Designing Suitable Metal Amidinate Sources for TiN and Ba/Sr-containing Thin Films

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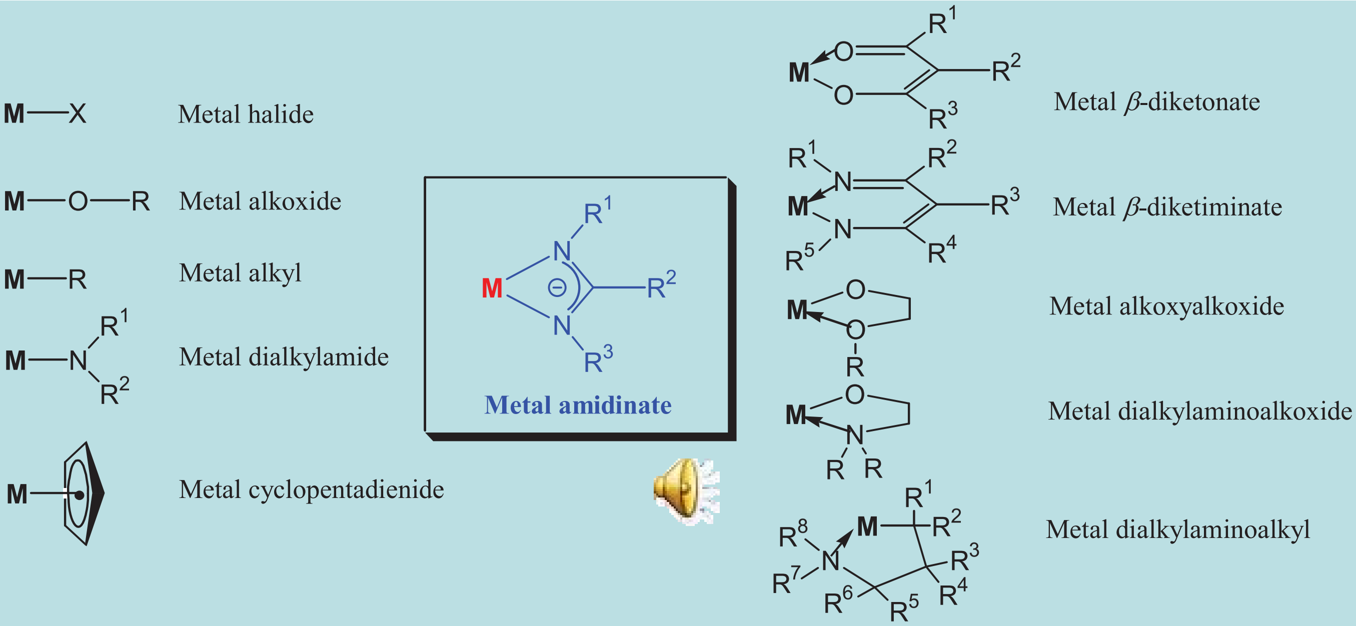
Selection of Suitable Platforms for ALD



Metal Amidinates

- **Bidentate "chelating" effects** ⟹ Improved thermal stability
- **$R^{1,2,3}$ tuning in amidinate** ⟹ Volatility and reactivity control
- **No direct M-C bonds** ⟹ Less carbon incorporation in films
- **Amidinates** of La, Cu, Co, Ru, Ni, Er, Gd, Zr, Hf, Y are used efficiently in ALD.

New Amidinate Sources for Ba, Sr and Ti

- TiN is an excellent barrier and also a good electrode material.

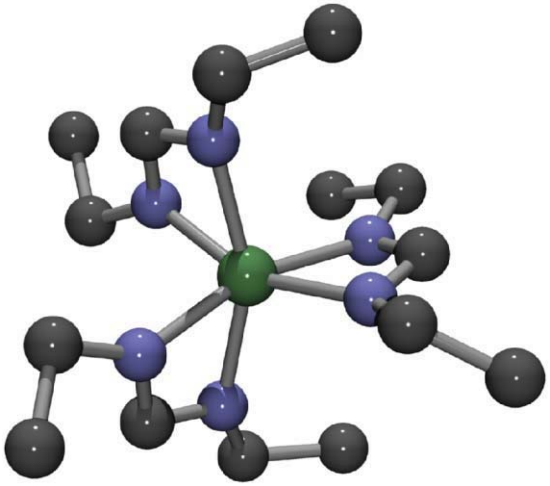
- The current titanium sources (TDMATi and TDEATi)
  - lack thermal stability and decompose at elevated temperatures
  - may lead to inferior quality TiN films.

