Designing Atomic Level Process Chemistries: The Role of Atomistic Simulation in Developing Sustainable Deposition and Etch Processes

Dr. Michael Nolan

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Semicon Europa 2023, *Materials Innovation*

16/11/2023

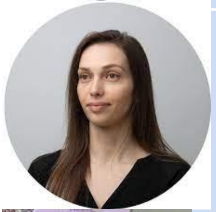
Materials Modelling for Devices Group

Tyndall National Institute
Institiúid Náisiúnta

Materials Modelling for Devices Members and Atomic Level Processing Research Directions

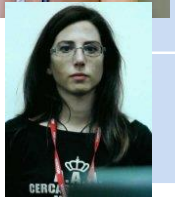
Michael Nolan (Head of Group/Tyndall interim Chief Scientist, MMD-MNS)
ALD/ALE of Oxides, Metals, Nitrides, Hybrid Materials, Polymers
Materials Discovery

Ji Liu (MMD-MNS)
ALD of Oxides, Metals, Nitrides
Precursor Chemistry



Arbresha Muriqi (MMD-MNS)
Hybrid Materials MLD and VPI
Precursor Chemistry
Interfaces

Rita Mullins (MMD-MNS)
Atomic Layer Etching of Oxides,
Metal ALD



Alessandra Imbrogno (MMD-MNS)
MLD of Polymers, ALD of Nitrides

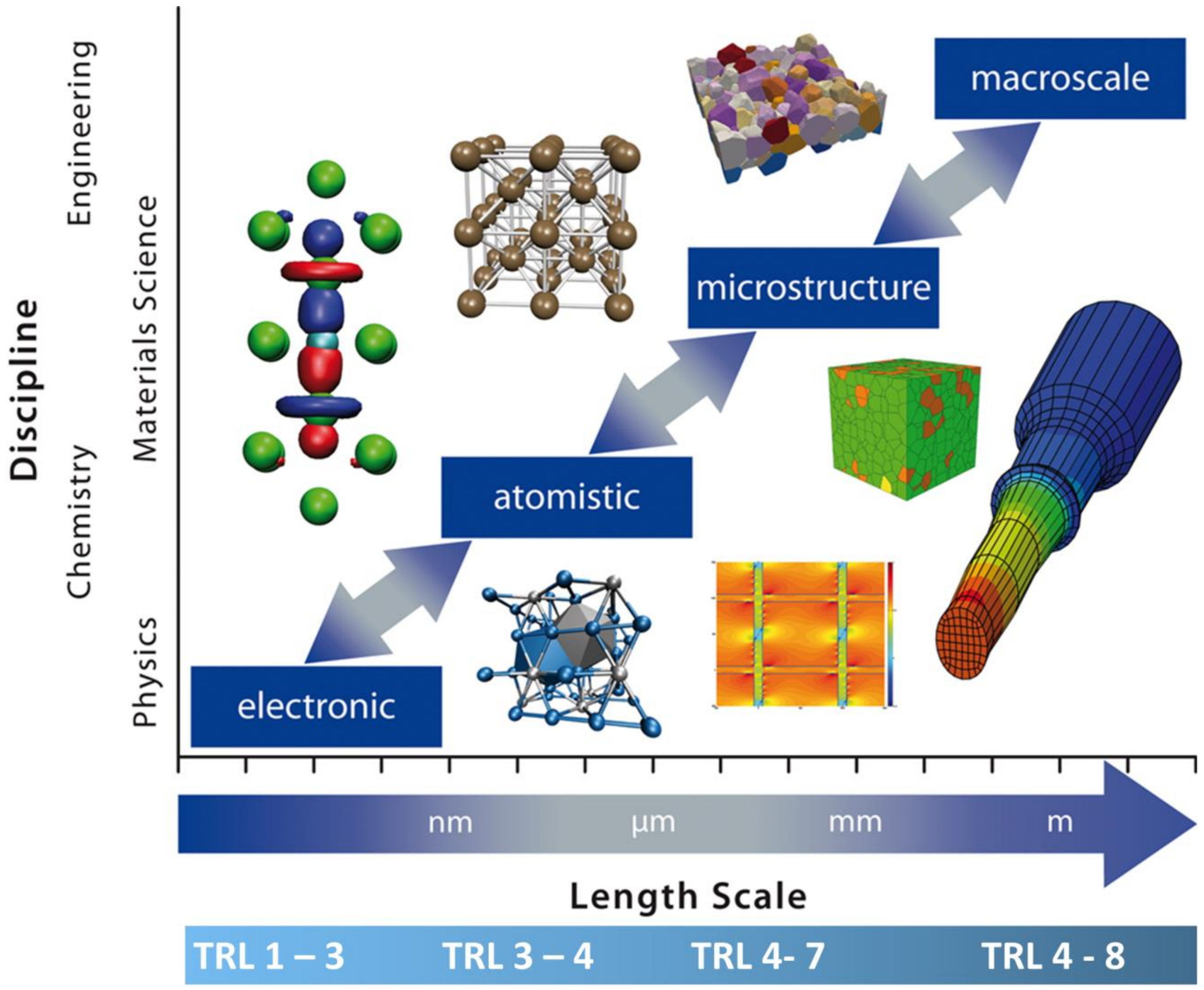
New in 2024: Postdoc on kMC, PhD & MSc on ALE

Tyndall 4000 CPU Core High Performance Computing Cluster

Irish Centre for High End Computing (Tier-2) National Service, 13600 CPU Core – 40x upgrade in 2024 through EuroHPC

EuroHPC Tier-2 Service: e.g LUMI, LE0NARDO, Mare Nostrum, VEGA, …

Introduction to Atomic-Scale Simulation and Modelling



Mathematical Description of phenomena

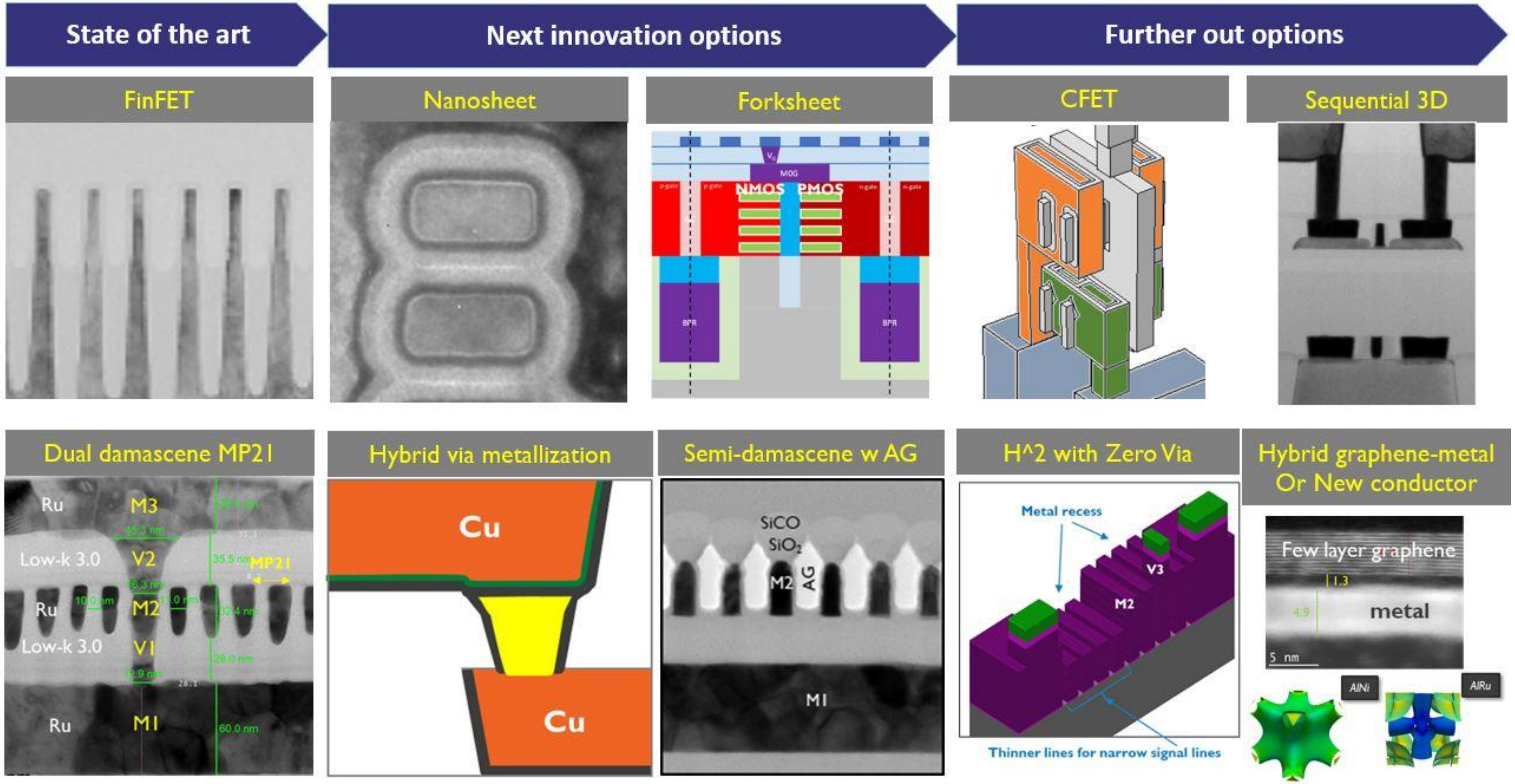
electronic
atomistic
structural
devices
processing
wave propagation

Range of Length and Timescales

$10^{-15} – 10^{-12}$ s / 10^{-9} m
$10^{-9} – 10^{-3}$ s / $10^{-9} – 10^{-6}$ m
$10^{-3} – 10^{6}$ s / $1 – 10^{3}$ m

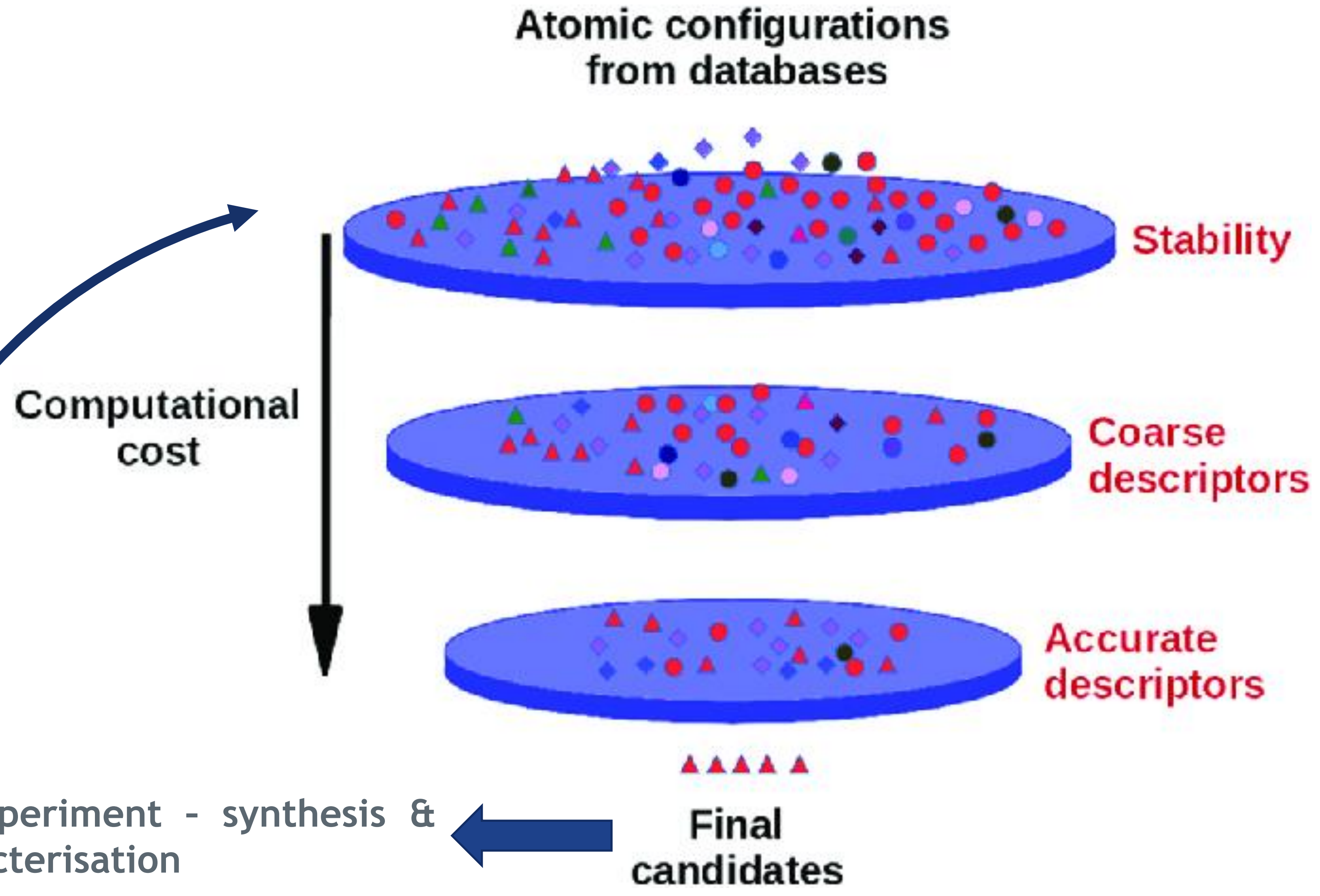
Coarsening of Information upon increasing length scale

