RUHR-UNIVERSITÄT BOCHUM

# PRECURSOR CHEMISTRY FOR SPATIAL ATOMIC LAYER DEPOSITION

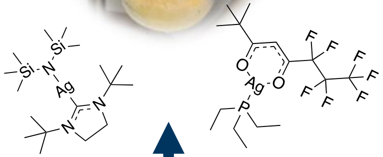
Nils Boysen, Inorganic Materials Chemistry

Spatial ALD Day – 09.06.2022

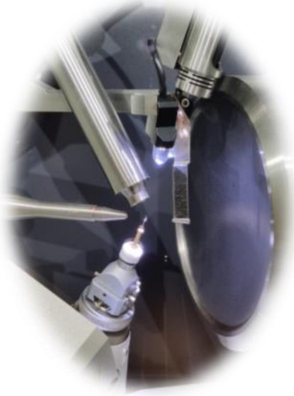
# Are you familiar with precursor chemistry?

# Our Expertise

**Precursor Synthesis**

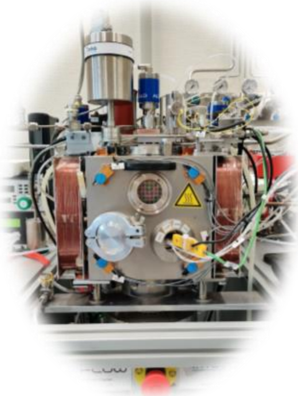


**Precursor Evaluation**



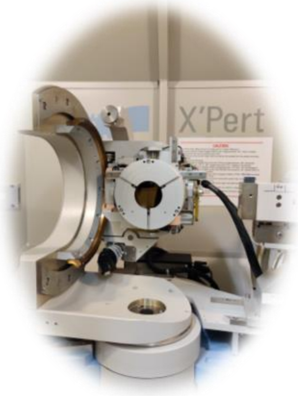
NMR, EA, IR, EI-MS, SC-XRD, TG, isoTG

**Thin Film Deposition**



MOCVD, t-ALD, PE-ALD, s-ALD, CSD

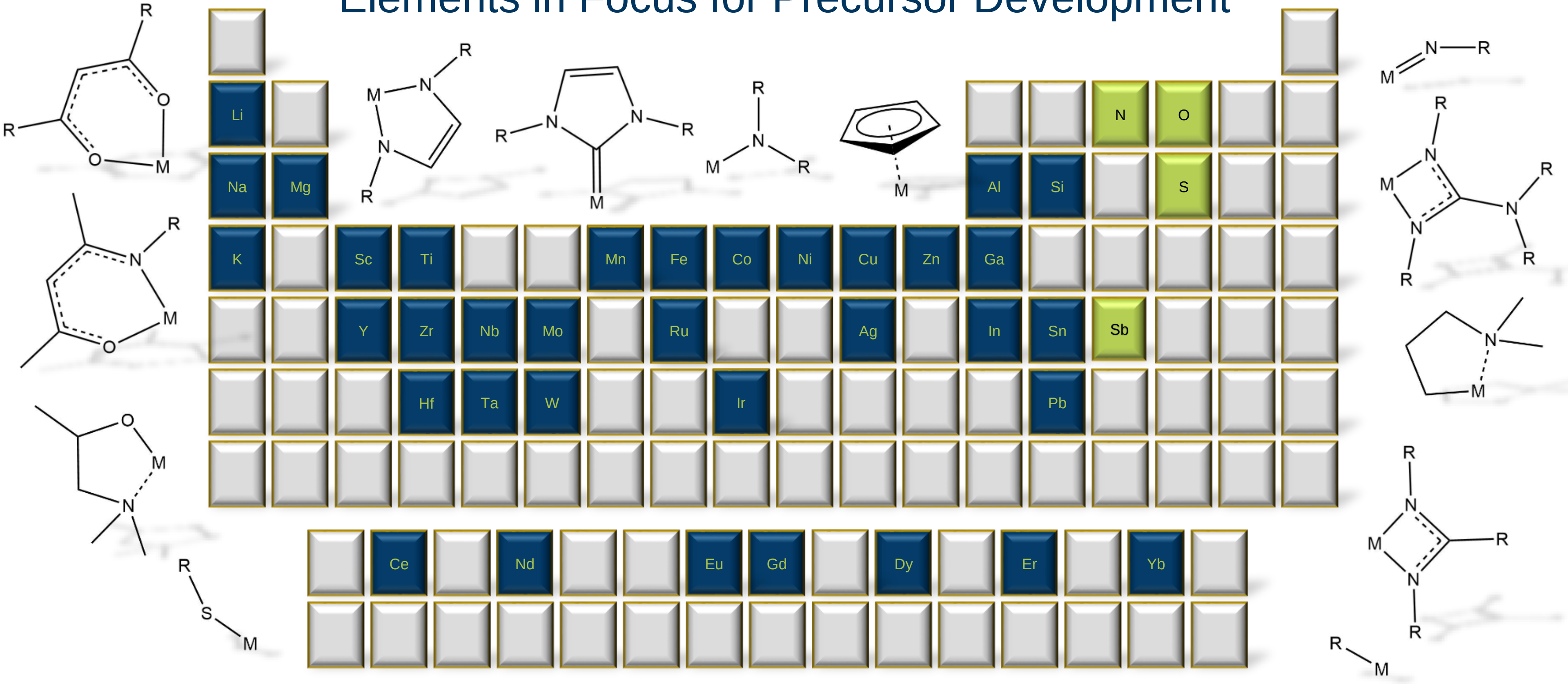
**Thin Film Analysis**



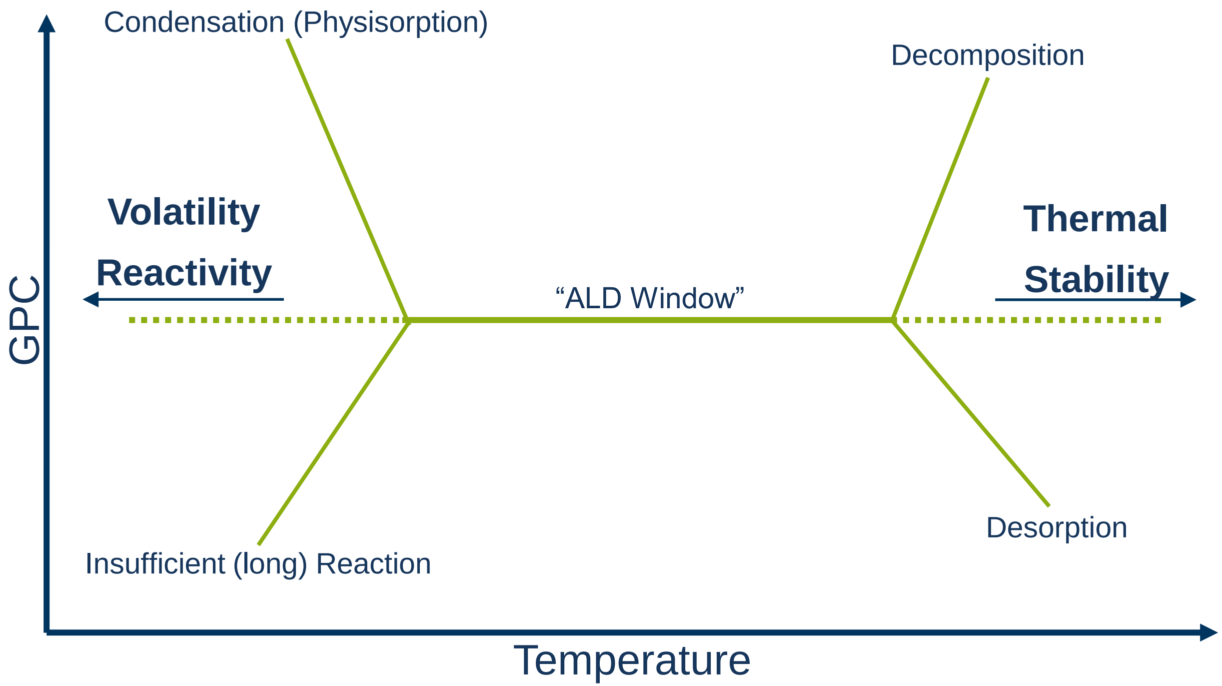

XRD, XRR, RBS/NRA, XPS, SEM, AFM, …

**Application** in cooperation with partners

# Elements in Focus for Precursor Development



# Precursor Parameters for "ALD Windows"



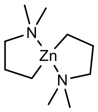

➢ **How are these parameters influenced by precursor chemistry?**

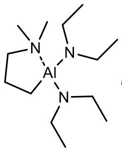
# Precursor Chemistry Parameters

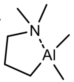
