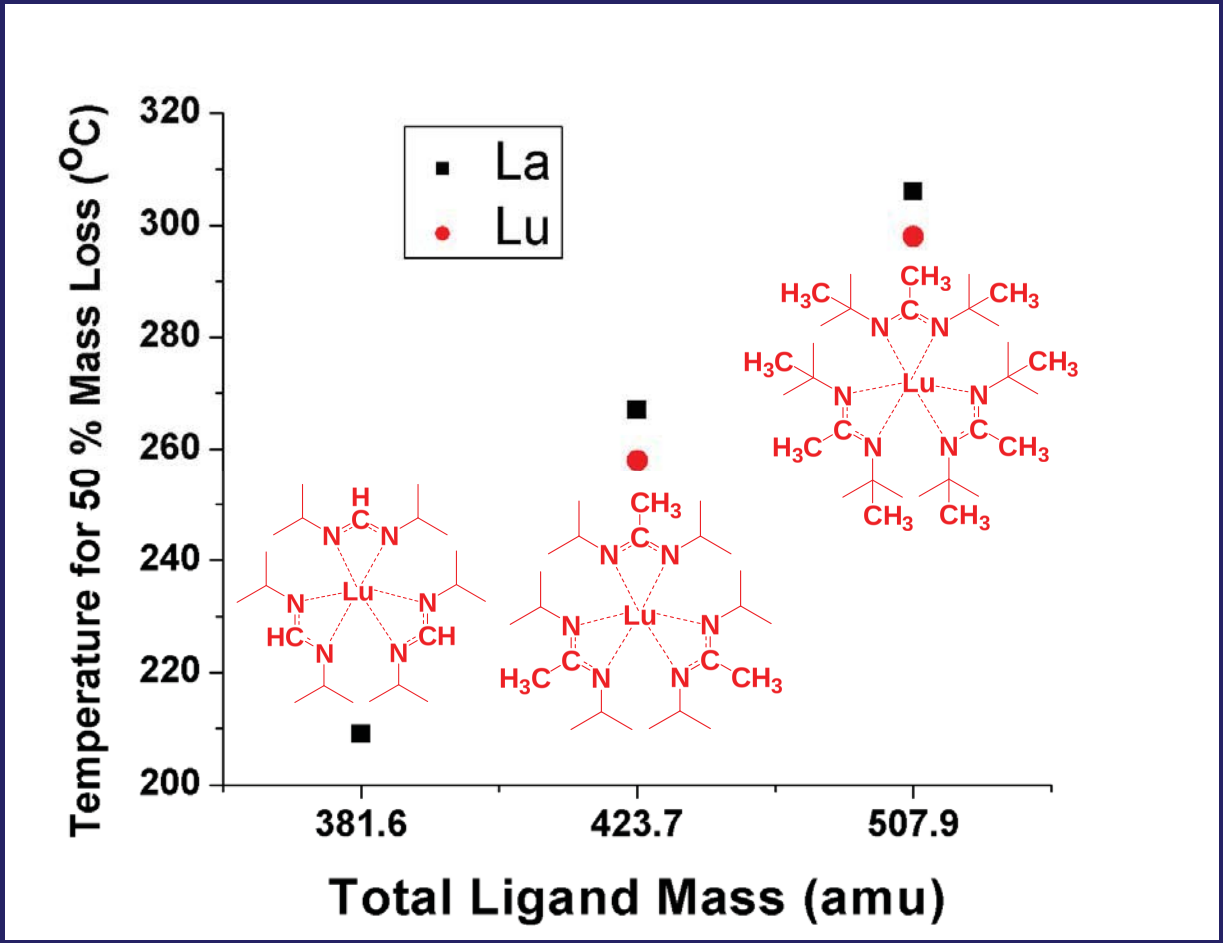
Thermal Gravimetric Analysis of Lutetium tris(N,N'-diisopropylacetamidinate)



Evaporation with negligible residue

=> Sufficient volatility and thermal stability for ALD

Thermal Gravimetric Analyses of Lanthanum and Lutetium Amidinates



=> Lu amidinates are slightly more volatile than La amidinates

ALD of Lu_2O_3 and $LaLuO_3$

ALD experiments and film characterization are underway. . . .

Conclusions

Hf amidinates are more stable than Hf amides

Hf amidinates are suitable as ALD precursors

$LaLuO_3$ is a very promising high-k dielectric

La and Lu amidinates are volatile ALD precursors

Current work on ALD of $LaAlO_3$, Lu_2O_3 and $LaLuO_3$

Acknowledgements

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