Why is atomic level simulation so important?



An imec view on the CMOS technology scaling roadmap.

Computational Materials Screening



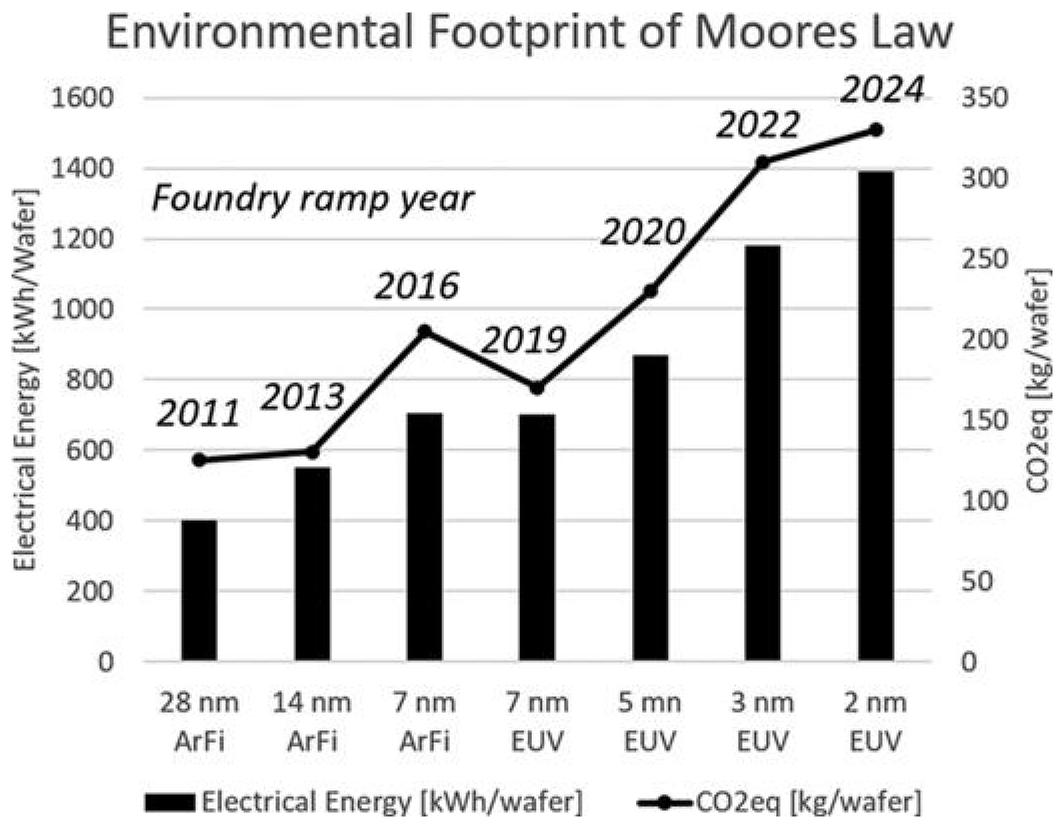
Large set of possible materials

First criterion to reduce set of possible materials

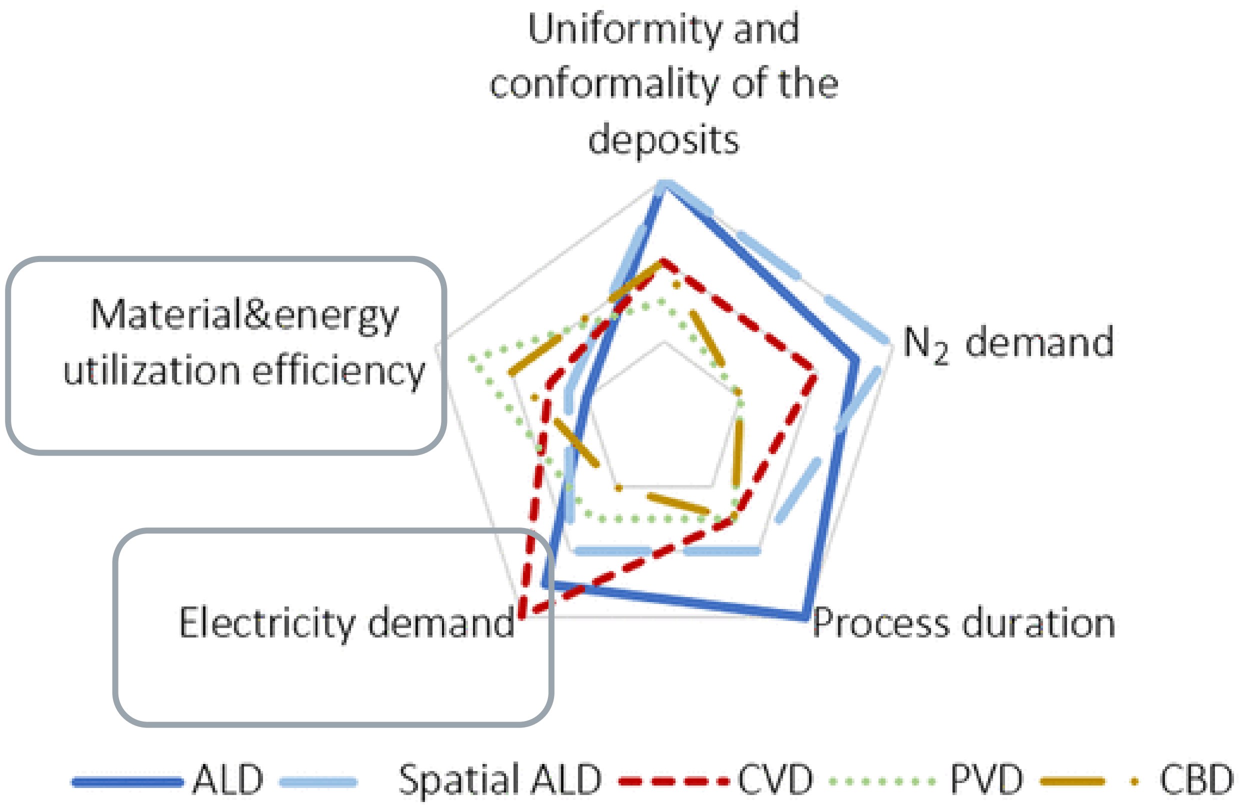
Second criterion to reduce to a manageable set of possible materials

To experiment - synthesis & characterisation

Sustainability Challenges in Atomic Level Processing

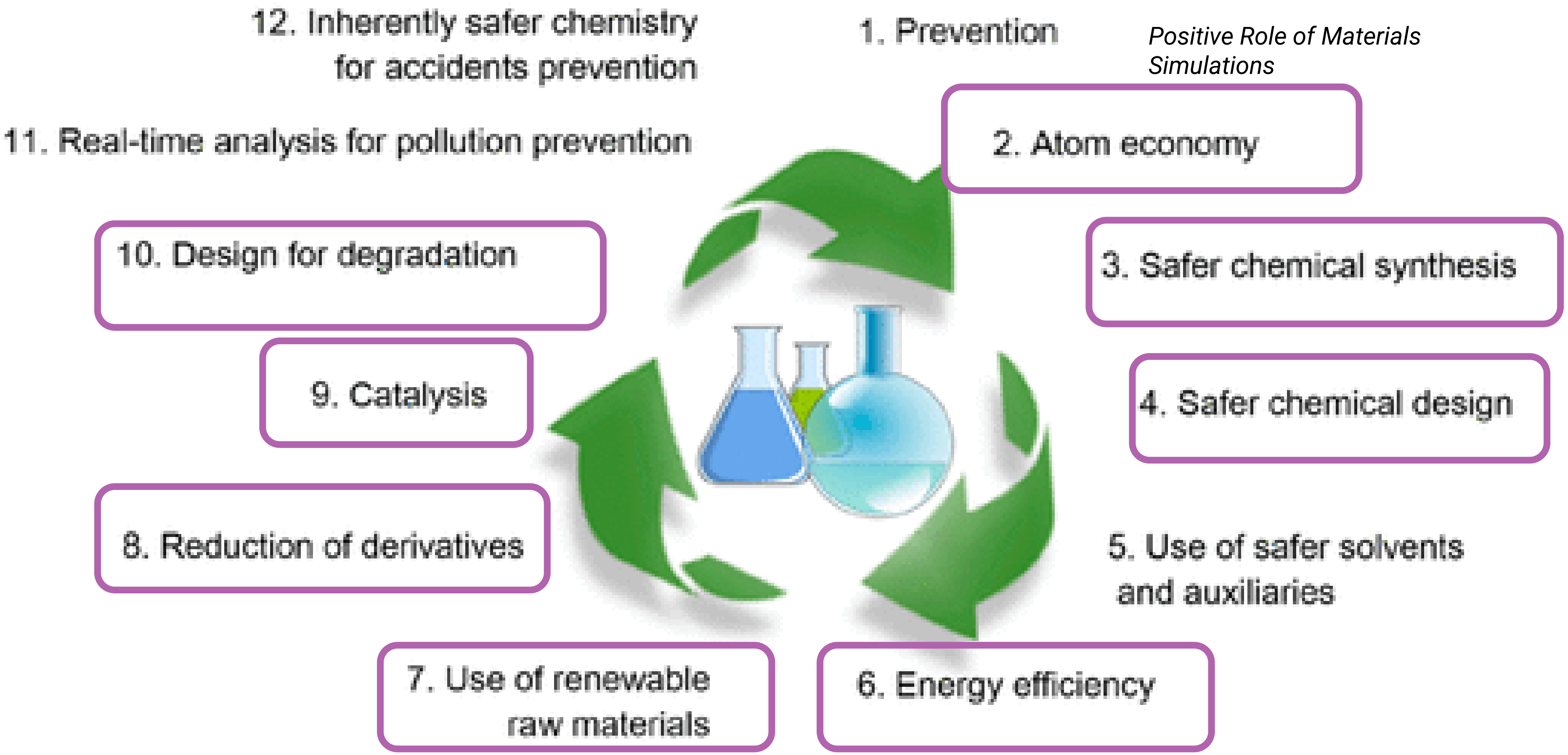


https://doi.org/10.1116/6.0001125



Weber et al ACS Mater Au 2023, 3, 274

Principles and Green/Sustainable Chemistry



Weber et al ACS Mater Au 2023, 3, 274
Anastas and Eghbali. *Chem. Soc. Rev.* **2010**, *39* (1), 301– 312, DOI: 10.1039/B918763B
Saudi Pharm. J. **2019**, *27* (1), 1– 8, DOI: 10.1016/j.jsps.2018.07.011

Sustainability Benefits of Simulation

Modelling and Simulation Based Materials and Process Development

Explore scenarios, e.g. “what if we take this option?”