- New Ti (III) Amidinate is designed to overcome these limitations

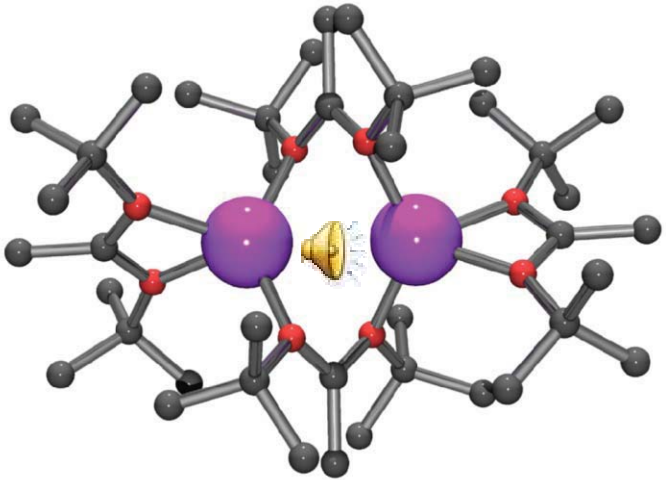
- STO, BTO and BST find applications in
  - NVFeRAM, microwave, DRAM, MEMs.

- Ba and Sr amidinates are also developed as alternative sources.

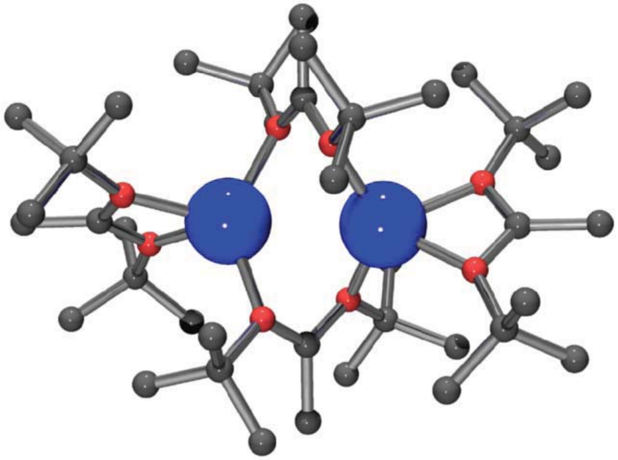
New Ti, Sr, and Ba Sources from Rohm and Haas



