17th International Conference on Atomic Layer Deposition
Denver, Colorado, USA
2017

What theory can tell us about ALD mechanism

Simon D. Elliott & co-workers
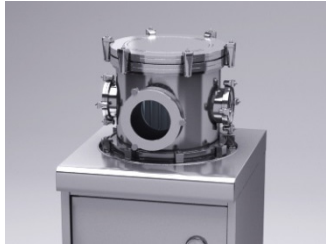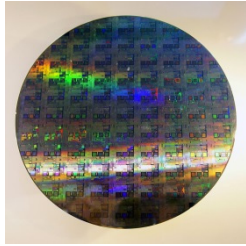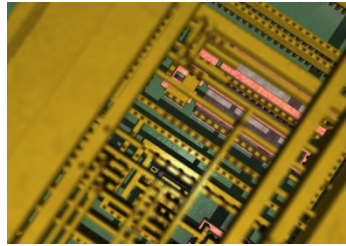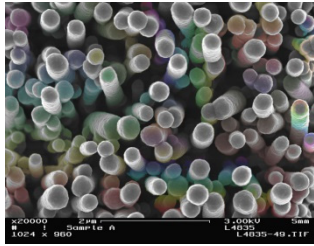
simon.elliott@tyndall.ie
www.tyndall.ie

metre

micro

nano

atomic

The length scales of ALD modelling

metre
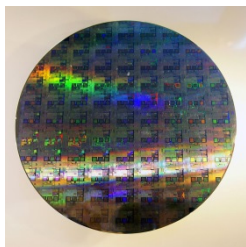
micro

nano

atomic

Computational fluid dynamics
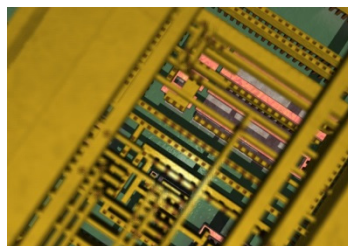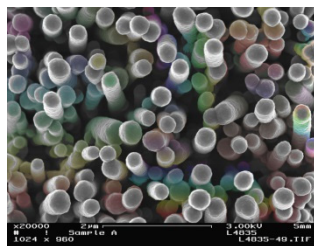
Coarse grained models
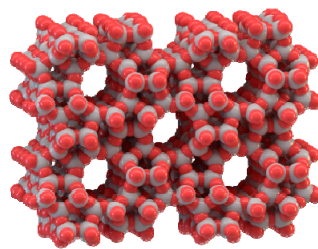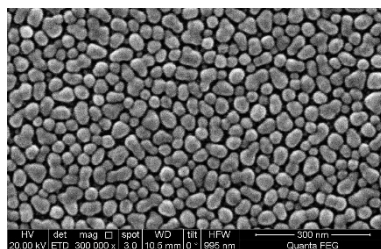
Atomistic simulations
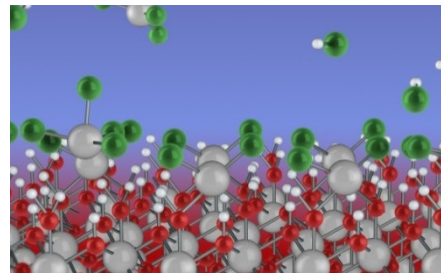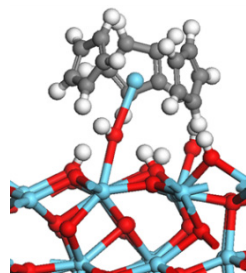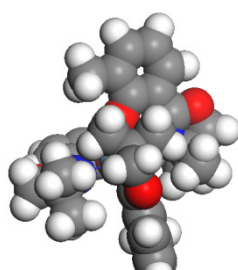
Density functional theory

atomic
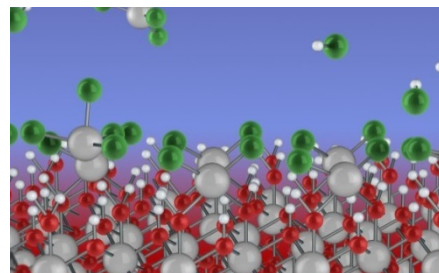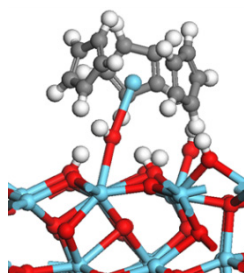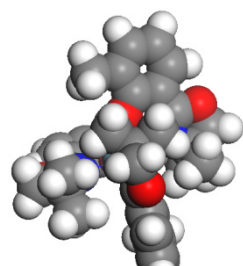
Density functional theory
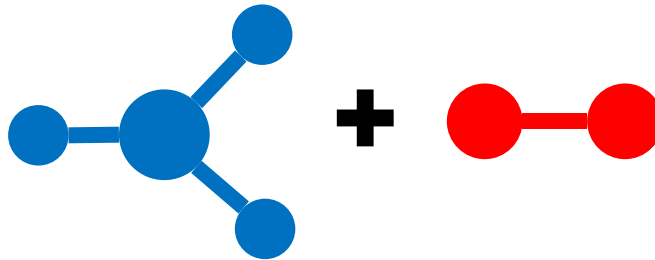
PRECURSOR PROPERTIES

S. D. Elliott, *Semicond. Sci. Technol.* **27**, 074008 (2012);
S. D. Elliott *et al.*, *Adv. Mater.* **28**, 5367 (2016).
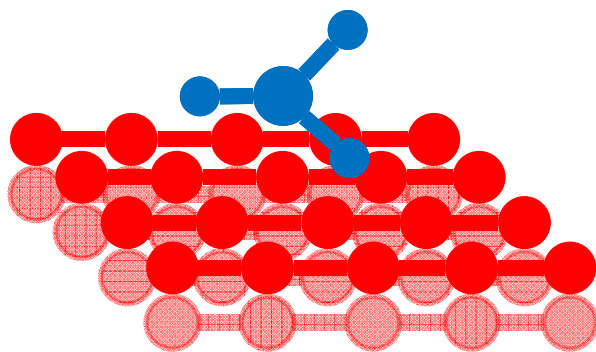
SUBSTRATE MODELS

S. D. Elliott, *Semicond. Sci. Technol.* **27**, 074008 (2012);
S. D. Elliott *et al.*, *Adv. Mater.* **28**, 5367 (2016).