Predict chemistries before going to lab

Optimised deposition chemistries

Recued use of (expensive, dangerous, etc) chemicals

Reduced implementation time and cost

Sustainability Benefits of Simulation

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Equipment Manufacturers: Better ALD and MLD chemistries

Intel: Better ALE Chemistries

Logitech: non-fluorinated materials + Deposition

MedTech: ultra-thin low friction materials + Deposition. Piezoelectrics

Sustainability Benefits of Simulation

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Our Examples:

- "Digital Twin" for ALP development and optimisation

- Processes with less harsh and lower energy intensity chemistries

- Precursors for Atomic and Molecular Layer Deposition

Sustainability Benefits of Simulation

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- Replace fluorinated chemicals for etch and other processes

    replace halogens for etch

Sustainability Benefits of Simulation

Tyndall National Institute
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- “Digital Twin” for ALP development and optimisation

- Processes with less harsh and lower energy intensity chemistries

- Precursors for Atomic and Molecular Layer Deposition

- Replace fluorinated chemicals for etch and other processes
  replace halogens for etch

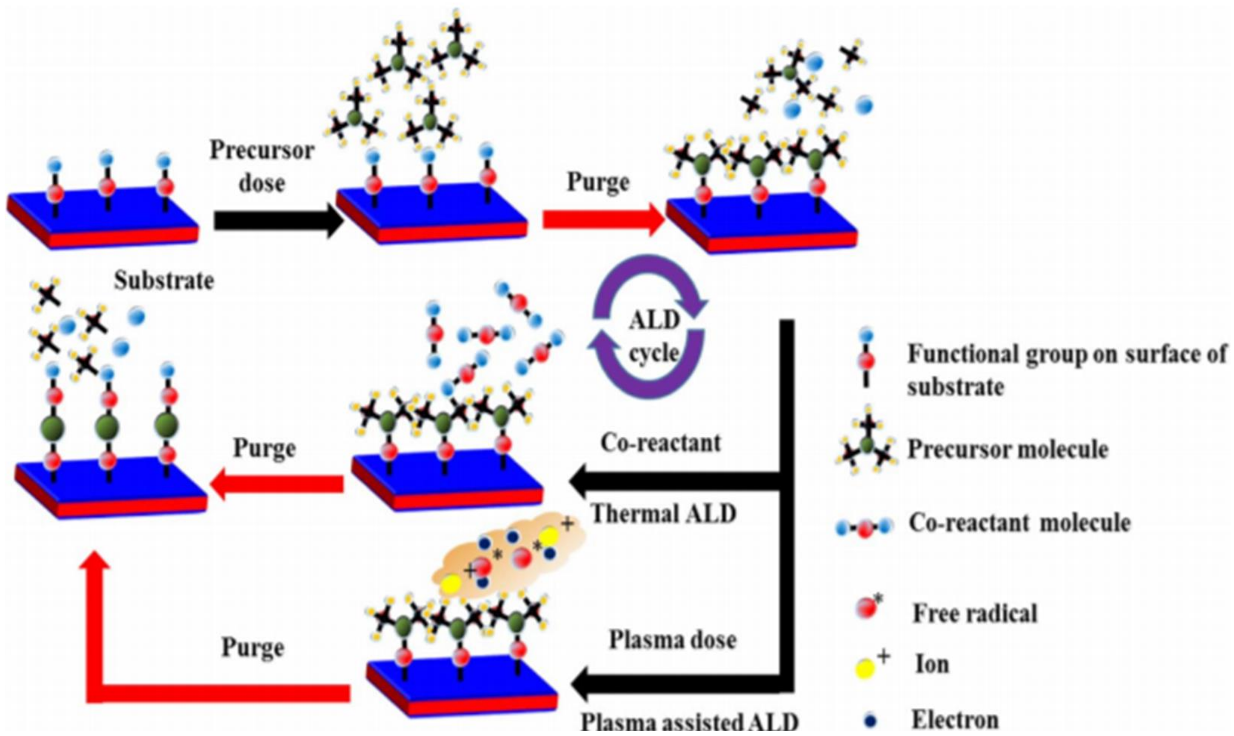
- Avoid precious and critical materials

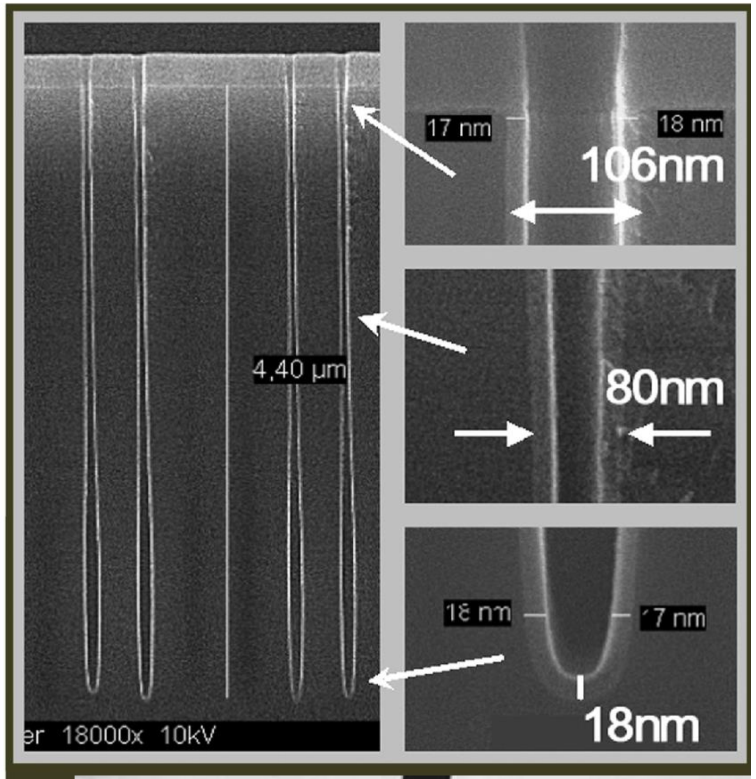
- MLD process chemistry for thin lubricious coatings

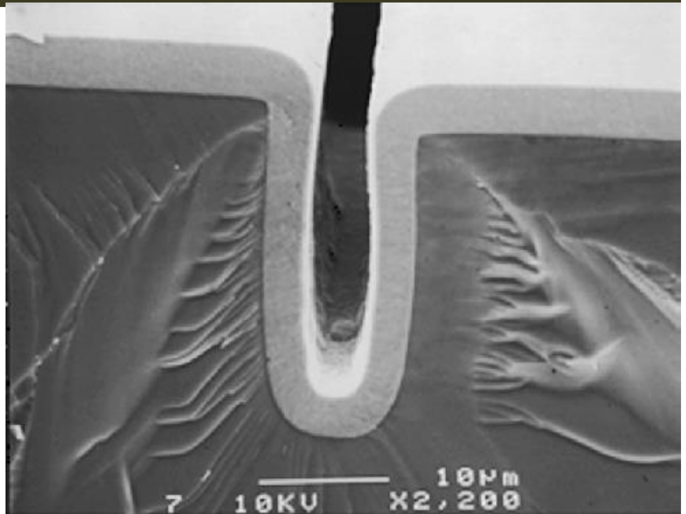
- Non-fluorinated low friction coatings for gaming peripherals

Surface Chemistry for Atomic Level Processing

Deposition

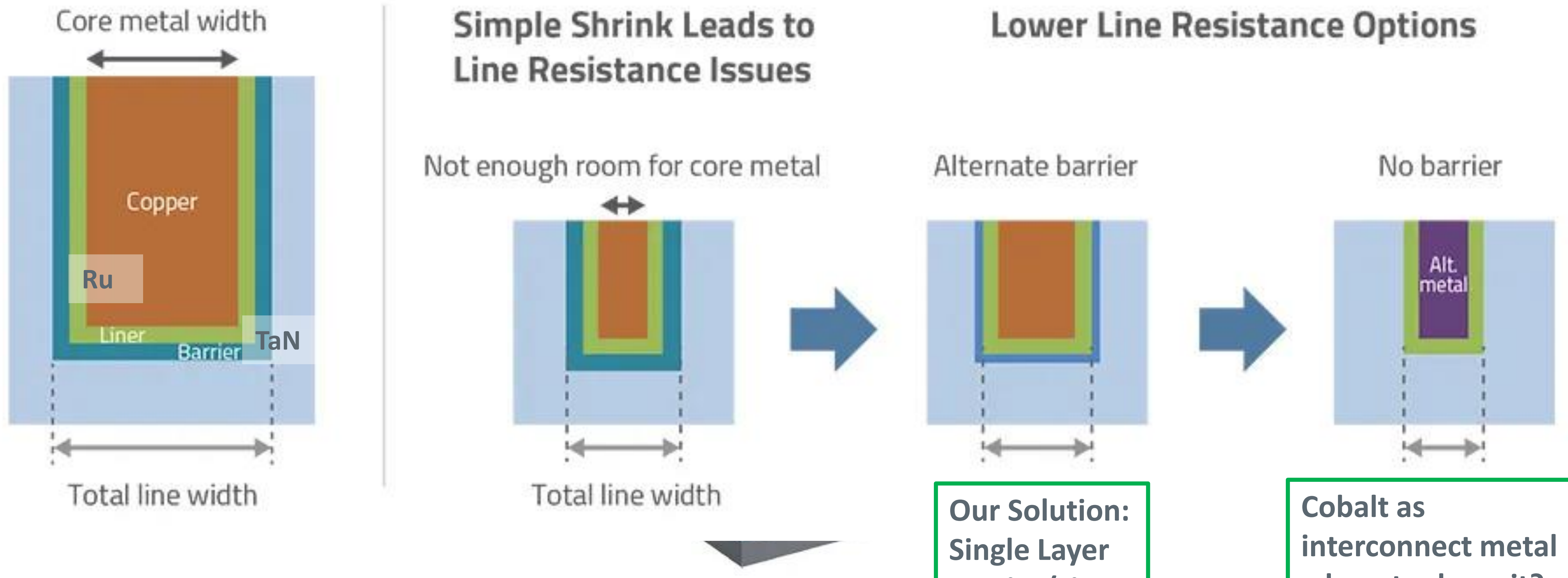






Ultra thin coatings
Complex structures
Uniformity (< 1%)
Conformal

Example – Metal Interconnects



Our Solution: Single Layer Barrier/Liner

Cobalt as interconnect metal – how to deposit?