**<u>Organic Ligands surrounding the metal center are the most important factor for:</u>**

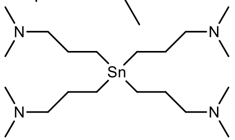
- **Volatility** (VdW-interactions, molecular weight, symmetry, phase)
- **Thermal Stability** (bond strengths, inter- and intramolecular reactions, decomposition)
- **Reactivity** (towards the functional substrate groups and co-reactant)

## DMPs







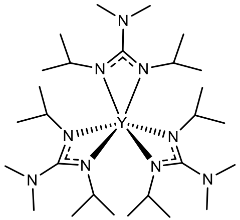


L. Mai et al., *Small*, 2020, **16**, 1907506.

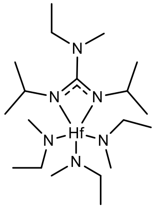
L. Mai et al., *Chem. Eur. J.*, 2019, **25**, 7489–7500.

L. Mai et al., *Appl. Mater. Interfaces*, 2019, **11**, 3169–3180.

## Guanidinates

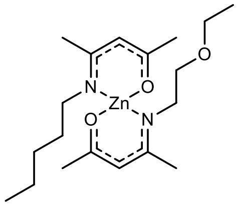


L. Mai, N.Boysen et al., *RSC Advances*, 2018, **8**, 4987–4994.



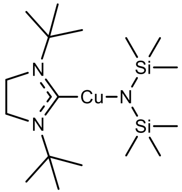
D. Zanders et al., *Appl. Mater. Interfaces*, 2019, **11**, 28407–28422.

## Ketoiminates

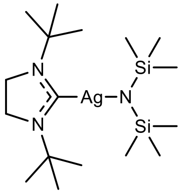


R. O' Donoghue et al., *Dalton Trans.*, 2016, **45**, 19012–19023.

## NHCs



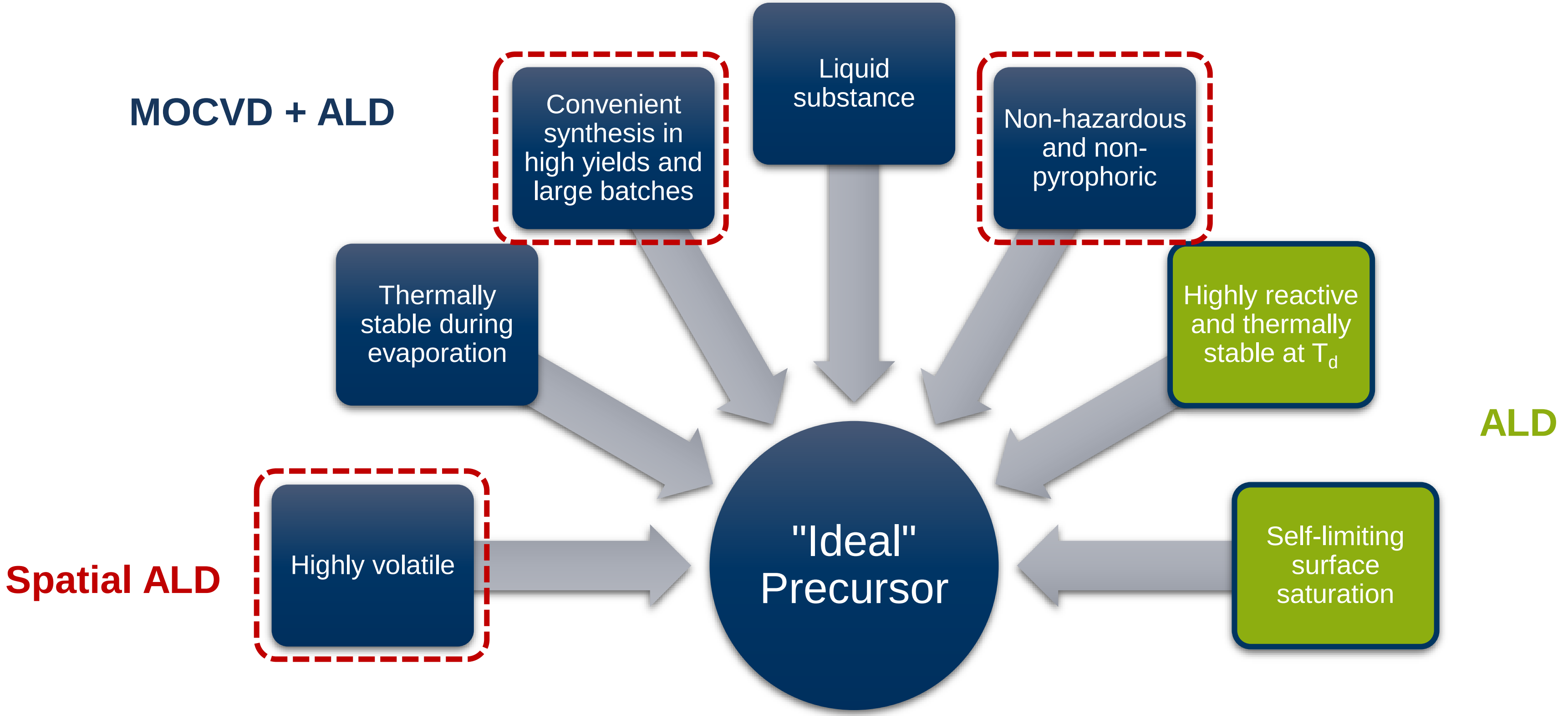
N. Boysen et al., *Chem. Commun.*, 2020, **56**, 13752–13755.