Ti-FAMD

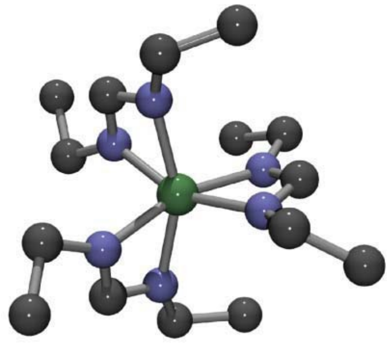


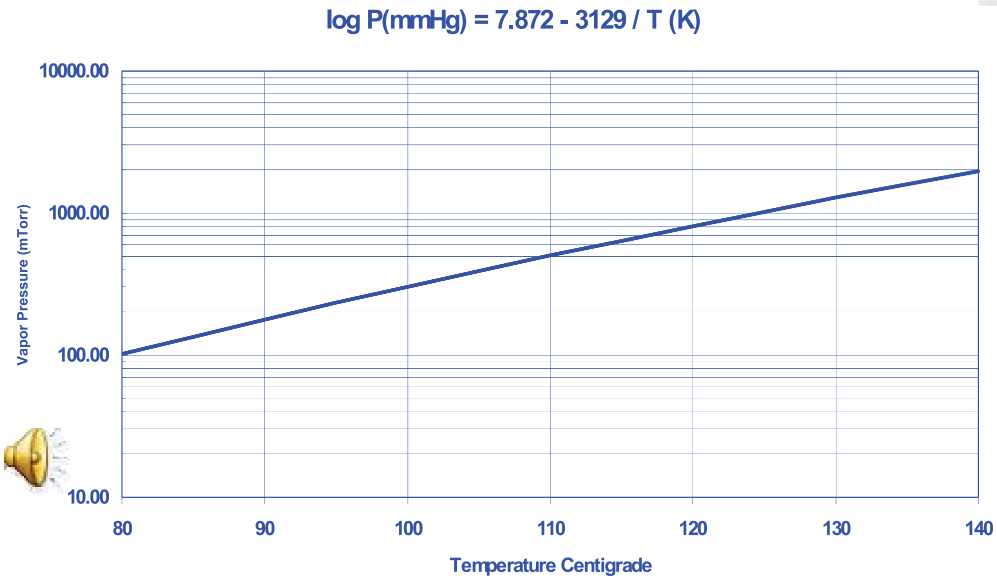
Sr-AMD

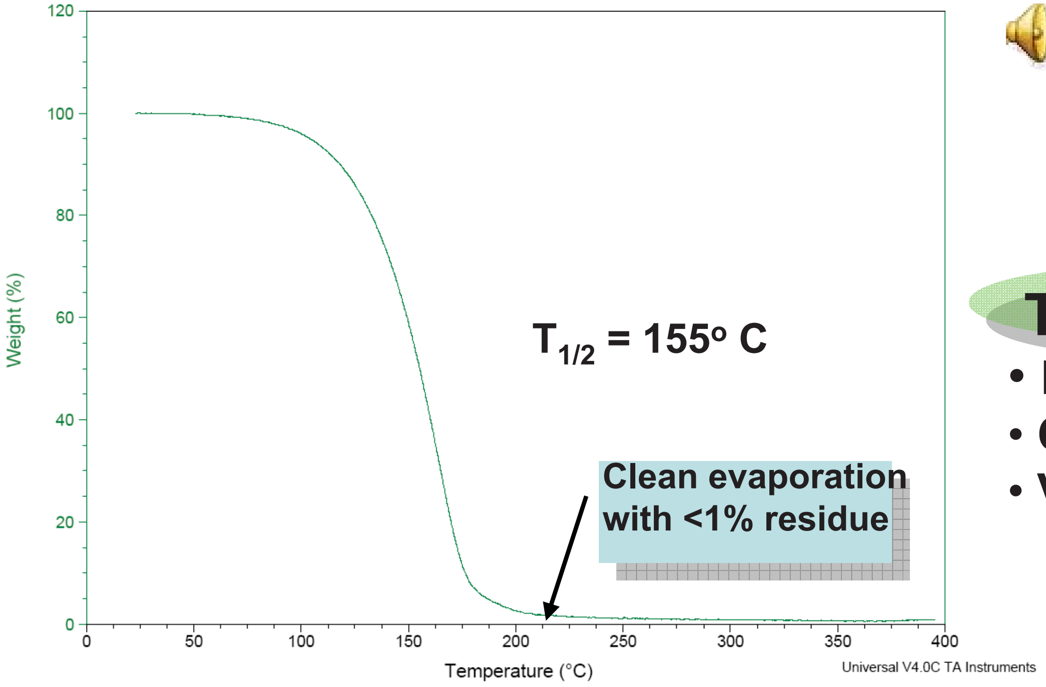


Ba-AMD

TGA and Vapor Pressure Curve for Ti-FAMD




log P(mmHg) = 7.872 - 3129 / T (K)