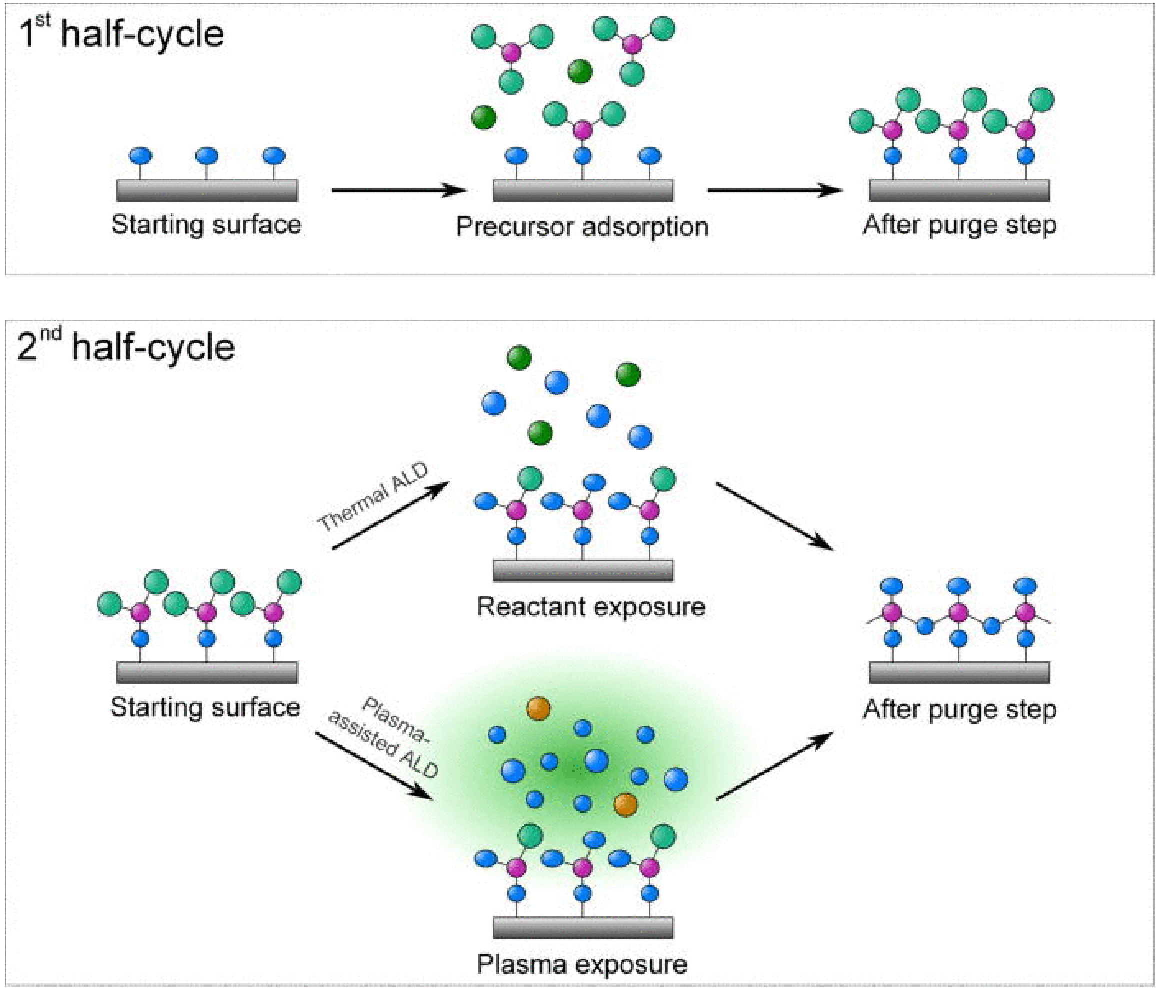
Vos, Martijn FJ, et al. "Atomic layer deposition of cobalt using H2-, N2-, and NH3-based plasmas: on the role of the Co-reactant." *J. Phys. Chem. C* 122.39 (2018): 22519-22529.

ALD of Alternative Interconnect

PE-ALD of Ru and Co with H_2/NH_3 plasma

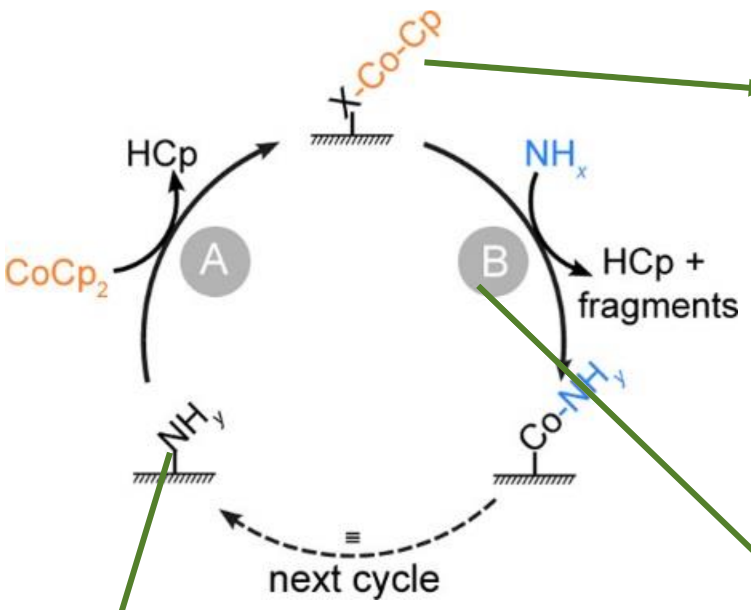
Precursor reaction mechanism is not clear

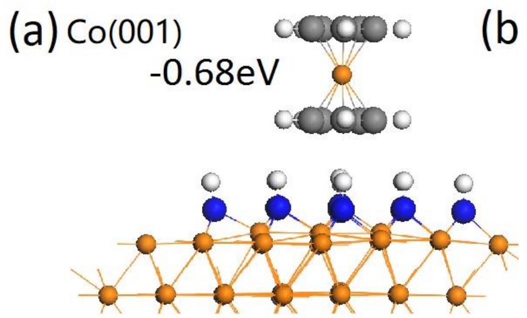
- I: coverage and stability of NH_y-terminations
- II: precursor reaction mechanism at first half cycle
  - (hydrogen transfer)
- III: final structure/termination after metal precursor pulse
- IV: reaction mechanism at second half cycle
  - (plasma step)

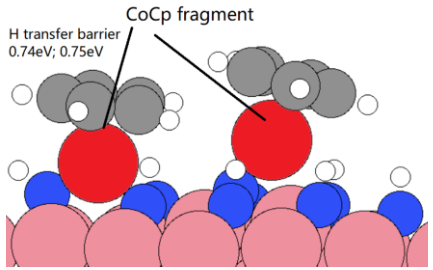


Vos, Martijn FJ, et al. "Atomic layer deposition of cobalt using H2-, N2-, and NH3-based plasmas: on the role of the Co-reactant." *J. Phys. Chem. C* 122.39 (2018): 22519-22529.