MULTIPLE ADSORBATES
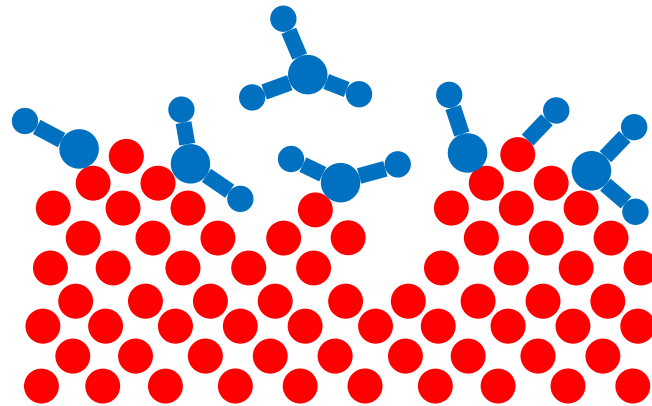
S. D. Elliott, *Semicond. Sci. Technol.* **27**, 074008 (2012);
S. D. Elliott *et al.*, *Adv. Mater.* **28**, 5367 (2016).
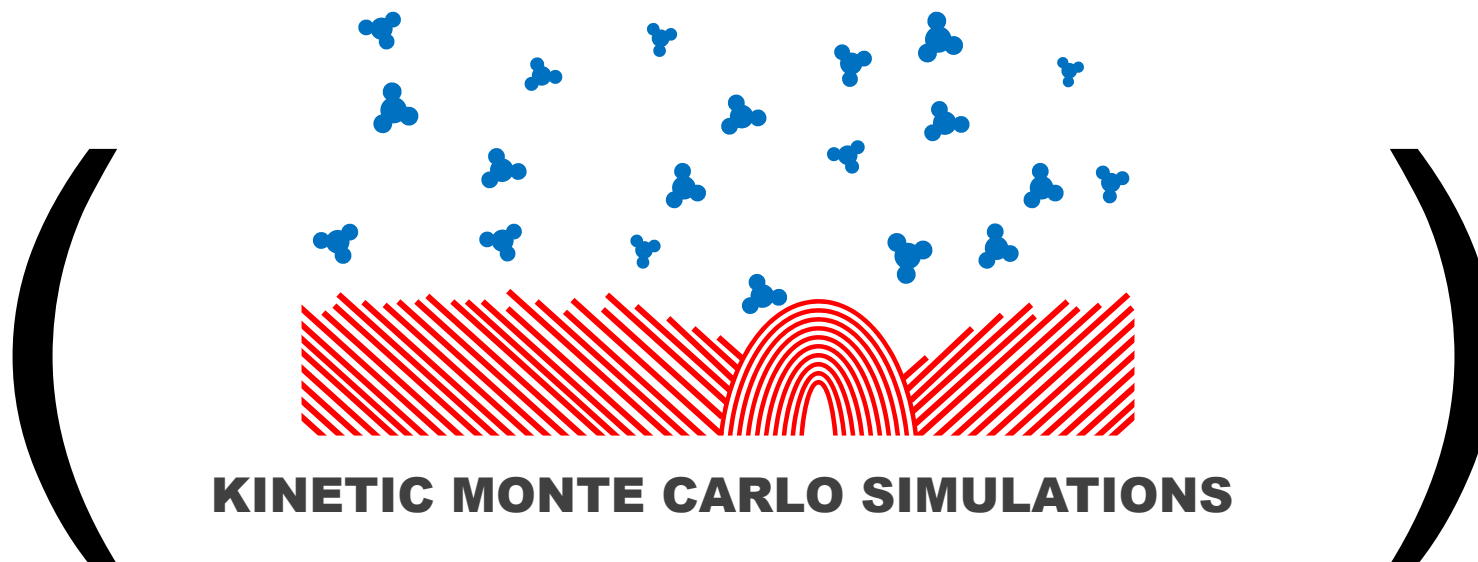
KINETIC MONTE CARLO SIMULATIONS

https://www.youtube.com/watch?v=tR1AQicsLRY

S. D. Elliott, *Semicond. Sci. Technol.* **27**, 074008 (2012);
S. D. Elliott *et al.*, *Adv. Mater.* **28**, 5367 (2016).

electrons

nuclei

Nuclei & electrons in external field

System is stationary in time

or

System undergoing transition, *e.g.* due to light

Solve the time-independent non-relativistic Schrödinger equation $\mathcal{H}\Psi = \mathcal{E}\Psi$

Atomic-scale simulations

electrons

nuclei

Nuclei & electrons in external field

| System is stationary in time | or | System undergoing transition, *e.g.* due to light |

Solve the time-independent non-relativistic Schrödinger equation $\mathcal{H}\Psi=\mathcal{E}\Psi$

| Coupled electron-nuclear dynamics | or | Quantum mechanics for electrons | **+** | Quantum or classical mechanics for nuclei |

Solve the many-electron Schrödinger equation $H\psi=E\psi$

Solve motion of nuclei on potential energy (PE) hypersurface, E

electrons

nuclei

Quantum mechanics for electrons **+** Quantum or classical mechanics for nuclei

Solve the many-electron Schrödinger equation $H\psi=E\psi$ → Solve motion of nuclei on potential energy (PE) hypersurface, E

Atomic-scale simulations

electrons

nuclei

| Quantum mechanics for electrons | **+** | Quantum or classical mechanics for nuclei |

Solve the many-electron Schrödinger equation $H\psi = E\psi$ → Solve motion of nuclei on potential energy (PE) hypersurface, E

| analytical potential E fitted to expt/theory | semi-empirical methods (*e.g.* Hückel, TB) | single determinant; $h\varphi = \varepsilon\varphi$ (HF or DFT) | post-HF methods (*e.g.* CAS, CCSD) |

$<10^6$ atoms $<10^5$ atoms $<10^3$ atoms $<10^2$ atoms

approximate   as exact as needed

| analytical potential E fitted to expt/theory | semi-empirical methods (*e.g.* Hückel, TB) | single determinant; $h\varphi=\varepsilon\varphi$ (HF or DFT) | post-HF methods (*e.g.* CAS, CCSD) |

Fixed potential energy function, varying only with interatomic geometry.