N. Boysen et al., *Angew. Chem. Int. Ed.*, 2018, **57**, 16224–16227.

➢ **What about additional, but highly important parameters?**

# General Requirements for MOCVD and ALD Precursors



# Metal and Ligand Interactions: Volatility

**Al** → **$AlCl_3$** → **$Al(CH_3)_3$** TMA

| Al | $AlCl_3$ | $Al(CH_3)_3$ (TMA) |
|---|---|---|
| Boiling Point: 2470 °C | Sublimation: 180 °C | Boiling Point: 125 °C |

Highly volatile, liquid, reactive and thermally stable

**Pyrophoric**

➢ **TMA is close to an “ideal” precursor but not perfect !**

# Accidents with TMA

JOURNALS | COVID-19 Science

Commentary Home Opinion Analysis Blogs

HOME > COMMENTARY > BLOGS > IN THE PIPELINE > TRIMETHYLALUMINUM EXPLOSION IN MASSACHUSETTS

IN THE PIPELINE | SAFETY WARNINGS

## Trimethylaluminum Explosion in Massachusetts

7 JAN 2016 • BY DEREK LOWE • 1 MIN READ • COMMENTS

Word has come of a bad industrial accident in the town of North Andover, about 25 to 30 miles north/northwest of Boston. There's a Dow facility there, the Advanced Materials division, and what makes this particularly bad is that they had an explosion and death there as recently as 2013.

https://www.science.org/content/blog-post/trimethylaluminum-explosion-massachusetts

➢ **TMA can be handled with precautions, but it is still extremely hazardous**

# Alternatives for TMA

$Al(CH_3)_3$

TMA

$Al(OiPr)(CH_3)_2$

DMAI




$Al(DMP)(CH_3)_2$

DMAD




- **We always have to make trade-offs**
- **Precursor choice should depend on your desired application**




at RT
Highly volatile
Termally stable

Processes at RT
Highly volatile

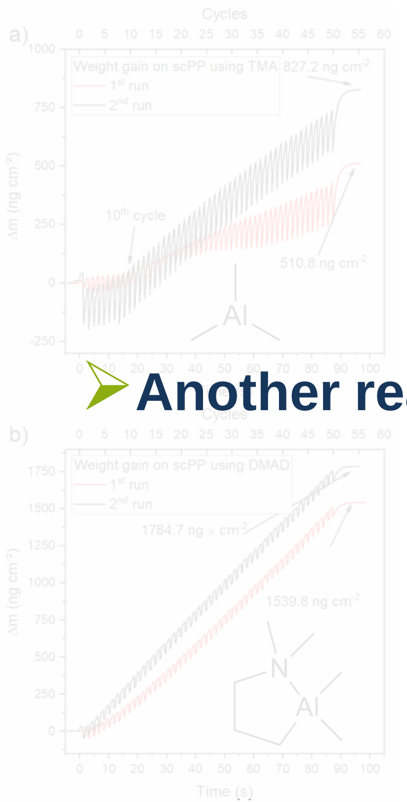
**Pyrophoric**

**Non-Pyrophoric**
Potts et al. (2012)

**Non-Pyrophoric**
Mai et al. (2018)

- **Alternatives are available, but their synthesis (and upscaling) might be more challenging**

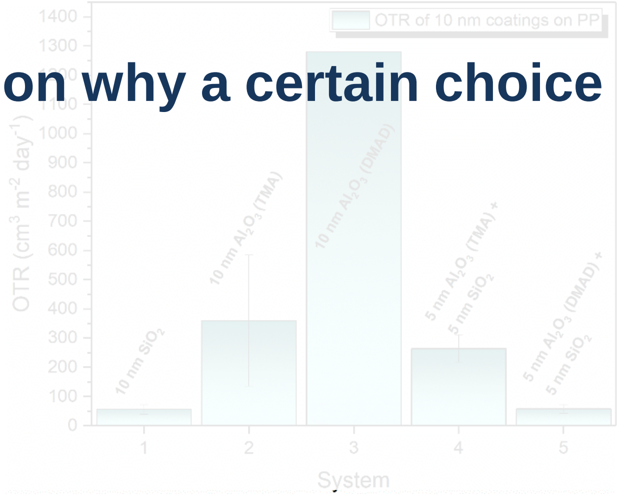
# Precursor Choice for Gas Barrier Coatings

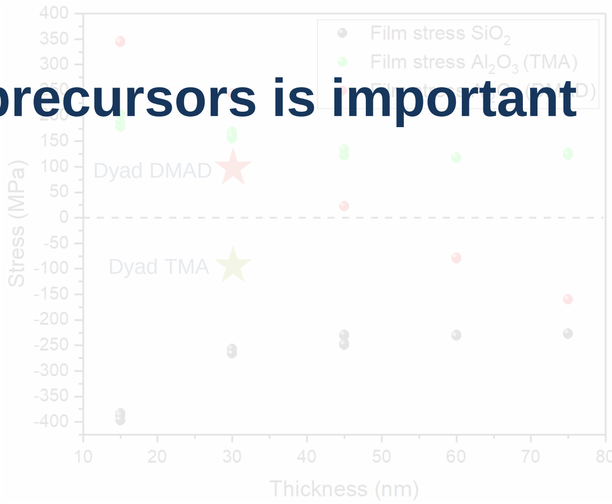






- PE-ALD Process at 80 °C
  - Stress of the dyads can be reduced with DMAD
  - **Better OTR performance**