Metal Plasma ALD: First Full ALD Cycle Study

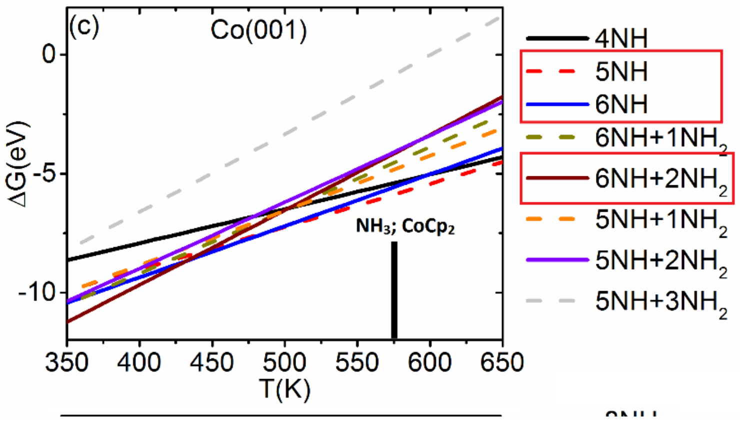


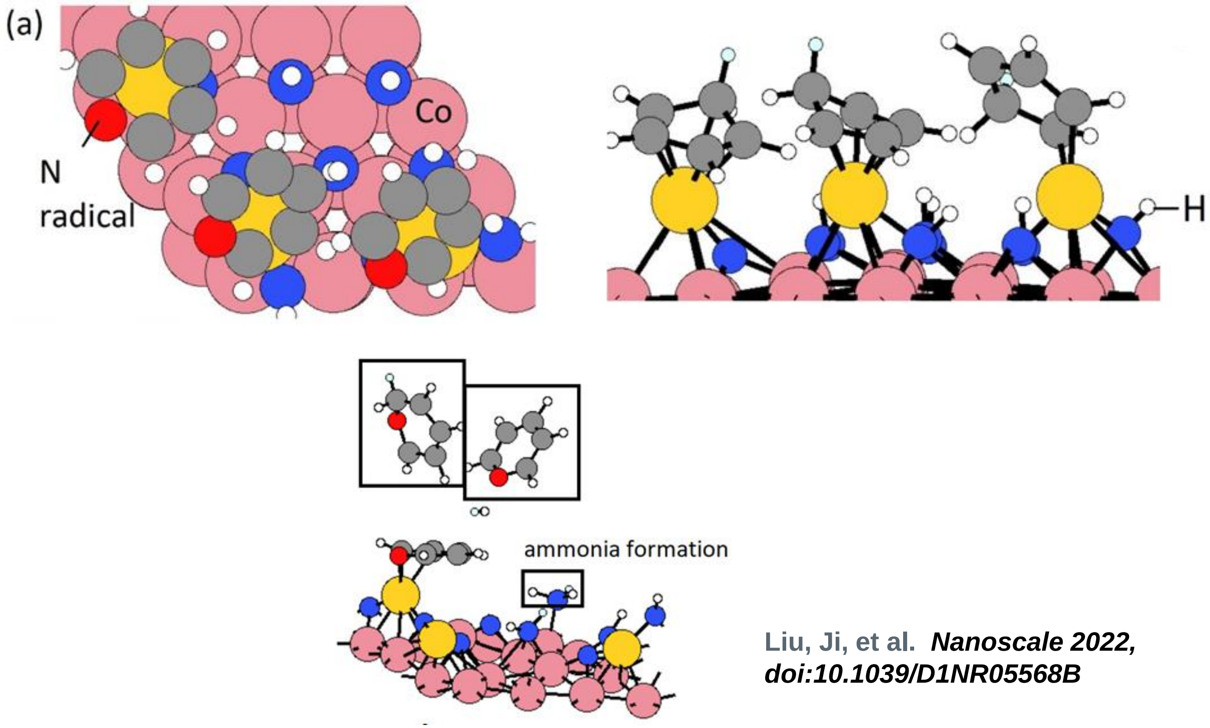




Liu, Ji, et al. *J. Phys. Chem. C* **2020, 124, 22, 11990–12000**

Liu, Ji, et al. *J. Mat Chem. C* **2021, 9 2919**





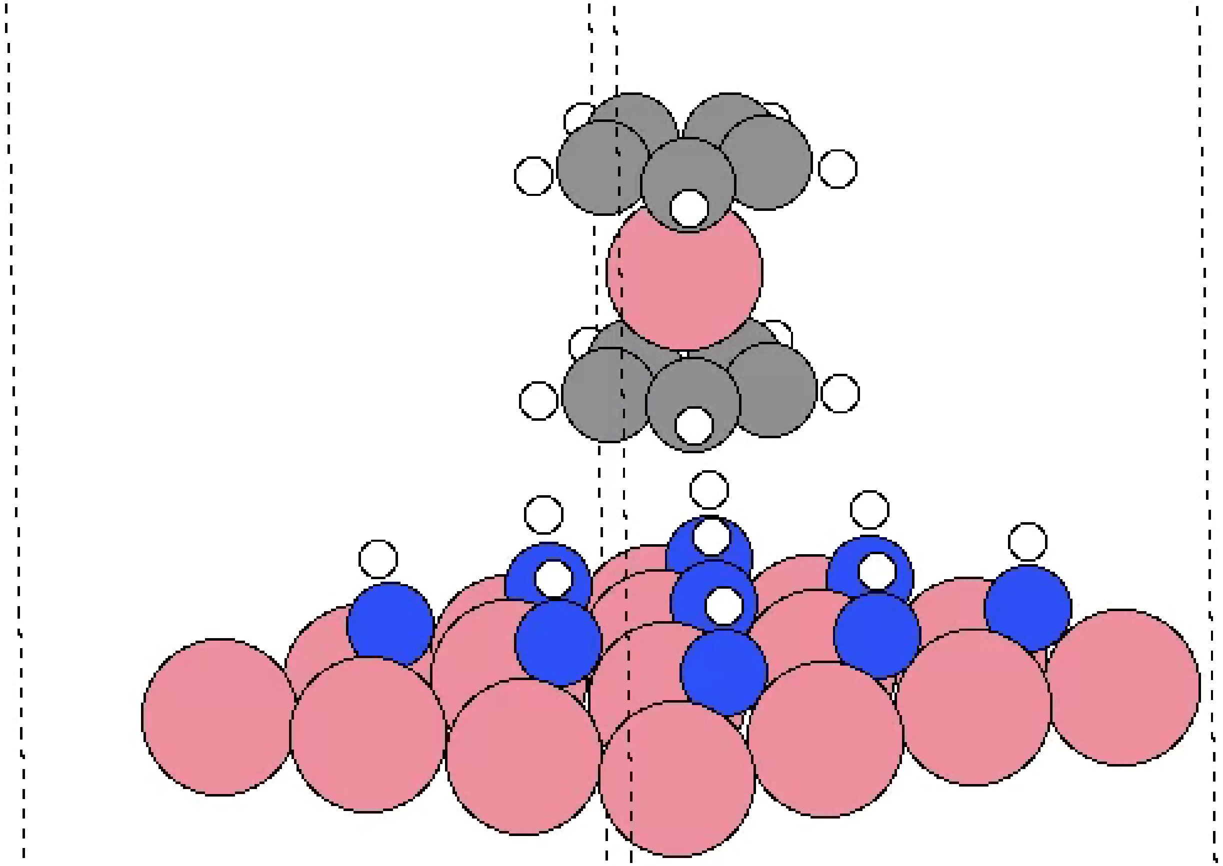
Liu, Ji, and Michael Nolan." J. Phys. Chem. C 123.41 (2019): 25166-25175.

Liu, Ji, et al. *Nanoscale 2022, doi:10.1039/D1NR05568B*

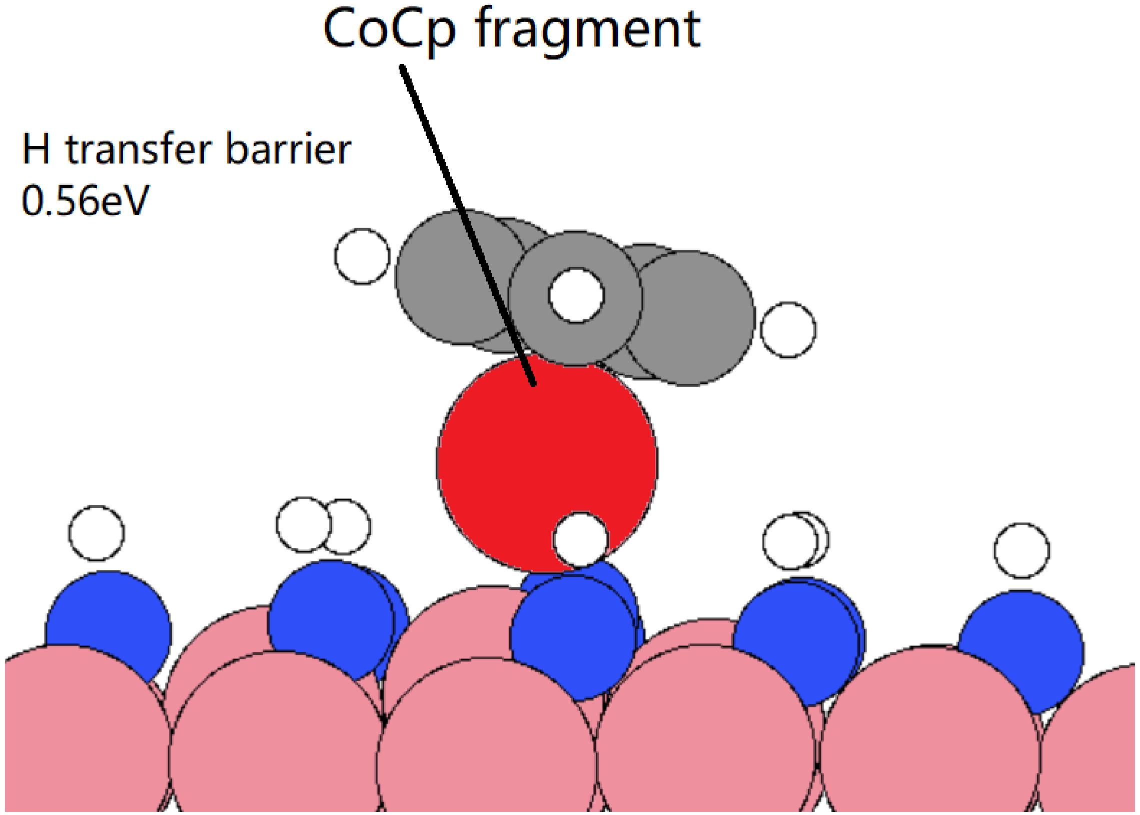
Precursor reaction mechanism

Simulation to predict:

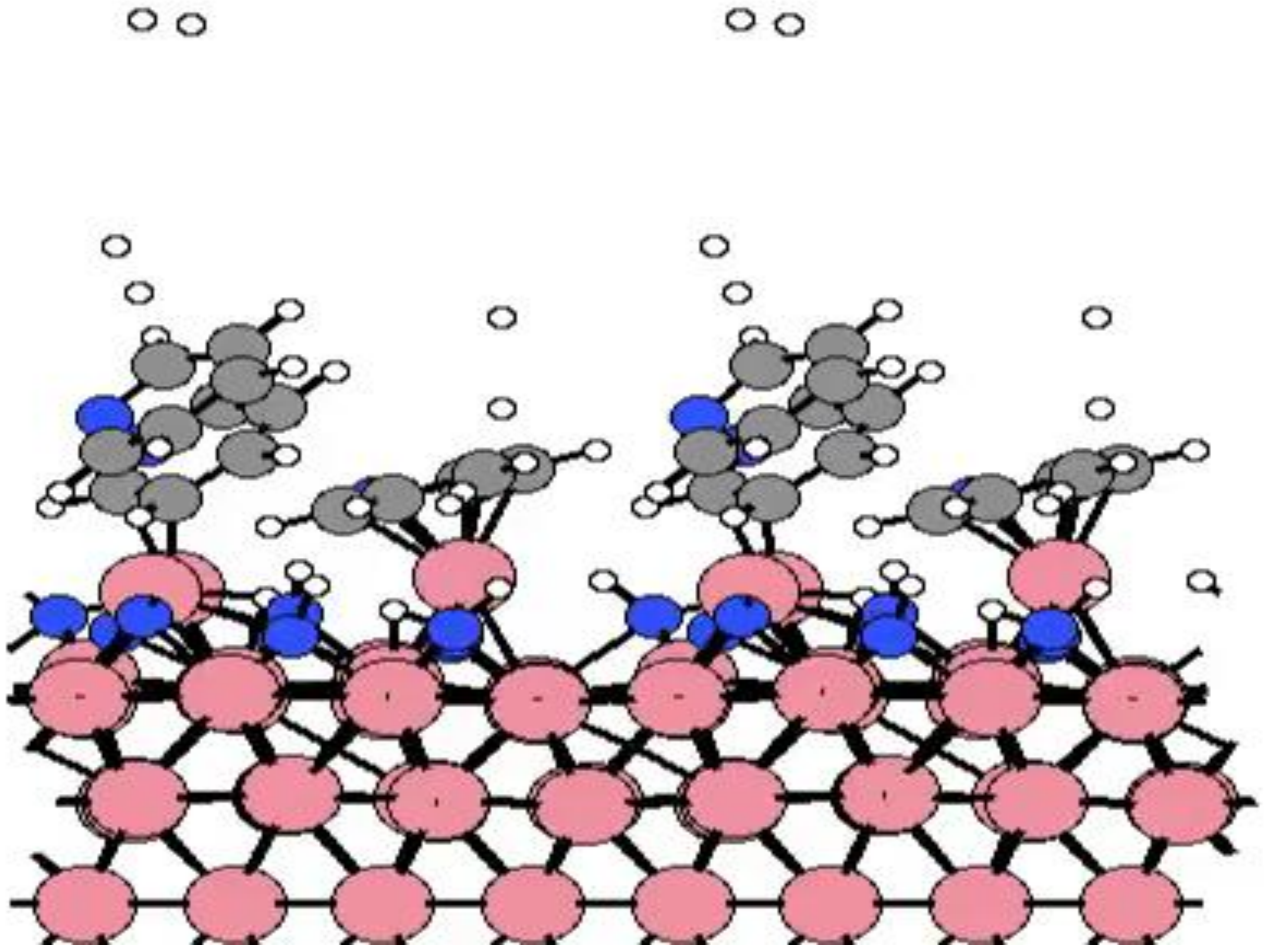
- Thermodynamics of reaction of precursor at surface: *is the possible chemistry favourable?*
- Kinetics: *calculating activation barrier of key process step(s)*
- Screening precursors without doing lab experiments



Single $CoCp_2$



N-plasma half-cycle



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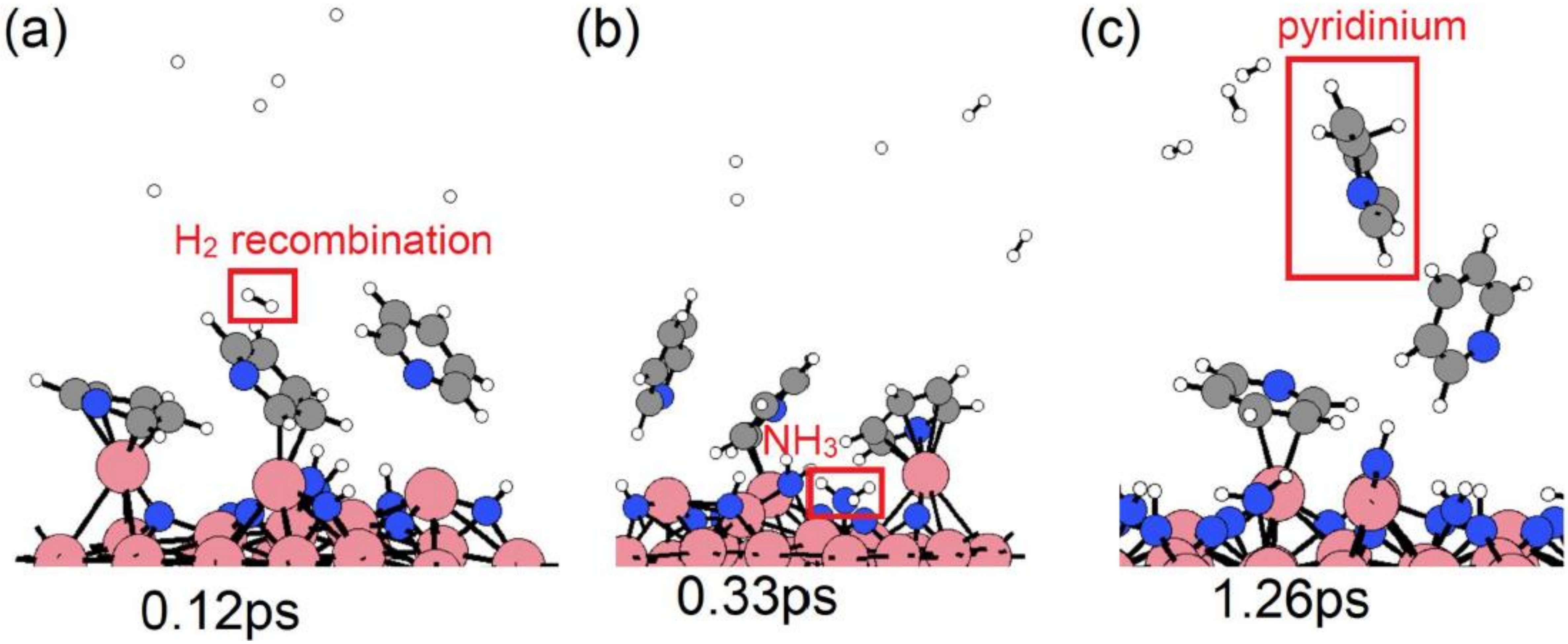
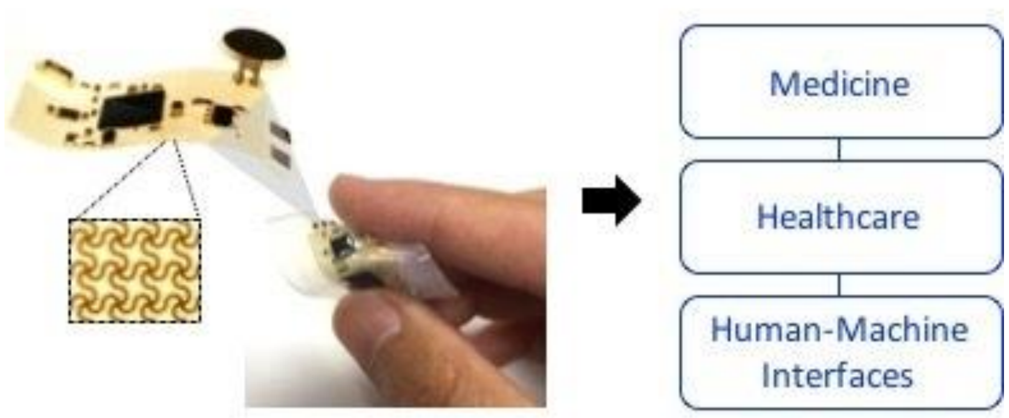