Analogy: always bring an umbrella, just in case it will rain.

Atomic-scale simulations

analytical potential E fitted to expt/theory	semi-empirical methods (*e.g.* Hückel, TB)	single determinant; $h\varphi=\varepsilon\varphi$ (HF or DFT)	post-HF methods (*e.g.* CAS, CCSD)

Wavefunction-based description of electrons, but solutions fitted to known data.

Analogy: bring umbrella if weather statistics for this day averaged over many years indicate high likelihood of rain.

Weather statistics for **Linköping**, Östergötland (Sweden)

⭐ Add to My places
Forecast as PDF

≣ Overview
🕐 Hour by hour
📅 Long term
📈 Statistics
📍 Maps

Malmslätt weather station: 93 m.a.s.l., 5.0 km away from Linköping
Jönköping: 111.0 km fra Linköping
Jönköping flygplats: 115.0 km fra Linköping

RELEVANT PLACES

Linköping
Tórshavn

To the main menu at the page bottom

Average temperature per month
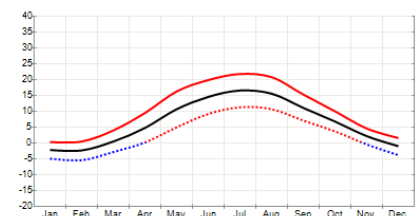
Average days with precipitation per month
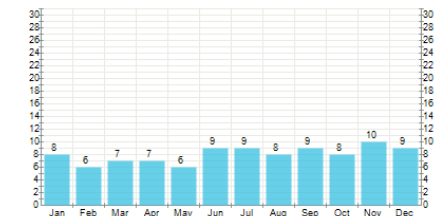
yr.no

www.tyndall.ie

Atomic-scale simulations

analytical potential E fitted to expt/theory	semi-empirical methods (*e.g.* Hückel, TB)	single determinant; $h\varphi=\varepsilon\varphi$ (HF or DFT)	post-HF methods (*e.g.* CAS, CCSD)

Many-electron wavefunction is anti-symmetric product of many one-electron wavefunctions ("orbitals").

HARTREE-FOCK THEORY:

Solve one-electron problem in mean field due to other electrons

→ Missing dynamical correlation

Insist that each orbital is empty or doubly-occupied

→ Missing static correlation (e.g. when HOMO=LUMO)

Analogy: bring umbrella if rain is forecast for today.

Long term forecast for
Linköping, Östergötland (Sweden)

☰ Overview

Long term forecast

🕐 Hour by hour

📅 Long term

📈 Statistics

Ⅲ Maps

RELEVANT PLACES

	Monday 5 June 12–18	Tuesday 6 June 12–18	Wednesday 7 June 12–18	Thursday 8 June 14–20	Friday 9 June 14–20
	15°	21°	13°	14°	14°
	0 mm	0 mm	0 mm	4.7 mm	5.2 mm

yr.no

Atomic-scale simulations

analytical potential E fitted to expt/theory	semi-empirical methods (*e.g.* Hückel, TB)	single determinant; $h\varphi=\varepsilon\varphi$ (HF or DFT)	post-HF methods (*e.g.* CAS, CCSD)

Many-electron wavefunction is anti-symmetric product of many one-electron wavefunctions ("orbitals").

DENSITY FUNCTIONAL THEORY:

Solve one-particle problem in mean field that mimics electron correlation
→ Some dynamical correlation included

Insist that each orbital is empty or doubly-occupied

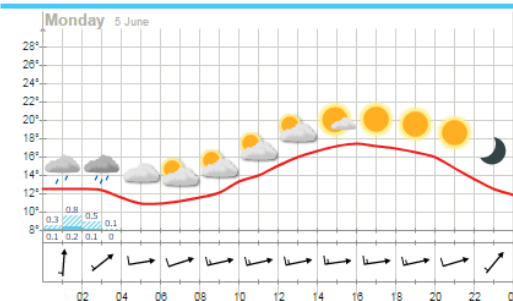   → Missing static correlation (e.g. when HOMO=LUMO)

Analogy: bring umbrella if hour-by-hour weather forecast indicates high likelihood of rain now.

Hourly forecast for
Linköping, Östergötland (Sweden)

- Overview
- Hour by hour
  - Detailed
- Long term
- Statistics
- Maps

Meteogram, next 48 hours

Monday 5 June

RELEVANT PLACES

Linköping
Copenhagen

yr.no

analytical potential E fitted to expt/theory	semi-empirical methods (*e.g.* Hückel, TB)	single determinant; $h\varphi = \varepsilon\varphi$ (HF or DFT)	post-HF methods (*e.g.* CAS, CCSD)

Many-electron wavefunction by mixing configurations and/or reference states from single-electron solutions.