$T_{1/2}$ = 155° C

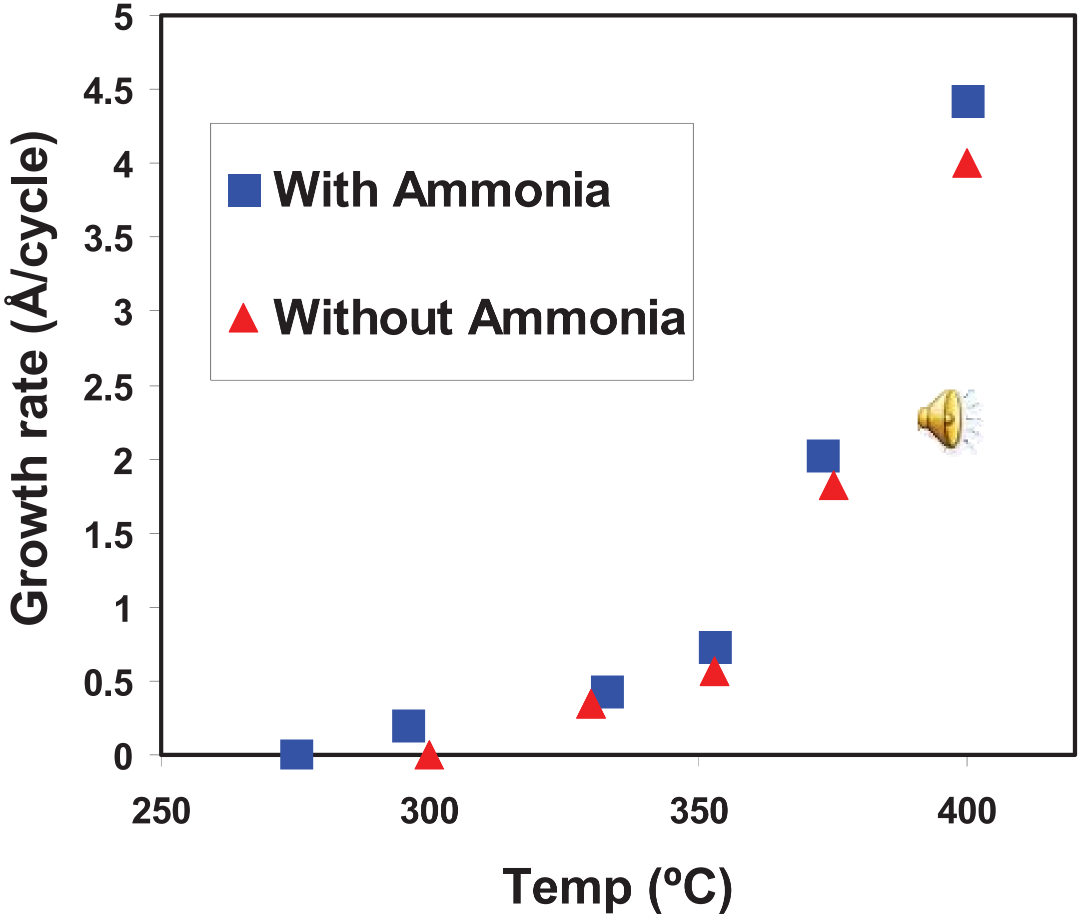
Clean evaporation with <1% residue

Universal V4.0C TA Instruments

Ti-FAMD offers:

- highly volatile liquid Ti (III) precursor
- Clean evaporation with negligible residues
- VP = 0.1 Torr at 80 ^{O}C, suitable for ALD