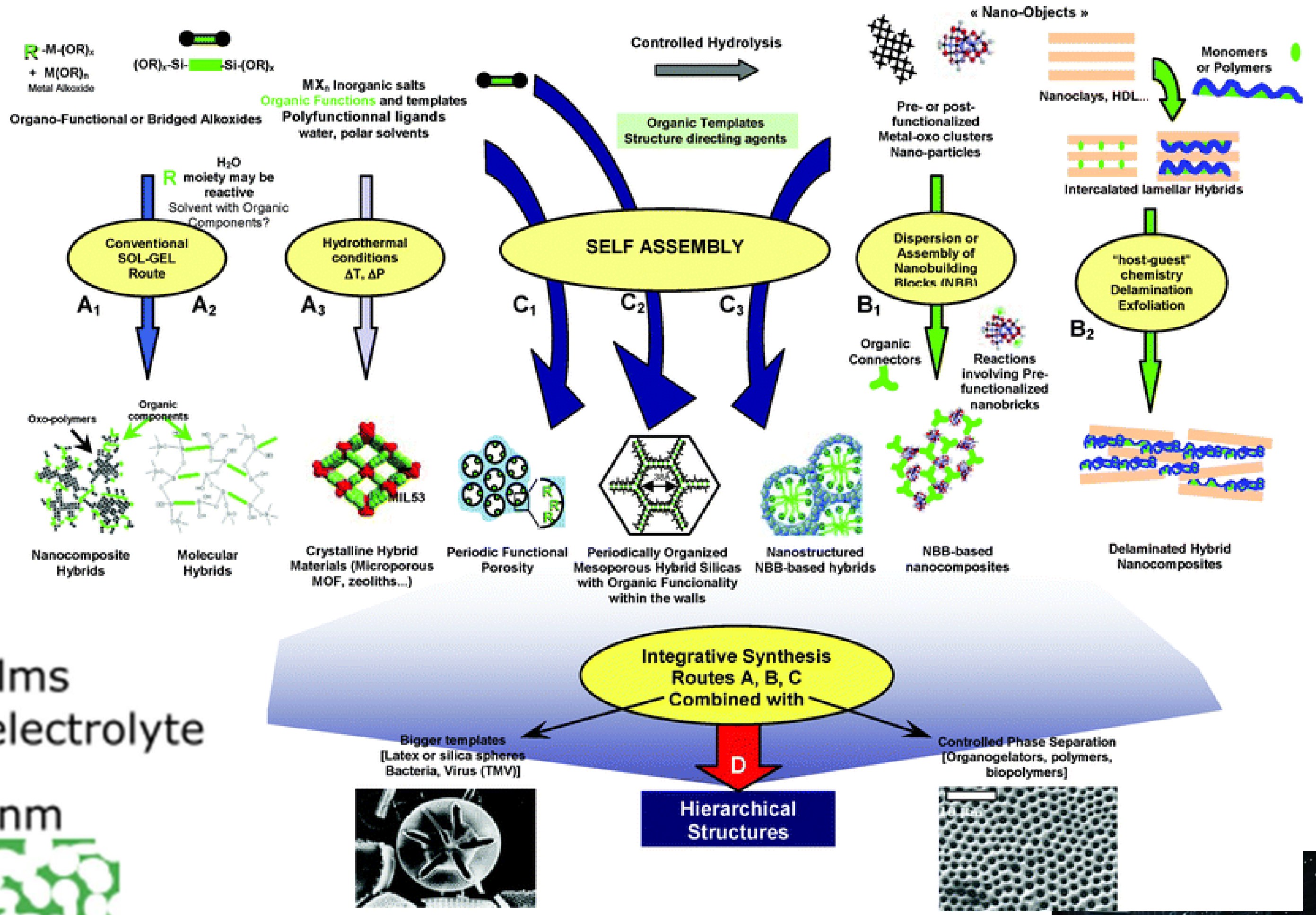
Liu, Ji, et al. Self-limiting nitrogen/hydrogen plasma radical chemistry in plasma-enhanced atomic layer deposition of cobalt. *Nanoscale* **2022**, https://doi.org/10.1039/D1NR05568B)

Example - Hybrid Polymer/Organic Materials

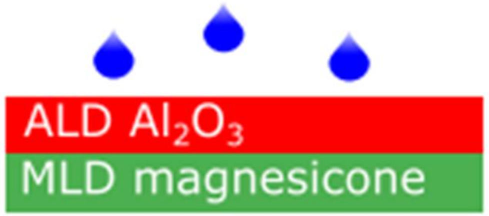
Hybrid inorganic-organic materials interesting across many technologies

Soft Material-Enabled, Flexible Hybrid Electronics

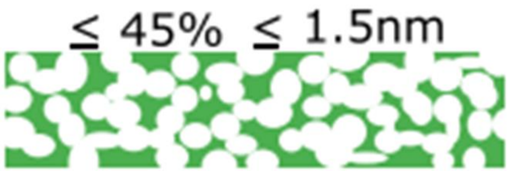




Moisture barrier



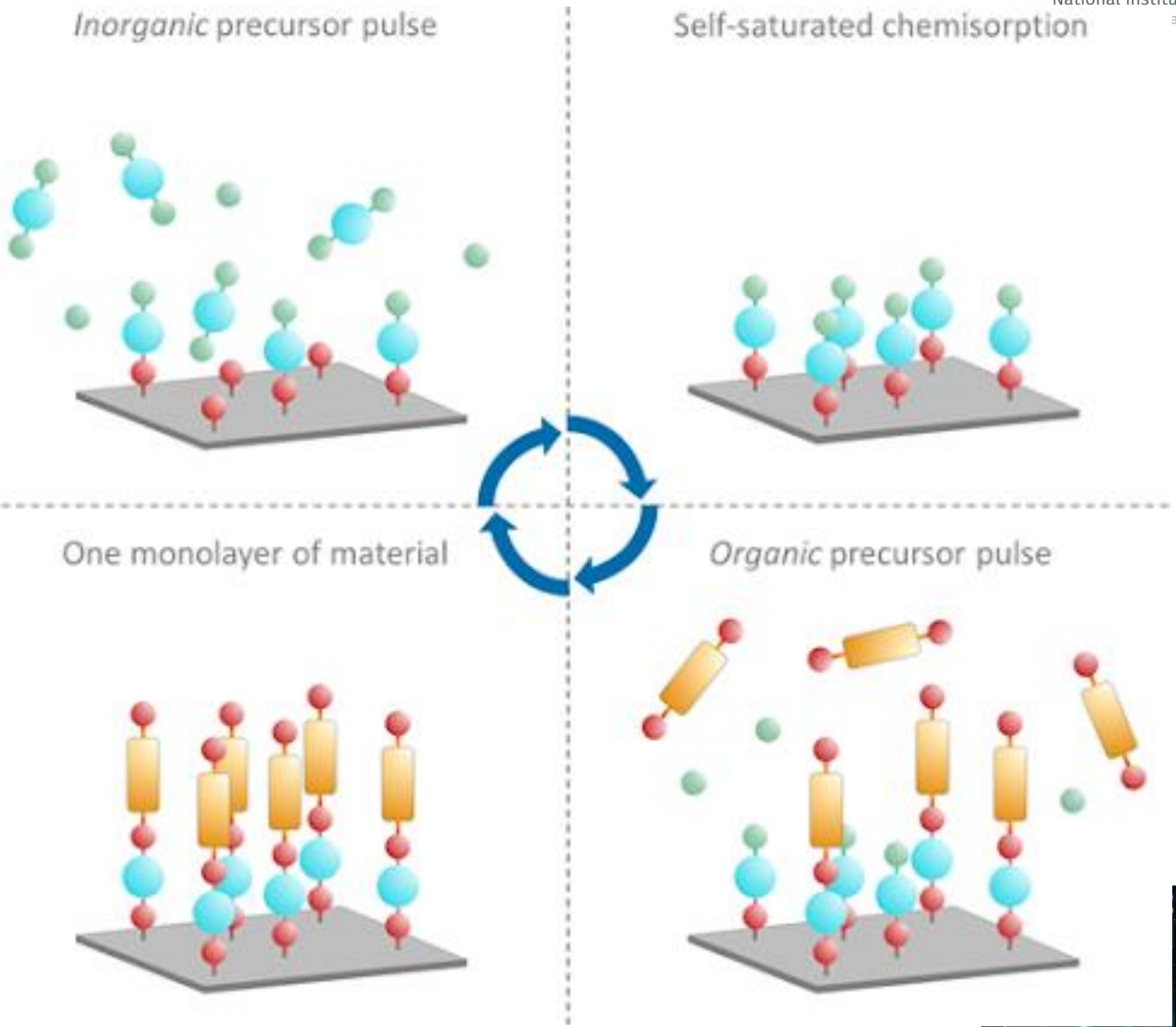
Porous MgO films
for solid composite electrolyte



Kint et al. Chem of Mat., 2020, 32, 11, 4451 - 4466

Example - Hybrid Polymer/Organic Materials

Exploit Molecular Layer Deposition



MLD benefits from atomistic simulations to understand/predict chemistries in advance of laboratory work