Analogy: bring umbrella if radar shows that rain is approaching.

yr.no
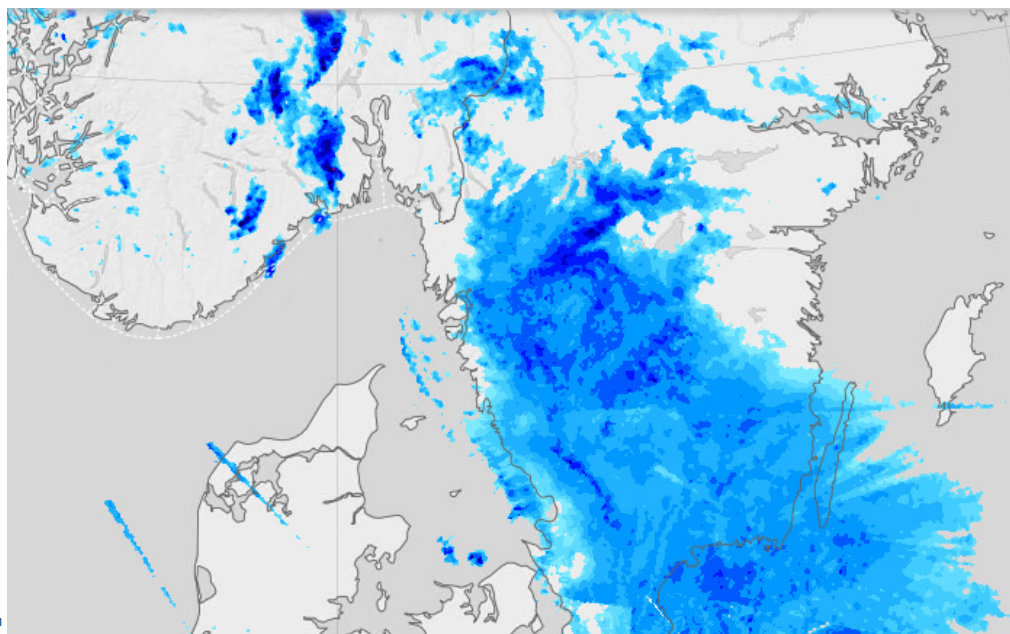
SHARE   RESEARCH ARTICLE

Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere[1,*], Gustav Bihlmayer[2], Torbjörn Björkman[3,4], Peter Blaha[5], Stefan Blügel[2], Volker Blum[6], Damien Calis...

+ See all authors and affiliations

PRE   Peer Reviewed
← see details

Lejaeghere *et al.* compared the calculated values for the equation of states for 71 elemental crystals from 15 different widely used DFT codes employing 40 different potentials. Although there were variations in the calculated values, most recent codes and methods converged toward a single value, with errors comparable to those of experiment.
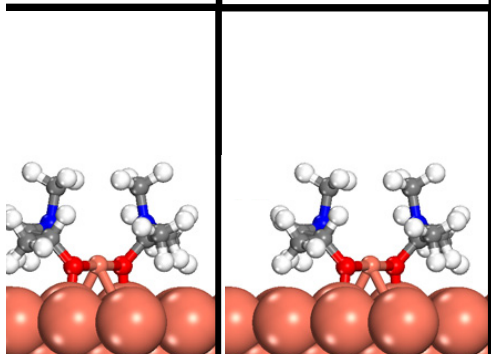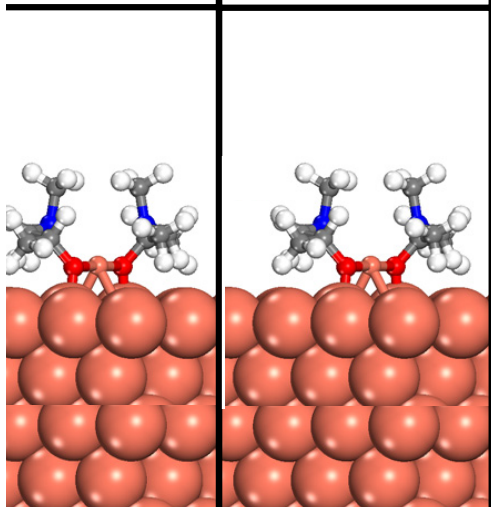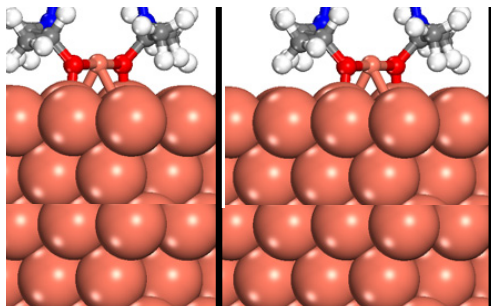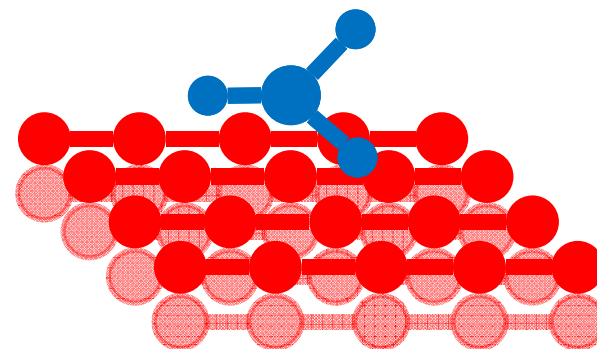
Density functional theory for slabs

10^3 atoms per cell

Length scale 10^{-9} m

Time scale 10^{-12} s

Surface represented by infinitely-repeating 4 layer slab of (111)-oriented fcc-Cu separated by vacuum;

- VASP program;
- Functional due to Perdew, Burke & Ernzerhof with vdW-optB88 correction;
- Plane waves to 450 eV cutoff;
- PAW treatment of cores;
- k-point at Γ is adequate for large p(6×6) cell with 18 Å vacuum;
- Self consistent steps to 10^{-4} eV;
- Geometry optimised by conjugate-gradient;
- Activation energies E_a by nudged elastic band.