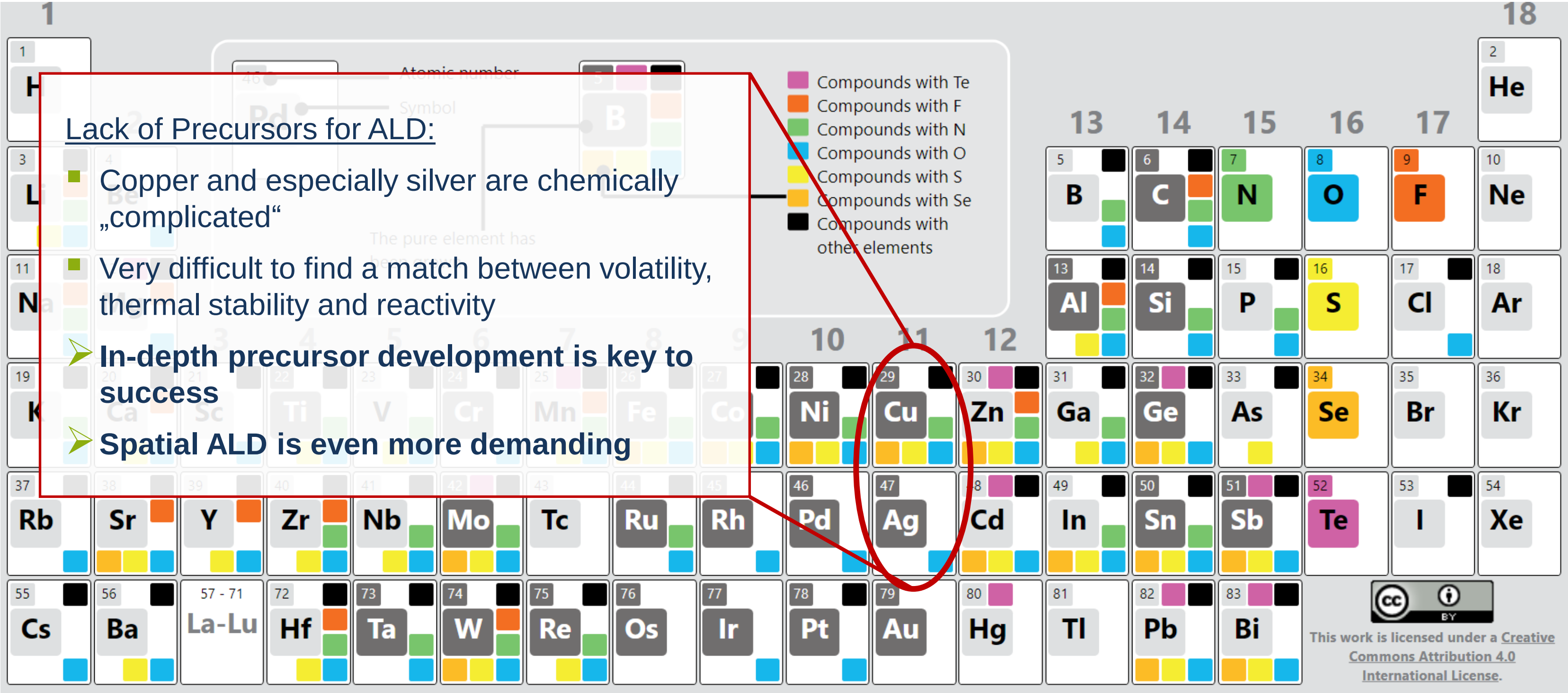




**Another reason why a certain choice of precursors is important**



M. Gebhard and A. Devi et al.
*ACS Appl. Mater. Interfaces* **2018** *10* (8), 7422-7434

# Motivation for this Workshop




Lack of Precursors for ALD:

- Copper and especially silver are chemically „complicated“
- Very difficult to find a match between volatility, thermal stability and reactivity
- ➢ **In-depth precursor development is key to success**
- ➢ **Spatial ALD is even more demanding**

➢ **Copper and Silver are good examples for precursor development**

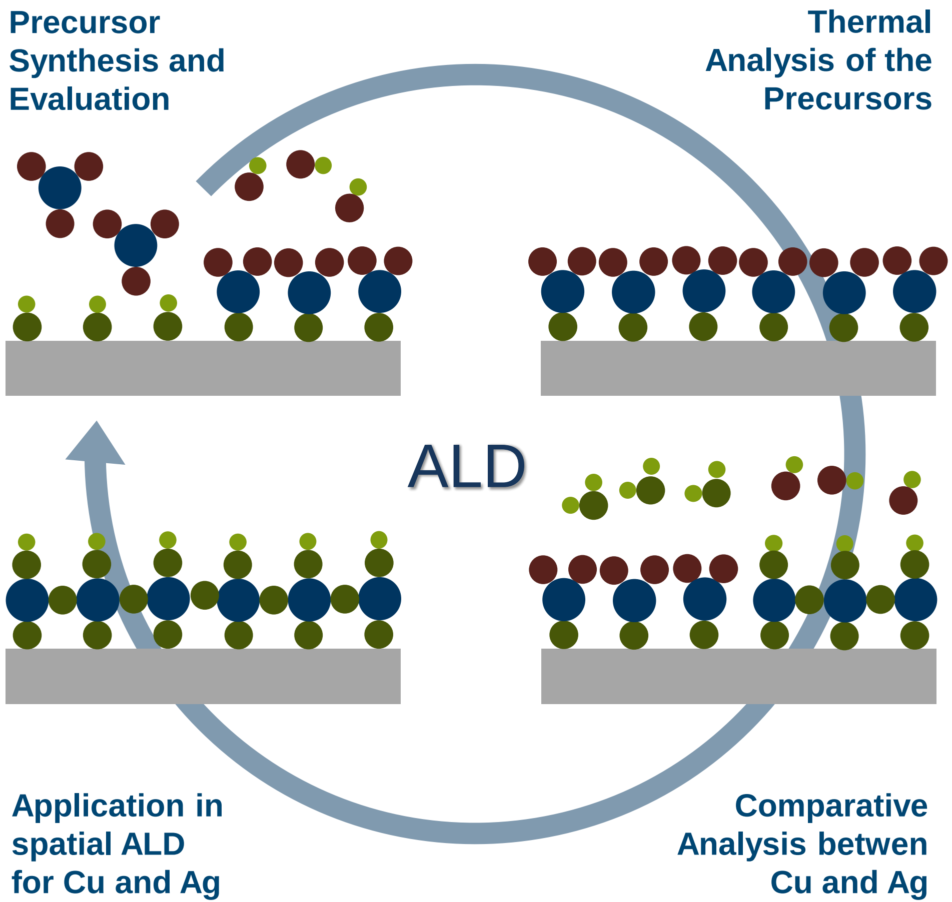


www.AtomicLimits.com - DOI: 10.6100/alddatabase

# Focus of this Workshop

**Silver Precursor Chemistry for spatial ALD**

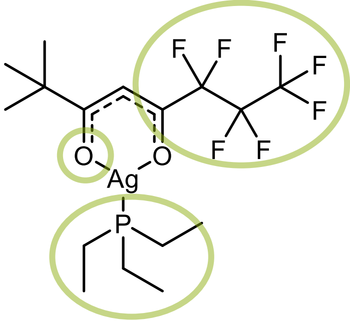
**Copper Precursor Chemistry for spatial ALD**



# Silver Precursor Chemistry for spatial ALD

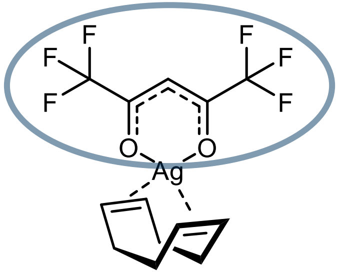
# Silver Precursors

## Known Ag Precursors:



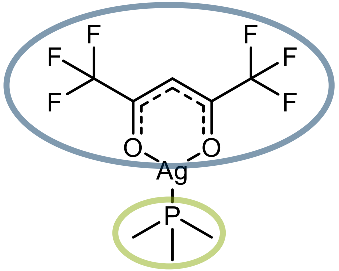

[Ag(fod)($PEt_3$)]