TiN Thin Film Processing from Ti (III) FAMD



Source Temp: 85 °C

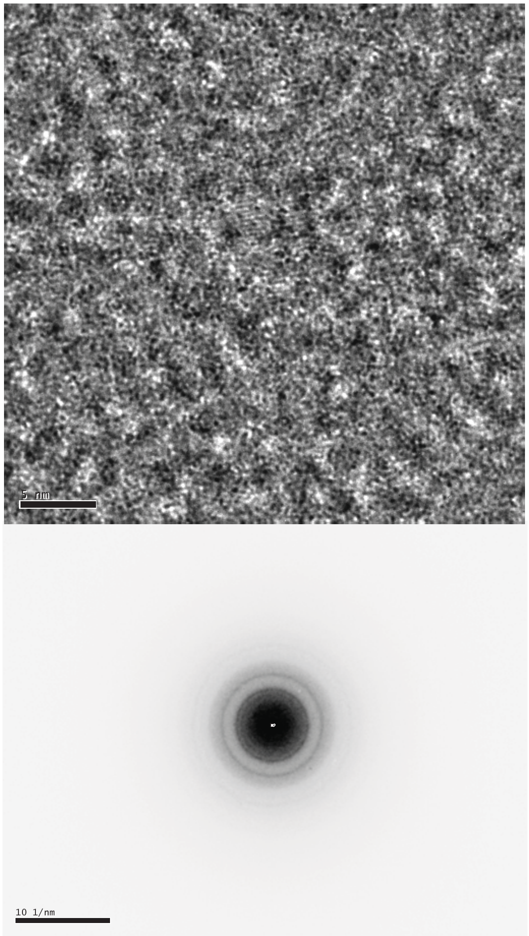
ALD TiN: 280 < T < 310 °C

CVD TiN: 310 < T < 335 °C

CVD TiCN: T > 335 °C

Ti FAMD ALD process window is 280 < T < 310 °C

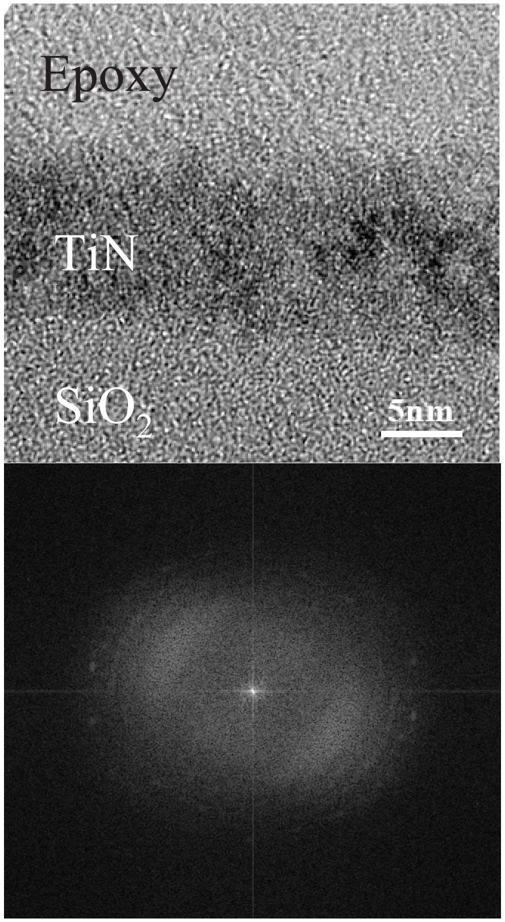
TEM of ALD TiN



Plane view

Real space image

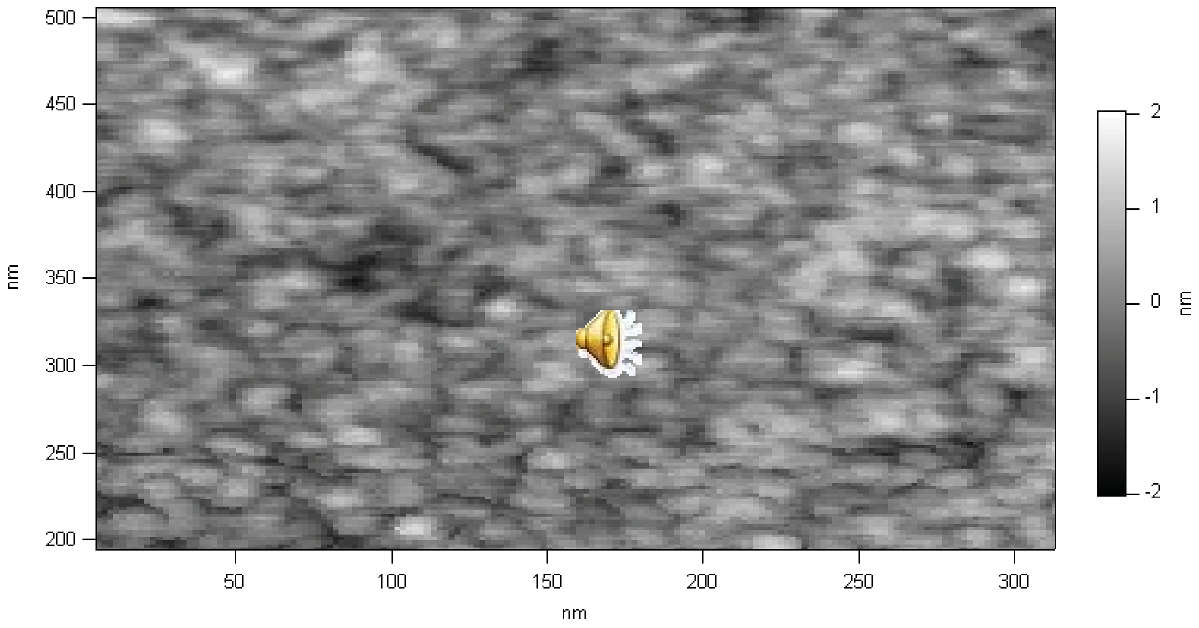
Diffraction pattern



Cross-section

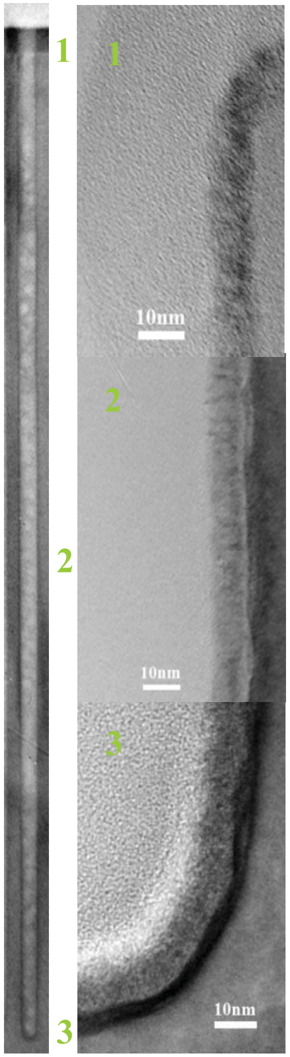
Amorphous with some tiny nanocrystalline regions