VASP: Kresse, G.; Hafner, J. *J. Phys.: Condens. Matter* 1994, 6, 8245.
PBE: Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* 1996, 77, 3865–3868.
Slab: Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* 1992, 64, 1045–1097.
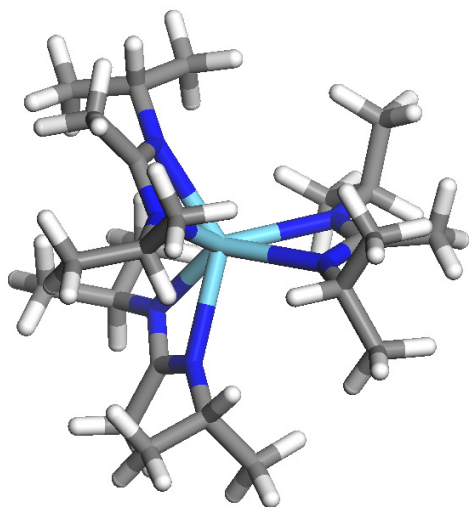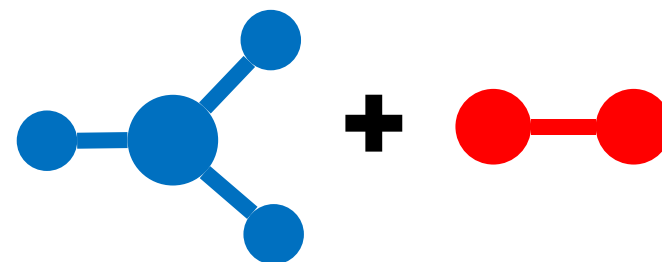
10^3 atoms in vacuum

Length scale 10^{-9} m

Time scale 10^{-12} s

- Isolated cluster of atoms in gas phase;
- TURBOMOLE program;
- Functional due to Becke & Perdew (1986) or Perdew, Burke & Ernzerhof (1996);
- Basis set of localised atomic orbitals: def2-TZVPP;
- Effective core potentials on heavy atoms;

TURBOMOLE: Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* 1989, 162, 165.
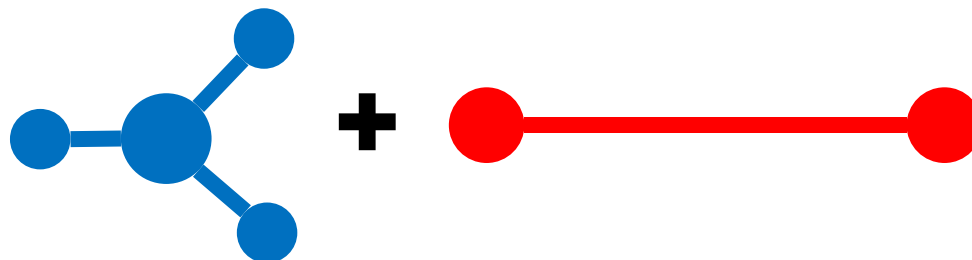Becke, A. D. *Phys. Rev. A* 1988, 38, 3098; Perdew, J. P. *Phys. Rev. B* 1986, 33, 8822.
Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* 1996, 77, 3865–3868.
Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* 1997, 97, 119.
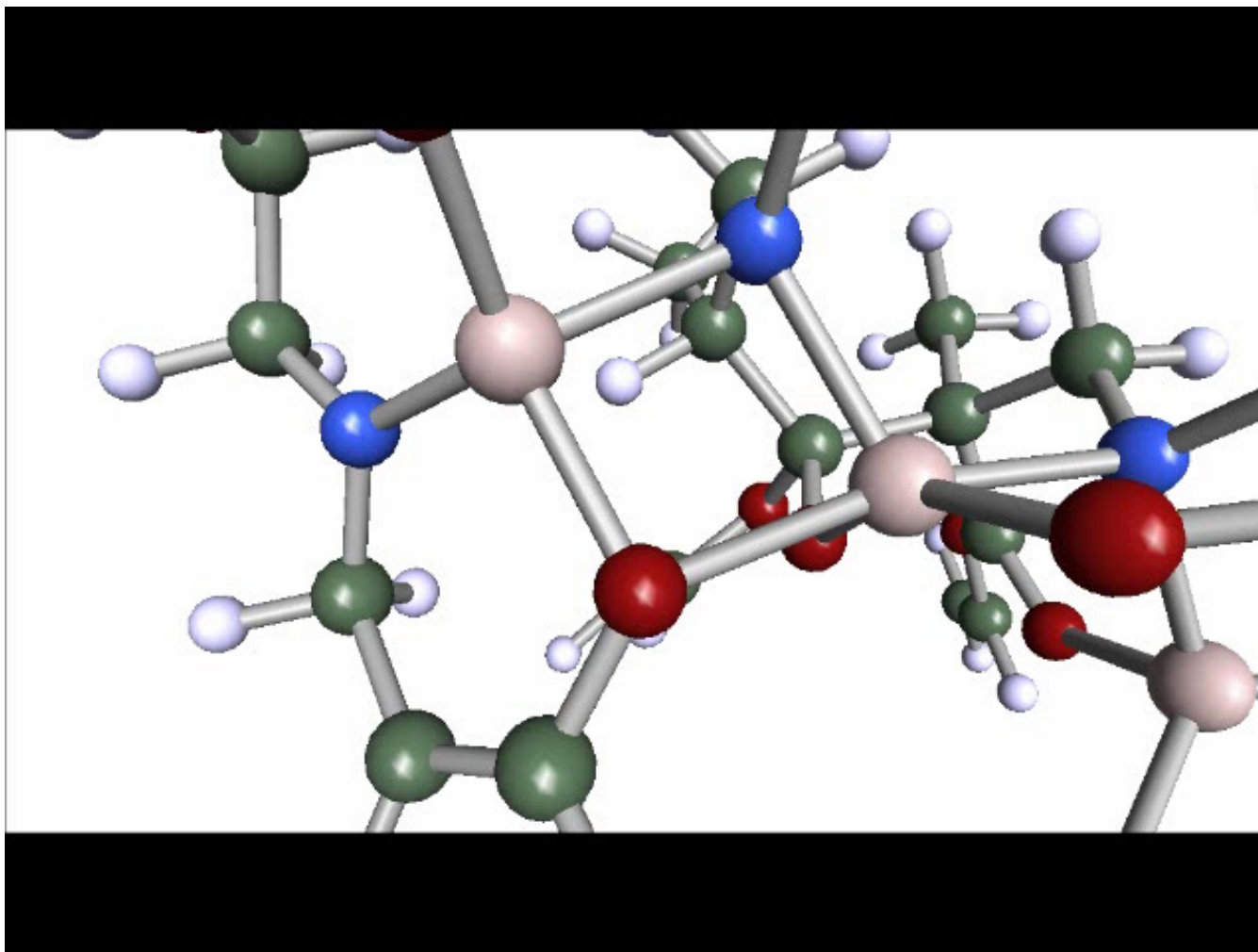
H. Ablat