M. Kariniemi et al., *Chem. Mater.* **2011**, *23*, 2901–2907.



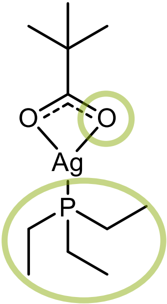

[Ag(hfac)(COD)]

Z. Golrokhi et al., *Appl. Surf. Sci.* **2017**, *399*, 123–131.



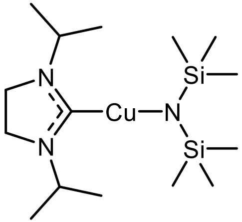

[Ag(hfac)($PMe_3$)]

S. S. Masango et al., *J. Phys. Chem. C* **2014**, *118*, 17655–17661.



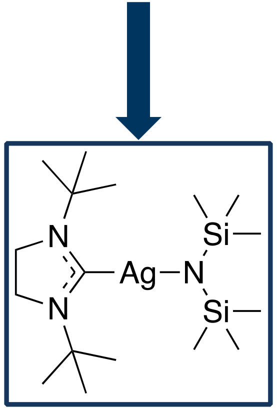

[Ag(piv)($PEt_3$)]

A. Niskanen et al., *Chem. Vapor Depos.* **2007**, *13*, 408–413.




J. P. Coyle et al., *Chem. Mater.* **2013**, *25*, 1132–1138.

[Cu(NHC)(hmds)]




<u>Problems with the known precursors:</u>

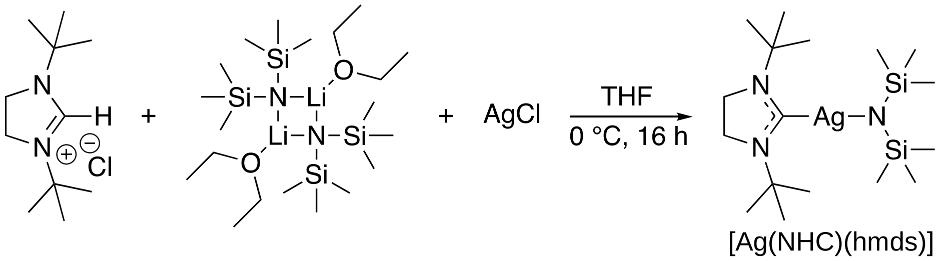
- O, P and F in the ligand sphere
- Low thermal stability (up to 200 °C) and low reactivity
- <u>Low growth rates</u> due to “hfac” poisoning

➢ **N-heterocyclic carbenes (NHC) as stabilizing ligand for highly reactive silver precursors**

N. Boysen, T. Hasselmann, T. Riedl, A. Devi et al., *Angew. Chem. Int. Ed.* **2018**, *57*, 16224–16227.

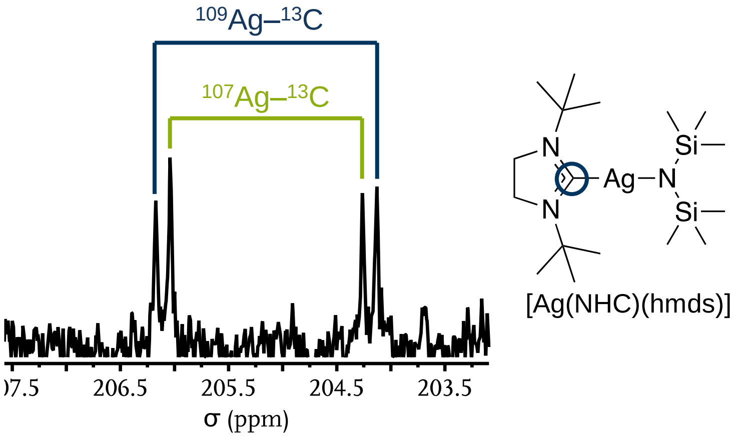
# Synthesis of a new Silver Precursor

## Synthesis of the precursor:




- One-pot synthesis (12 g), isolation with pentane
- Colorless crystalline solid, m.p. at 116 °C
- Average yields of 80 %
- ➢ Highly sensitive towards moisture and light

## $^{13}$C-NMR analysis:



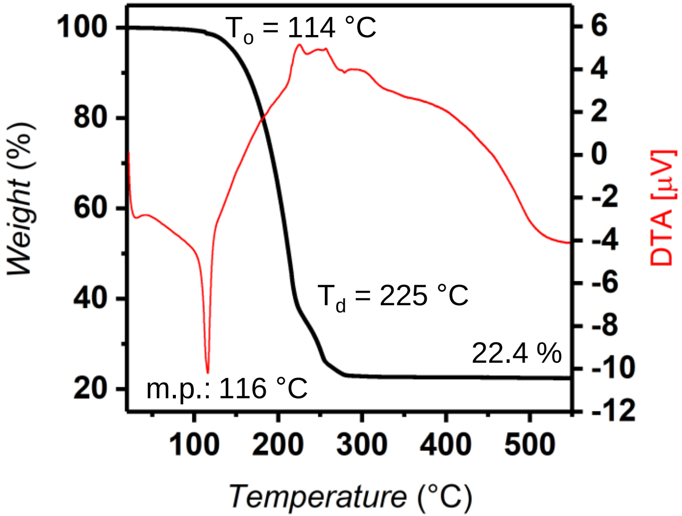

- C–Ag: dd at 205.1 ppm ($^{1}J_{C\text{-}Ag}$ = 190 Hz)
- Strong π-backdonation from Ag

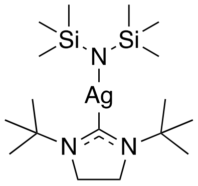
➢ **Successful synthesis of [Ag(NHC)(hmds)] confirmed by NMR**



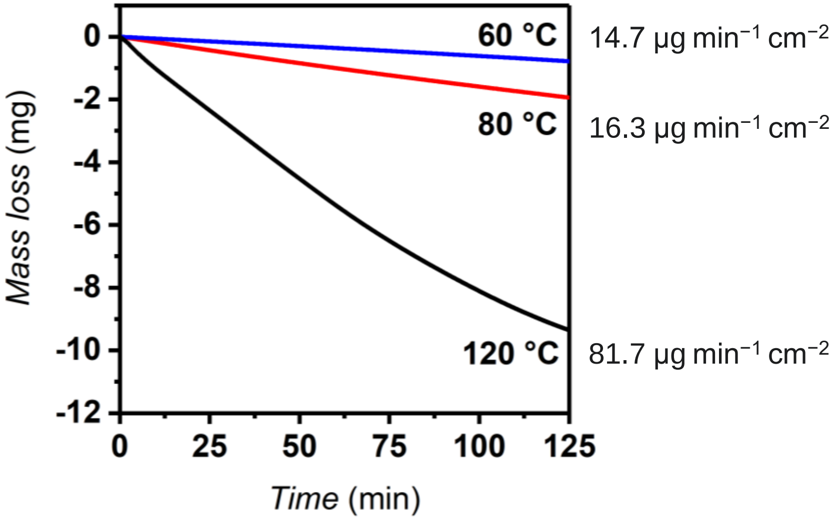
N. Boysen, T. Hasselmann, T. Riedl, A. Devi et al., *Angew. Chem. Int. Ed.* **2018**, *57*, 16224–16227.