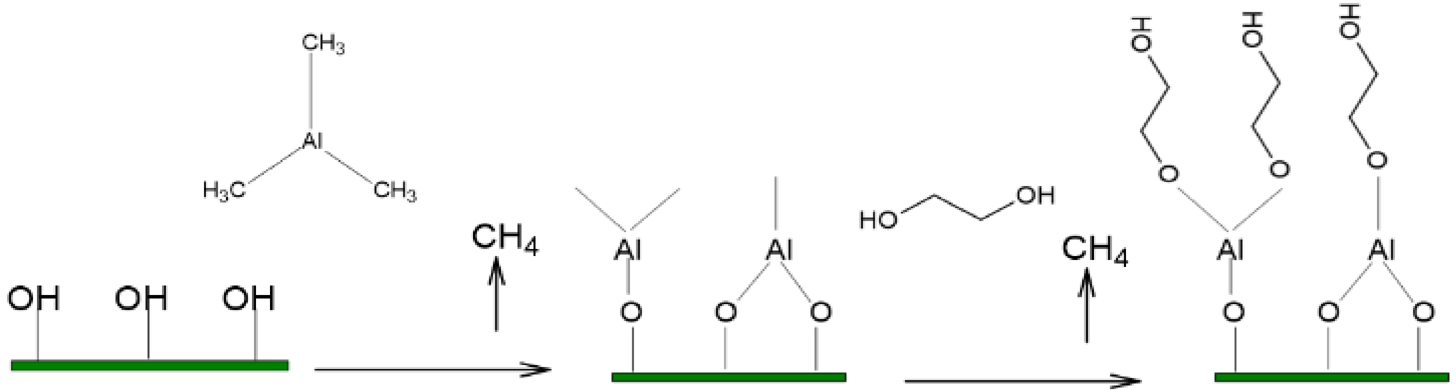
-> Eliminate non-performing chemistries

-> Avoid unsustainable materials and chemicals

AM, MN Chemistry of Materials, 2020, 32, 4451
Doi:10.1021/acs.chemmater.9b05116
Dalton Trans 2020, 49, 8710
Doi:10.1039/D0DT01376E

Example - Hybrid Polymer/Organic Materials

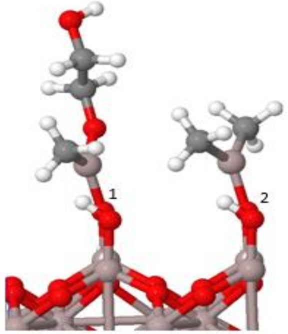
Alucone hybrid film growth



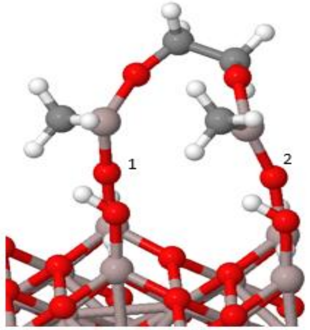
Ethylene Glycol

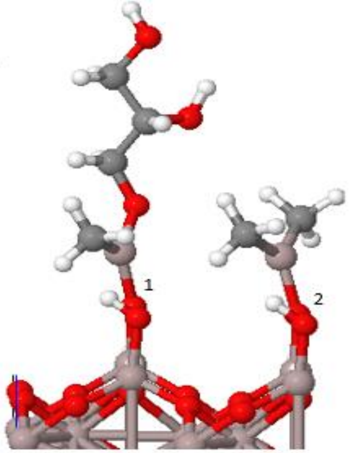
Glycerol

a)

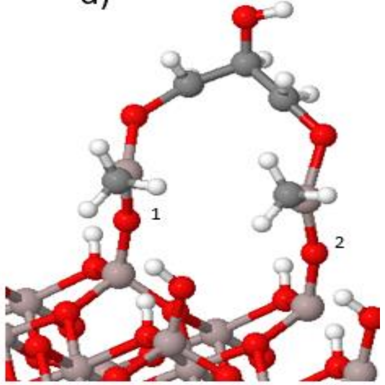


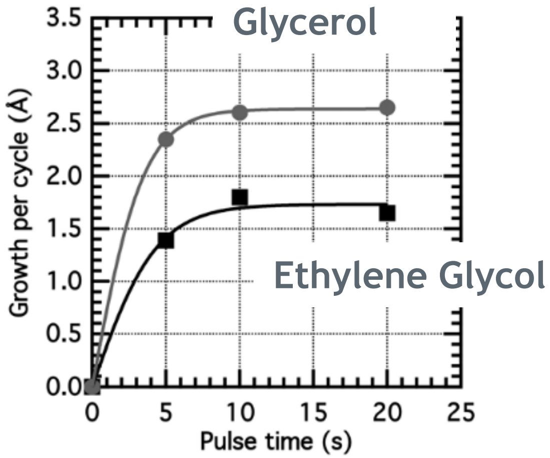
b)





d)





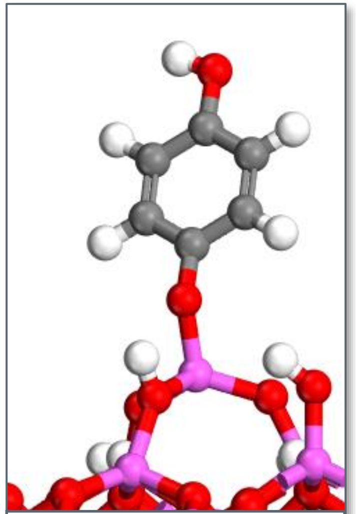
AM, MN Chemistry of Materials, 2020, 32, 4451
Doi:10.1021/acs.chemmater.9b05116
Dalton Trans 2020, 49, 8710
Doi:10.1039/D0DT01376E

Preference for both to lie flat

Glycerol grows thicker films because it has extra reactive sites
But alucones show poor stability in ambient

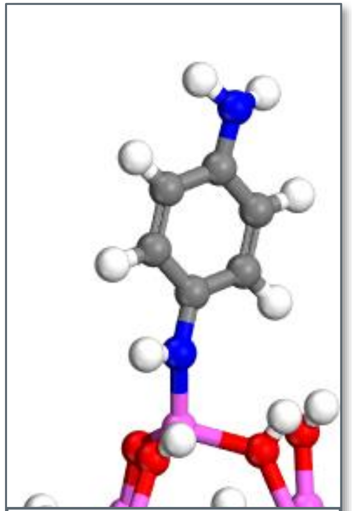
Hybrid Materials

Hydroquinone (HQ)



ΔE = -1.38 eV

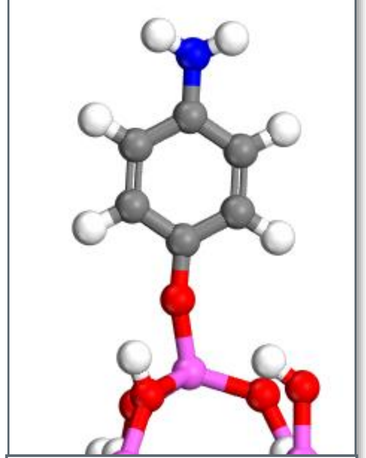
Phenylenediamine (PD)



ΔE = -1.12 eV

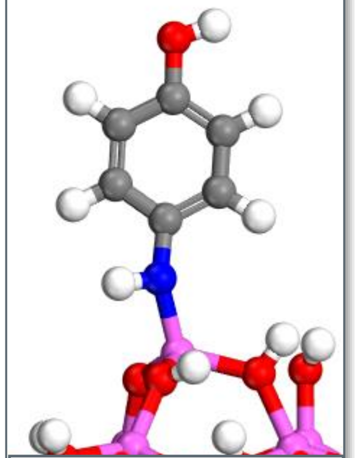
Aminophenol (AP)

AP (Al-O bonding)



ΔE = -1.25 eV

AP (Al-N) bonding)



ΔE = -0.86 eV

- All aromatic organic precursors react favorably with TMA adsorbed on the Al2O3 surface
- The energies indicate that formation of the Al-O bond is more favourable compared to the Al-N bond
- Key result is that the preference is for the upright and rigid configuration
- New class of organics for hybrid materials
- Idea Proved in MLD study with Aalto
  - A Tanskanen, P Sundberg, M Nolan, M Karppinen, Thin Solid Films 2021, 736, 138896

Sustainability Benefits of Simulation

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Modelling and Simulation Based Materials and Process Development

Explore scenarios, e.g. “what if we take this option?”

Predict chemistries before going to lab

Recued use of (expensive, dangerous, etc) chemicals

Reduced implementation time and cost

Access to European Infrastructure for Nanoelectronics

BENEFITS

Transnational Access Program: benefit from access & expertise of:

- Opportunities to **collaborate**
- Access to **state-of-the-art equipment** & unique platform technologies of 16 cleanrooms
- **Free-of-charge**

NANOFABRICATION

- Non-standard processing
- Industry-standard and non-standard fabrication
- Innovative materials and devices
- GaN-IC (on-SOI) platform for power electronics and fabrication via MPW shuttles
- Diamond CVD Growth and Nanofabrication, IPMS deposition tools for MRAM-stacks, NVM ferroelectrics, high-k and low-k dielectrics and IZM wafer-level packaging

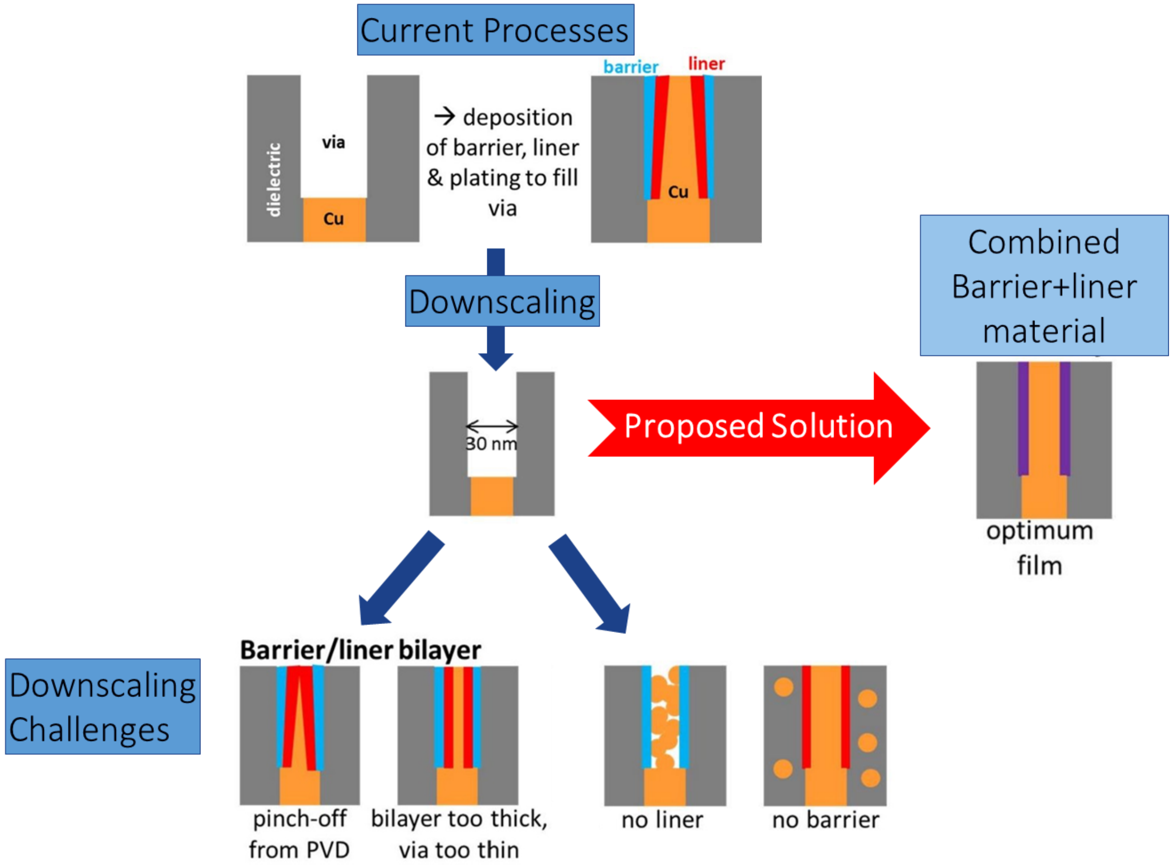
CHARACTERISATION SUITE

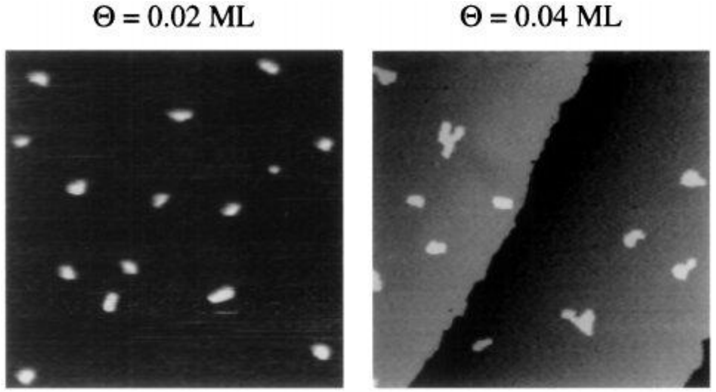
- Electrical test labs and device characterisation facilities
- Electron microscopy and spectroscopy
- Electrical test labs and Nano-Characterisation platform capabilities device
- Electrical & physical characterisation