Hybrid ALD - MLD

TMA + acrylate + ethanolamine

O-Al-N stretch computed at 511 cm^{-1}

...measured with FTIR at 514 cm^{-1}
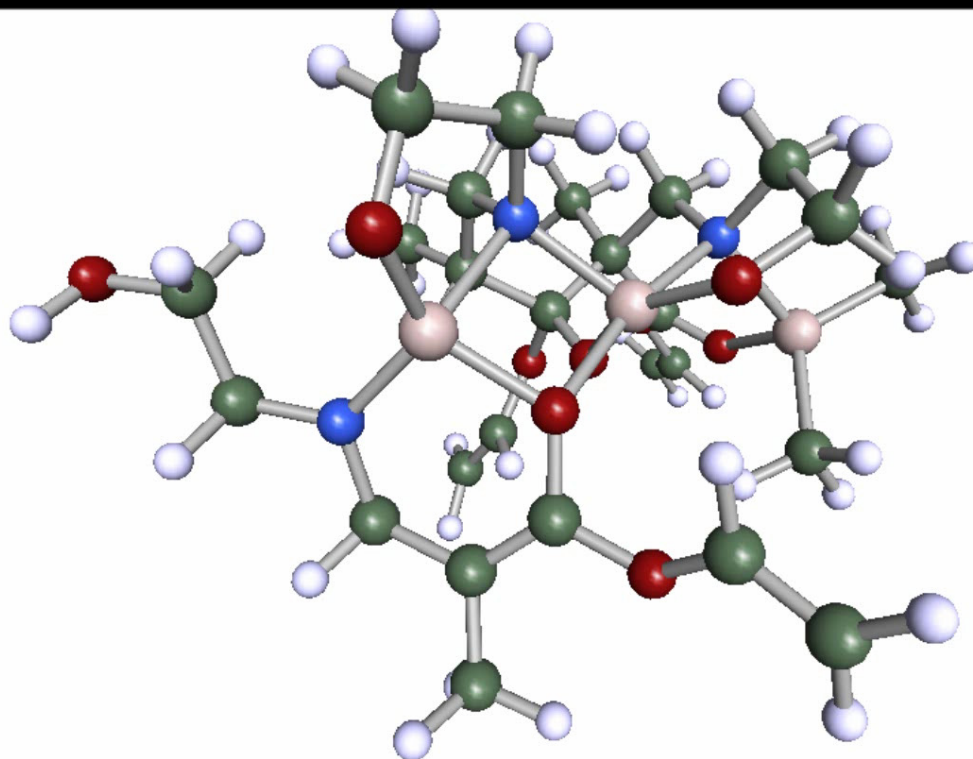
| H | C | O | N | Al |

O-Al-N stretch computed at 610 cm^{-1}

… measured at 610 cm^{-1} with FTIR

H	C	O	N	Al

O-Al-N stretch computed at 610 cm^{-1}

… measured at 610 cm^{-1} with FTIR

H	C	O	N	Al
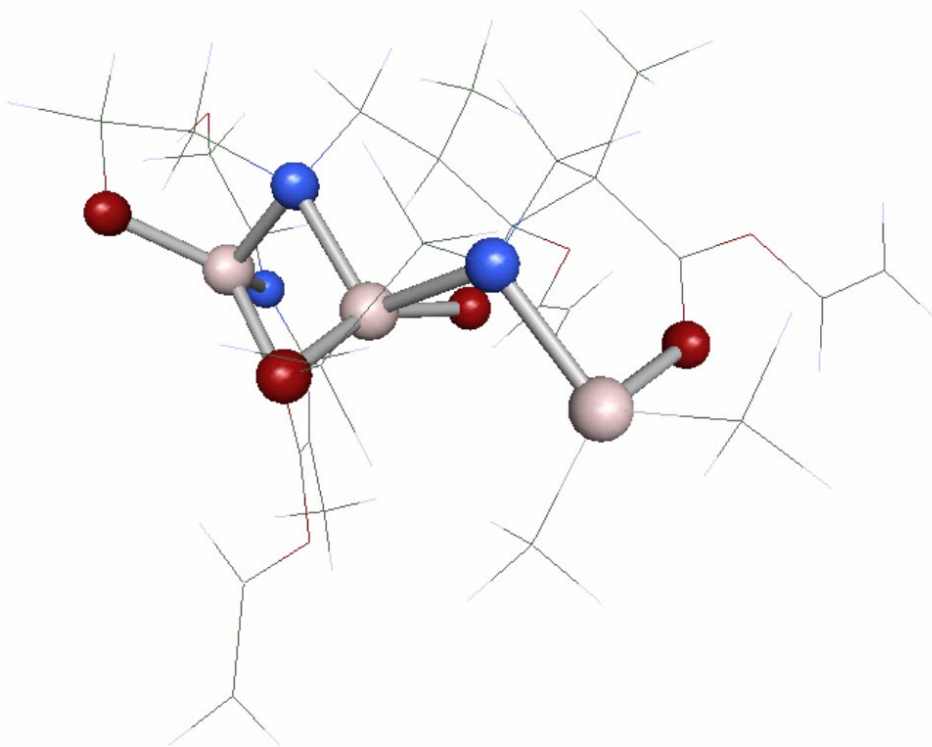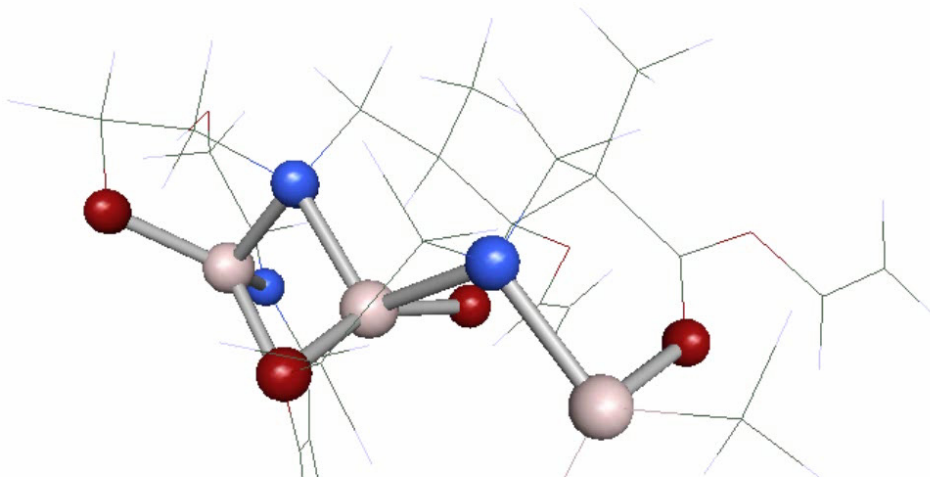
O-Al-N stretch computed at 610 cm^{-1}