# Thermal Analysis and Evaluation




[Ag(NHC)(hmds)]




**Thermogravimetric analysis:**

One-step evaporation and decomposition beyond 225 °C

**Isothermal analysis:**

Constant evaporation at 60 °C, 80 °C and 120 °C

➢ **High thermal stability of [Ag(NHC)(hmds)] for ALD application**



N. Boysen, T. Hasselmann, T. Riedl, A. Devi et al., *Angew. Chem. Int. Ed.* **2018**, *57*, 16224–16227.

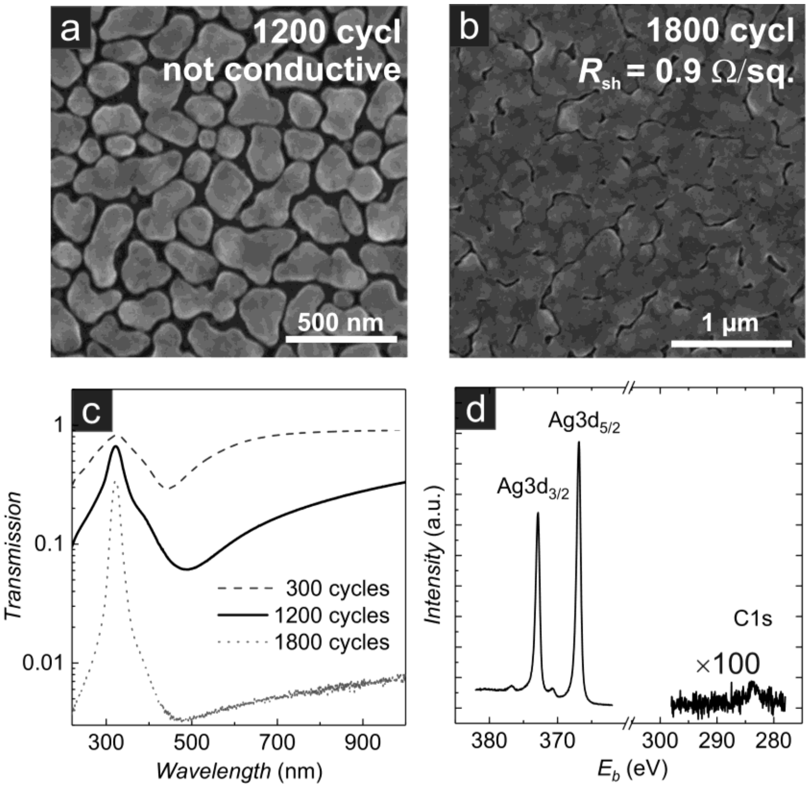
# ALD of Silver Nanostructures

**Deposition conditions:**

- Atmospheric pressure spatial PE-ALD reactor
- $H_2$/Ar DBD plasma at $T_s$ = 100 °C on Si(100)
- Bubbler with [Ag(NHC)(hmds)] at 120 °C

**Growth and compositional analysis**

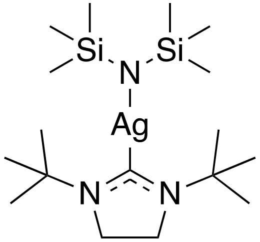
- RBS: GR = $2.1 \cdot 10^{14}$ Ag atoms/($cm^2 \cdot$ cycle)
  Corresponds to 0.36 Å/cycle
- XPS: low C (1.5 at.%) and low Si (0.8 at.%) contam.
- ➢ Resistivity of $10^{-5}$ Ωcm after 1800 cycles



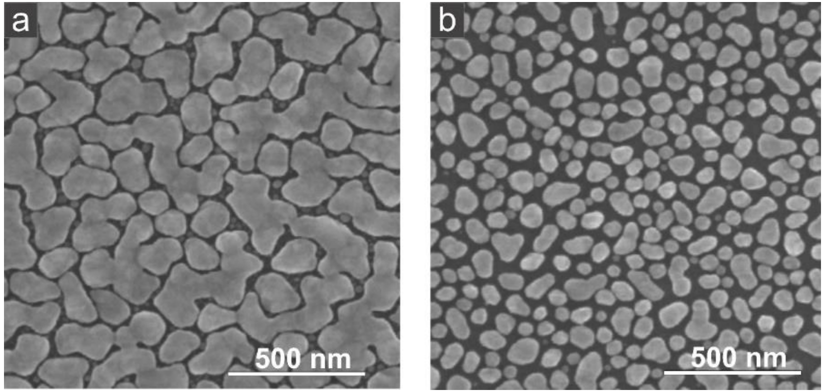

➢ **[Ag(NHC)(hmds)] enables high growth rates at low temperatures**

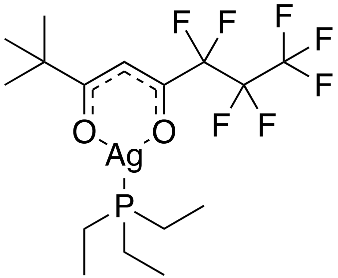
N. Boysen, T. Hasselmann, T. Riedl, A. Devi et al., *Angew. Chem. Int. Ed.* **2018**, *57*, 16224–16227.

# [Ag(NHC)(hmds)] vs. [Ag(fod)($PEt_3$)]




[Ag(NHC)(hmds)]




[Ag(fod)($PEt_3$)]

Area coverage: **85 %**

GR = **0.36 Å/cycle**

(RBS)

**Identical deposition conditions:**

Atmospheric pressure spatial PE-ALD reactor

$T_s$ = 100 °C, 1200 cycles, Si(100) substrates

Area coverage: **62 %**

GR = **0.14 Å/cycle**

(RBS)

- **Choice of the precursor significantly influences the growth characteristics**