PLATFORMS

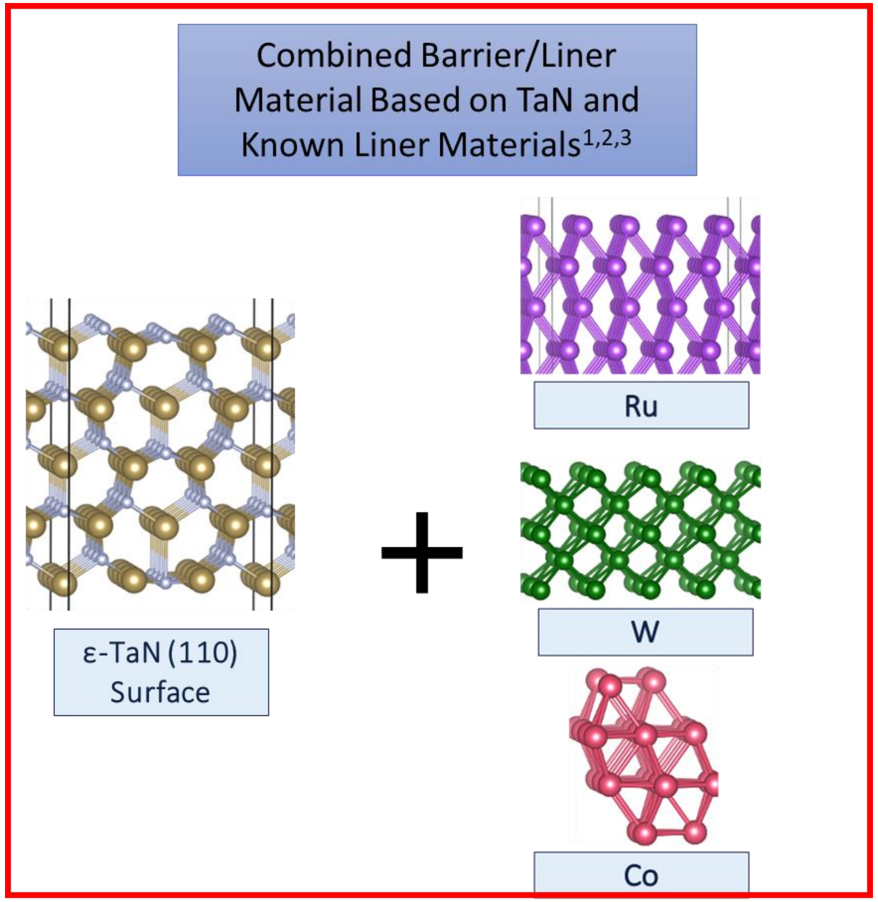
- Site-controlled quantum dots and quantum device fabrication
- Wafer-scale graphene device fabrication
- GaN-IC power electronic devices and test structures
- Diamond Platform and IISB 4H-SiC Line

Interconnect Barrier/Liner Challenge

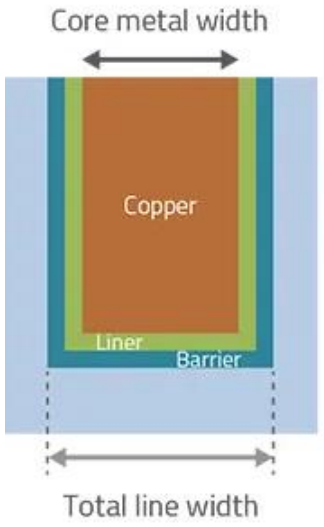




Copper Islands -> non-conducting



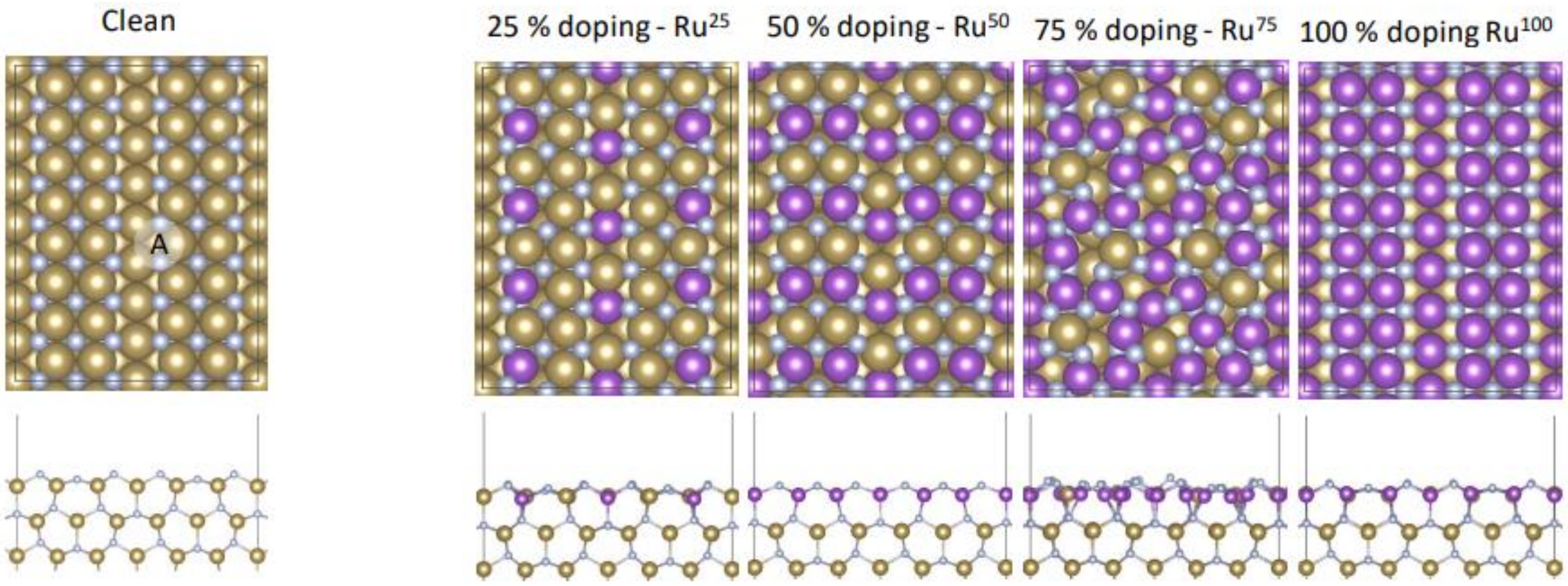
Continue to use Copper – Promoting Deposition of Conducting Copper



Increase volume available to the metal

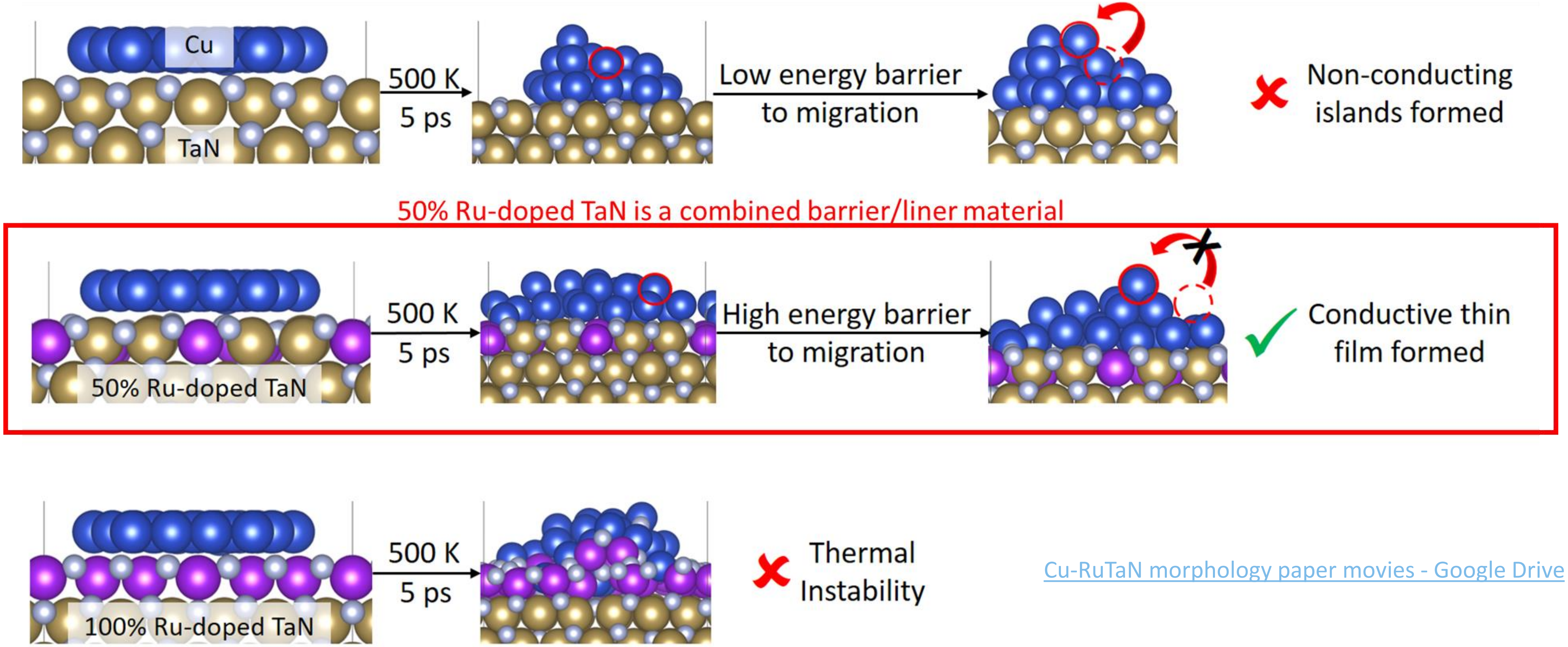
Devise <u>new</u> materials system:

TaN barrier that incorporates Ru directly into its surface layer (using Atomic Layer Deposition)



New Materials to Promote Copper Deposition

Cu Ru Ta N



[Cu-RuTaN morphology paper movies - Google Drive]

1 - SK Natarajan, Cara-Lena Nies, and M Nolan. J. Mat Chem C **(2019)** doi:10.1039/C8TC06118A

2 - Suresh Kondati Natarajan, Cara-Lena Nies, and Michael Nolan. J. Chem Phys. **(2020)** doi:10.1063/5.0003852

3 - Cara-Lena Nies, Suresh Kondati Natarajan and Michael Nolan. Chem Sci. **(2021)**. doi:10.1039/D1SC04708F