... measured at 610 cm^{-1} with FTIR

Little known about structure of exposed 'surface' during polymer MLD.

DFT can reveal how oligomers form.

H	C	O	N	Al
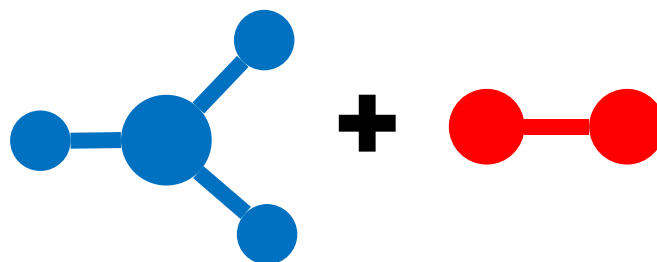
Combinatorial approach to precursor design

ALD of Si_3N_4

Quantum Mechanical Simulation for the Analysis, Optimization and Accelerated Development of Precursors and Processes for Atomic Layer Deposition (ALD)

Thomas Jeffrey Lomax Mustard, Hyunwook Shaun Kwak[*], Alexander Goldberg, Jacob Gavartin[**], Tsuguo Morisato[***], Daisuke Yoshidome[***], Mathew David Halls[†]

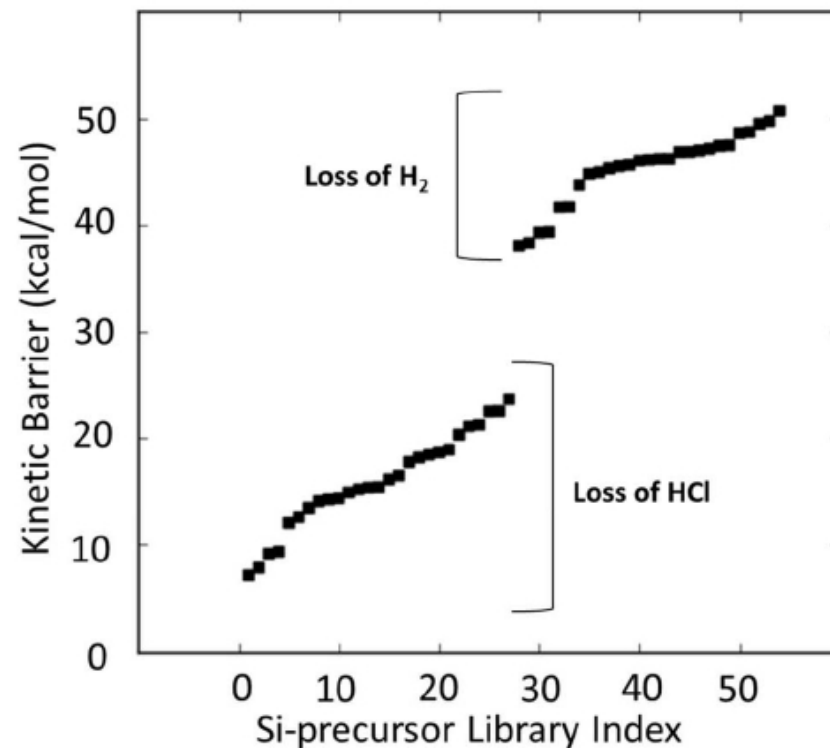Schrödinger Inc., San Diego, California 92121, United States

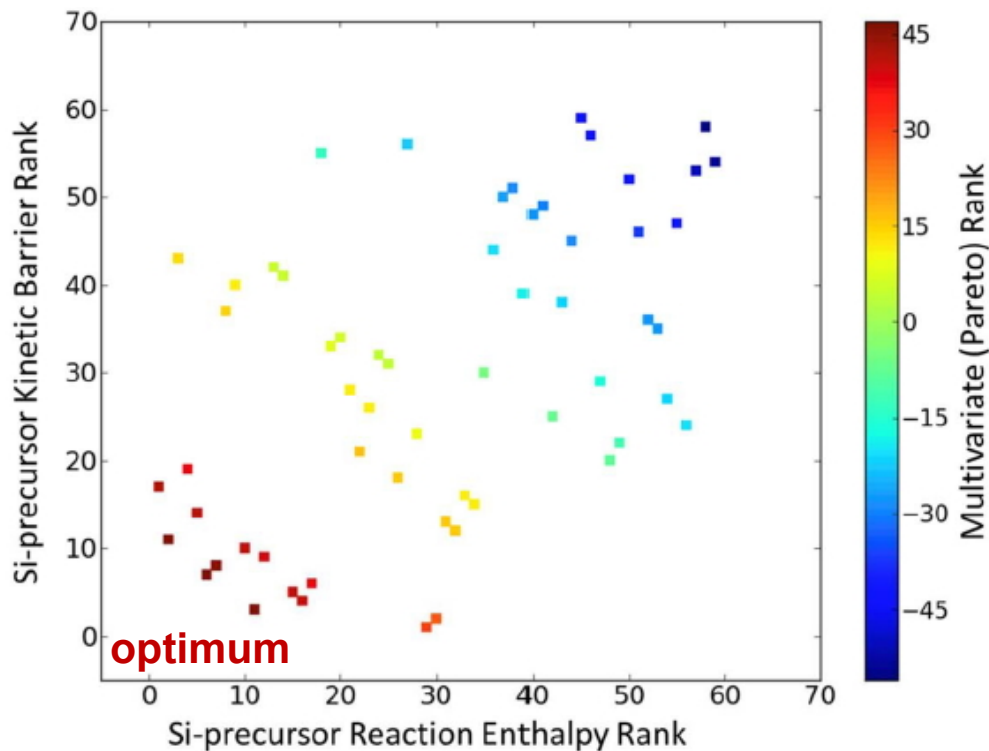[*]Schrödinger Inc., Cambridge, Massachusetts 02142, United States