N. Boysen, T. Hasselmann, T. Riedl, A. Devi et al., *Angew. Chem. Int. Ed.* **2018**, *57*, 16224–16227.

# Copper Precursor Chemistry for spatial ALD and Comparison to Silver

# Copper Precursors

## Known Copper Precursors for PE-ALD of Cu metal films:

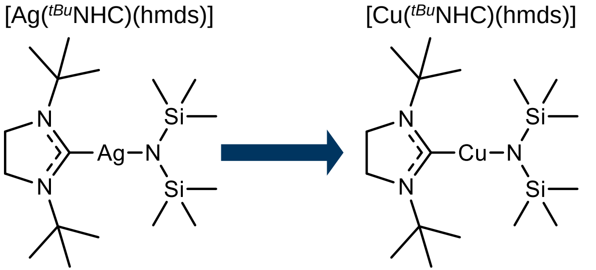
| Cu Precursor | Co-Reactant | $T_{dep}$ (°C) | GPC (Å) | Substr. | Reference |
|---|---|---|---|---|---|
| [CuCl] | $H_2$ | 375 – 475 | 0.8 | $SiO_2$ | Mårtensson et al. (1997) |
| [Cu(acac)$_2$] | Ar/$H_2$ plasma | 200 | 0.18 | Si | Niskanen et al. (2005) |
| [Cu(acac)$_2$] | $H_2$ plasma | 85 – 135 | 0.2 | $SiO_2$ | Wu et al. (2007) |
| [Cu(thd)$_2$] | $H_2$ plasma | 90 – 250 | 0.11 | $SiO_2$ | Jezewski et al. (2005) |
| [Cu(maboc)$_2$] | $H_2$ plasma | 100 – 180 | 0.65 | Ta | Moon et al. (2011) |
| [Cu($^{iPr}$amd)]$_2$ | $H_2$ plasma | 50 – 100 | 0.71 | Si | Guo et al. (2015) |
| [Cu($^{iPr}$NHC)(hmds)] | Ar/$H_2$ plasma | 225 | 0.2 | Si | Coyle et al. (2013) |

High deposition temperatures

Low growth rates

Oxygen in coordination sphere

➢ **No spatial (PE-)ALD process known for copper metal films**




J. P. Coyle et al., *Organometallics*, 2017, **36**, 2800–2810.

Why [Cu($^{tBu}$NHC)(hmds)]?:

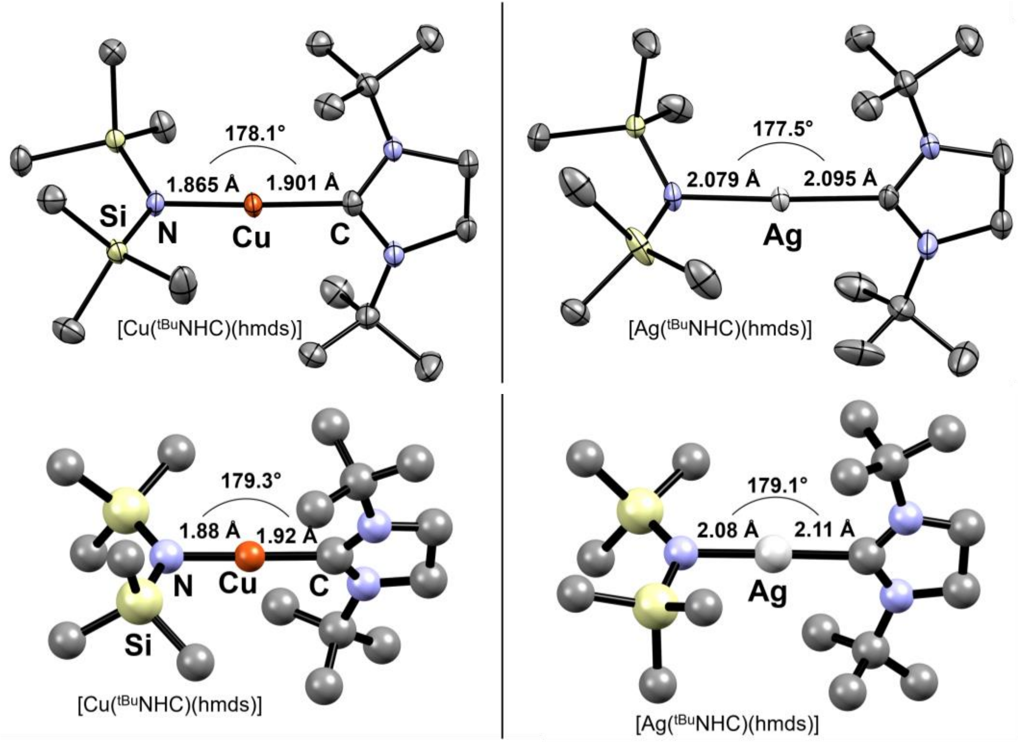
- [Cu($^{iPr}$NHC)(hmds)] already works in PE-ALD (Coyle et al.)
- Convenient and direct comparison to [Ag($^{tBu}$NHC)(hmds)] possible

➢ **Possible optimization of synthetic aspects and missing spectroscopic identity + spatial ALD process**



N. Boysen, T. Hasselmann, T. Riedl, A. Devi et al., *Angew. Chem. Int. Ed.* **2018**, *57*, 16224–16227.

# Comparative SC-XRD and DFT Structures




SC-XRD:

- Highly similar crystal structure (P$\bar{1}$, Z' = 1)
- Linear geometry around N–M–C
- Longer N–M–C bond lengths for Ag
- ➢ **Higher ionic radius for $Ag^+$**

DFT optimization:

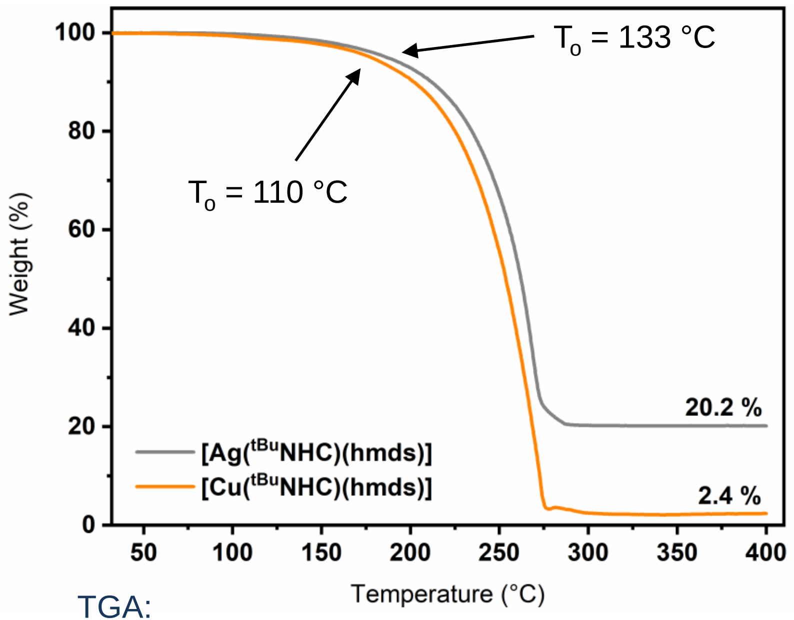
- DFT structure very similar to XRD structure
- Cu–N bond: $E_d$ = 446.33 kJ·mol$^{-1}$
- Ag–N bond: $E_d$ = 341.31 kJ·mol$^{-1}$
- ➢ **Higher thermal lability and reactivity for Ag?**