AFM of ALD TiN

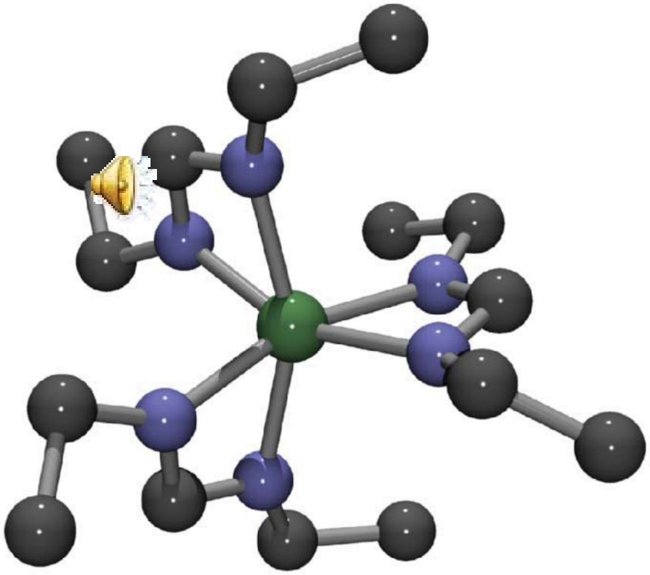


Smooth films (with RMS = 0.46nm) were obtained.

TiN ALD: Step Coverage by TEM



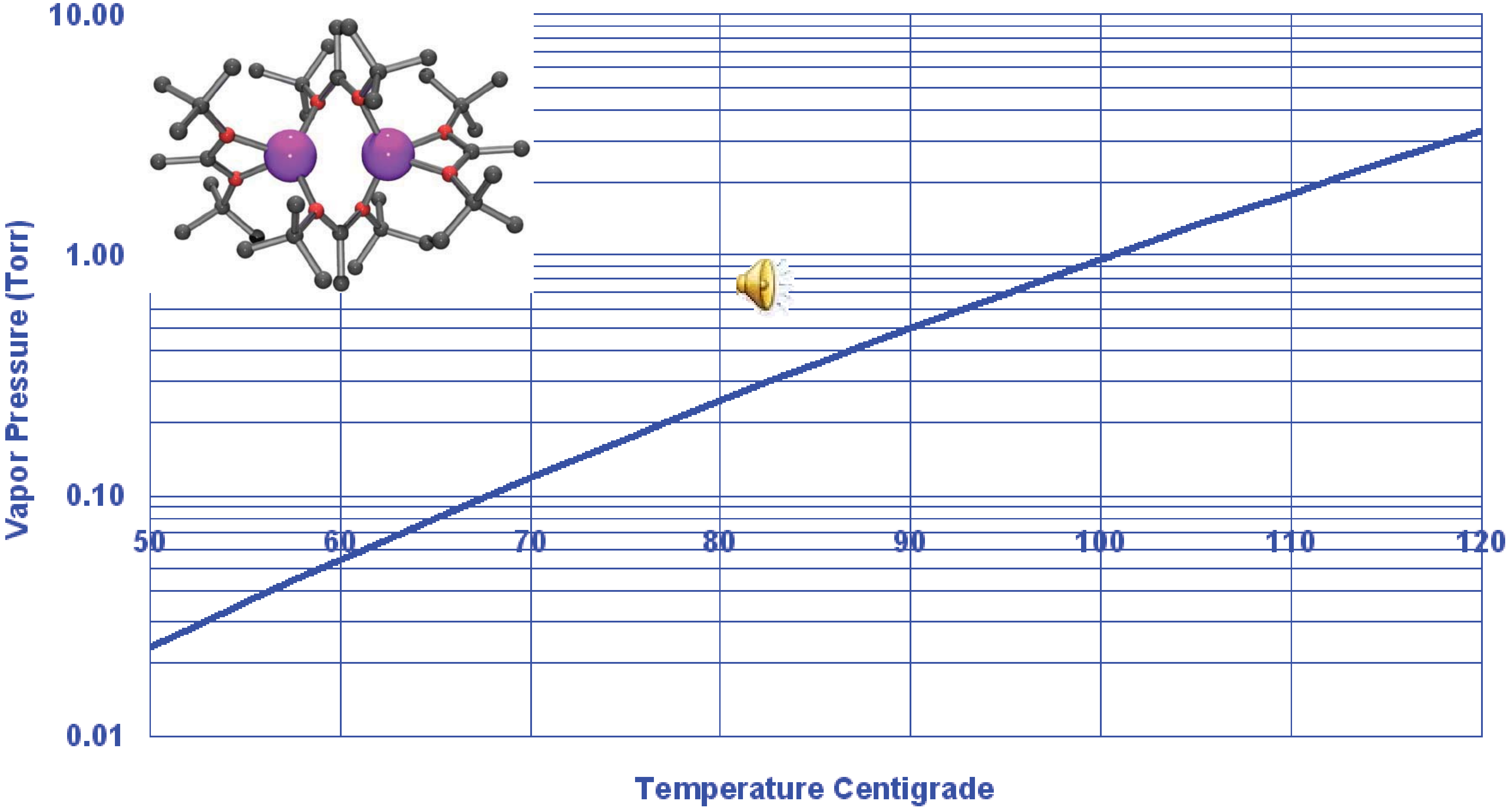
Conformal in 80:1 aspect ratio hole,
ALD at 335 ºC with ammonia
No C in the films at < 335 ºC by XPS