➢ **Similarities and differences in molecular structure and boding**



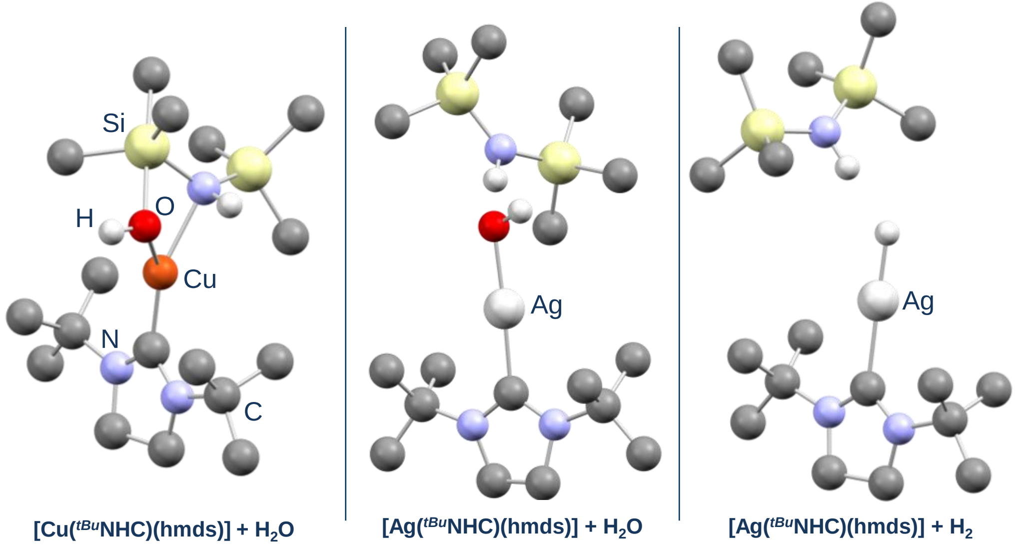
N. Boysen, A. Muriqi, M. Nolan, A. Devi et al., *Chem. Commun.*, 2020, **56**, 13752–13755.

# Comparative Thermal Analysis and DFT Reaction




TGA:

- Slightly lower onset of volatilization for Cu
- Higher thermal stability for Cu
- Lower melting point for Cu (93 °C vs. 114 °C)




DFT reaction analysis with $H_2$ and $H_2O$:

- No reaction of [Cu($^{tBu}$NHC)(hmds)] with $H_2$
- Interesting Ag-H species
- ➢ **Lower stability of [Ag($^{tBu}$NHC)(hmds)] but higher reactivity**



N. Boysen, A. Muriqi, M. Nolan, A. Devi et al., *Chem. Commun.*, 2020, **56**, 13752–13755.

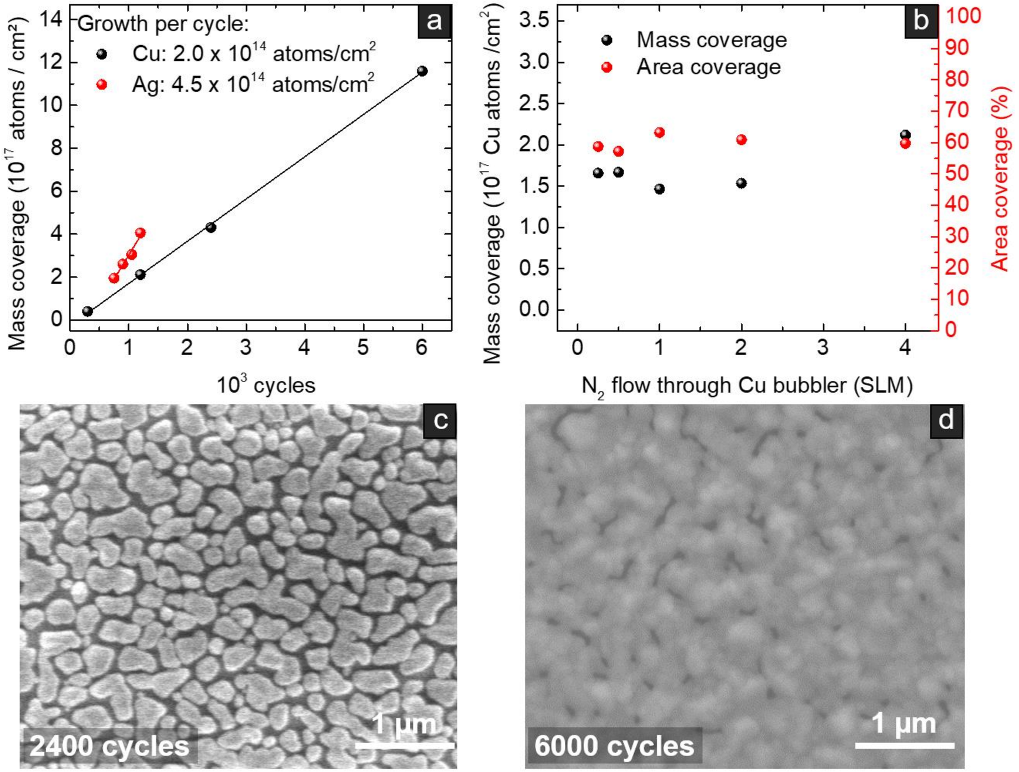
# APP-ALD of Copper Nanostructures

Deposition conditions:

- Atmospheric pressure spatial PE-ALD reactor
- $H_2$/Ar DBD plasma at $T_s$ = 100 °C on BSiG
- Bubbler with [Cu($^{tBu}$NHC)(hmds)] at 100 °C and [Ag($^{tBu}$NHC)(hmds)] at 120 °C

Growth conditions:

- Higher GPC for Ag (0.76 Å) vs. Cu (0.23 Å)
- Conductive and percolated Cu films after 6000 cycles with $\rho = 2.9 \cdot 10^{-5}$ Ωcm
- Contamination levels below detectable limits of XPS (< 0.5 at.%)
- **Limited reactivity towards $H_2$ plasma might be a factor for Cu ALD**




N. Boysen, B. Misimi, T. Riedl, A. Devi et al., *Chem. Commun.*, 2020, **56**, 13752–13755.

# Summary

**Synthesis of a new silver precursor [Ag(NHC)(hmds)]:**

- Synthesis in high yields, big batches und high purity
- Promising thermal stability and reactivity
- ➢ New spatial ALD process for silver thin films

**Comparison with copper precursor [Cu(NHC)(hmds)]:**

- Very similar structure and bonding situation
- Cu thermally more stable than Ag, but less reactive
- First spatial ALD process for copper thin films
- ➢ Pure and conductive copper thin films

**Precursor chemistry influences process parameters and is important for new sALD processes**

# Thank you for your attention!

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