Ti-FAMD

Vapor Pressure of Sr AMD

$\log P(\mathrm{Torr}) = 10.41 - 3887 / T\ (\mathrm{K})$



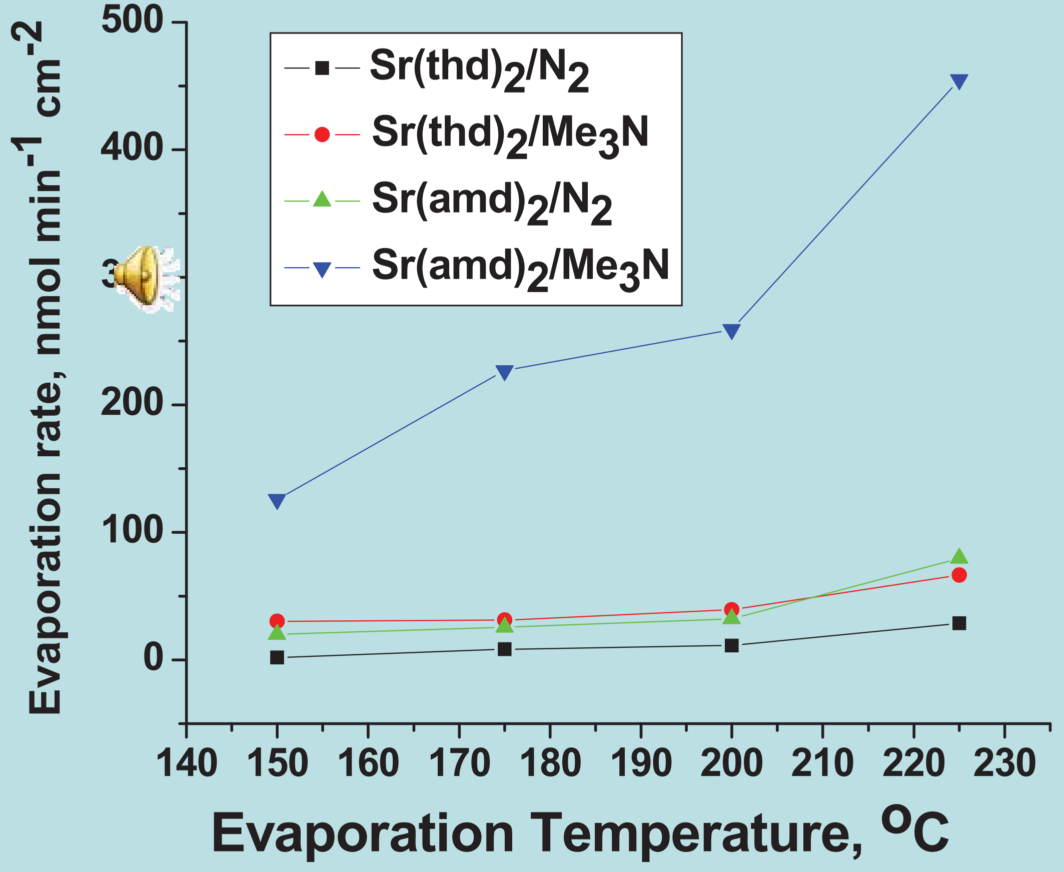
Enhanced Transport by Trimethylamine

- Using Me_3N as a carrier gas increases the TG vapor transport rate of $Sr(thd)_2$ and $Sr(amd)_2$

>3 x faster for $Sr(thd)_2$

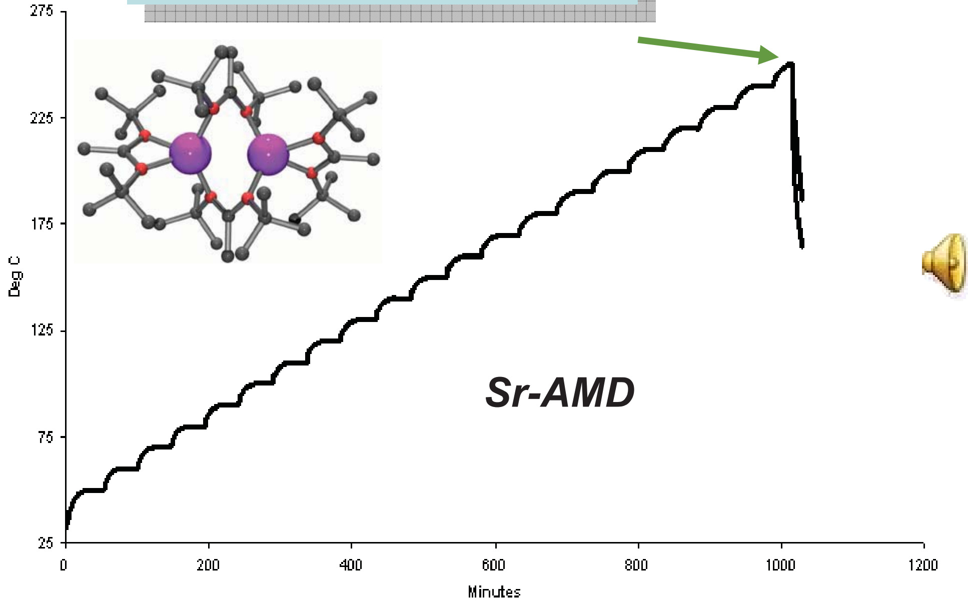
>6 x faster for $Sr(amd)_2$

$Sr(amd)_2/Me_3N$ >20 x faster than $Sr(thd)_2/N_2$

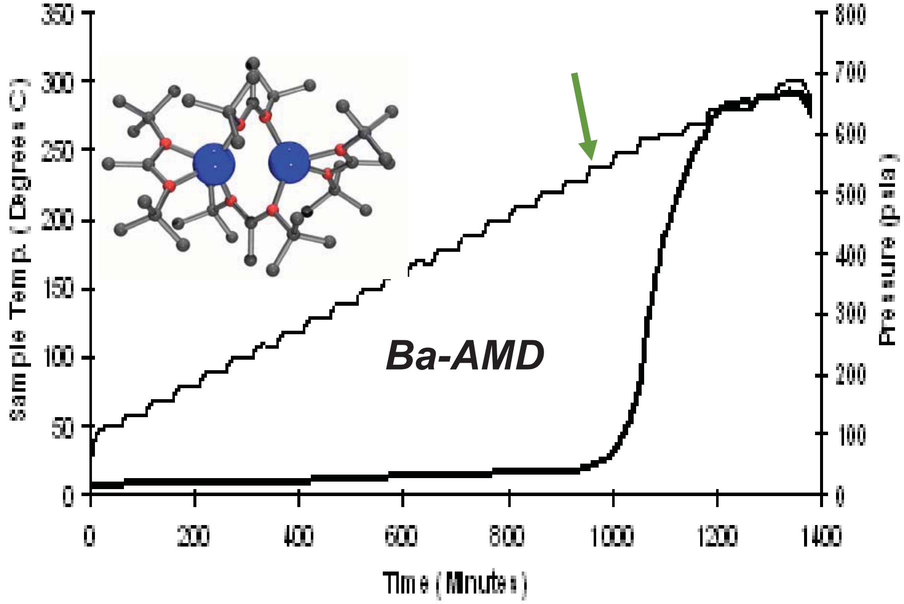


High Thermal Stability of Sr/Ba-AMD

Stable up to 250^{o} C



Stable up to 220^{o} C



Thermal stability studies by Accelerated Rate Calorimetry analysis (ARC)

Properties of the New Ti, Sr, and Ba Precursors

Name	Ti-FAMD	Sr-AMD	Ba-AMD
M. W. (g/mol)	289.37	852.38	951.79
Appearance	Deep Brown liquid	White solid	White solid
M.P. (ºC)	N/A	> 200 ºC	> 200 ºC
Density (g/mL)	0.90	0.50	0.54
Vapor Pressure	log P(Torr) = 7.872–3129/T(K)	log P(Torr) = 10.41-3887/T(K)	Data collection in progress
Thermal Stability	Data collection in progress	Stable to 250 ºC by ARC	Stable to 220 ºC by ARC
^{1}H NMR	Organic impurity N.D.	Organic impurity N.D.	Organic impurity N.D.
Solubility	Soluble in hydrocarbon solvents (> 0.1 M)	Soluble in hydrocarbon solvents (0.1 M)	Soluble in hydrocarbon solvents (0.1 M)
Shelf life	Stable over 3 months	Stable over 6 months	Stable over 4 months
TGA	Clean evaporation	Clean evaporation	Clean evaporation

Summary

- New sources of Ti, Sr and Ba are needed for TiN, STO and BST applications.

- Ti-FAMD, Sr-AMD and Ba-AMD with greater thermal stability are developed.

- Preliminary ALD results for TiN using liquid Ti (III) source are reported.

- Further growth studies on BST and STO are to be conducted.