[**]Schrödinger Inc., Cambridge, Cambridgeshire CB1 2JD, United Kingdom

[***]Schrödinger K.K., Chiyoda-ku, Tokyo 100-0005, Japan

[†]Corresponding author :Mathew David Halls, E-mail : mat.halls@schrodin
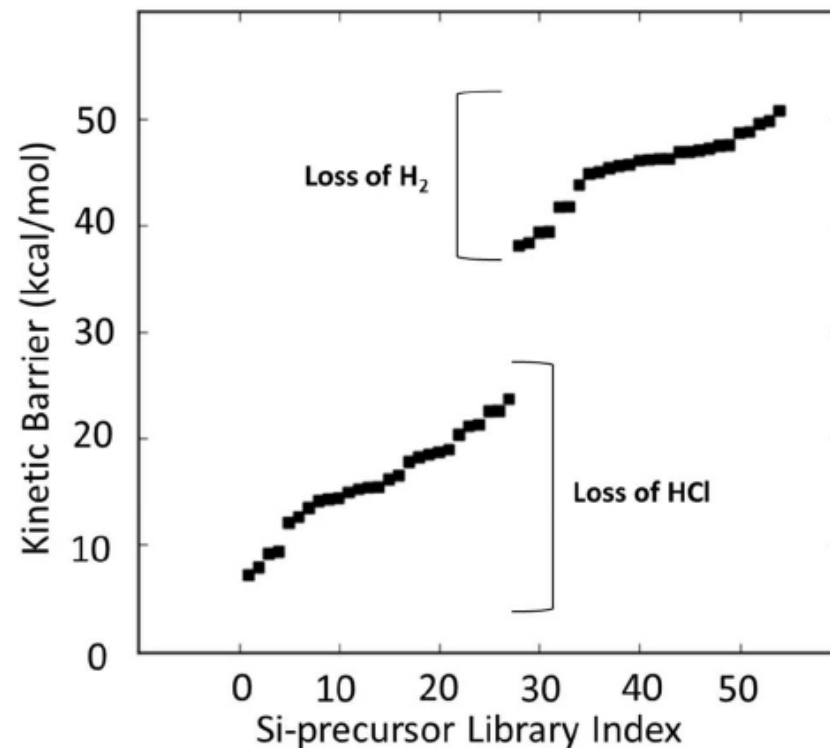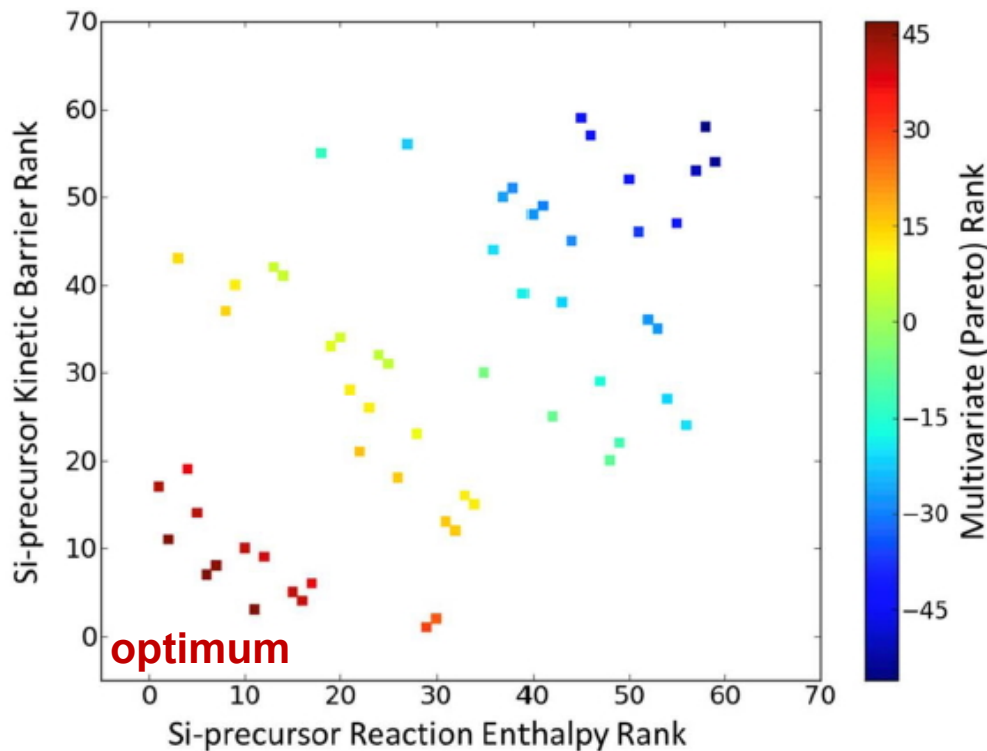299-4532

SCHRÖDINGER.

Precursors screened:

$Si(Cl)R_2$ with R=H, Cl or CH_3

$Si_2(Cl)R_5$ with R=H or Cl

Enthalpy and kinetic barrier evaluated for model reactions:

$NH_{3\,(g)} + Si(Cl)(H)R_{2\,(g)} \rightarrow H_2N\text{-}Si(H)R_{2\,(g)} + HCl_{(g)}$

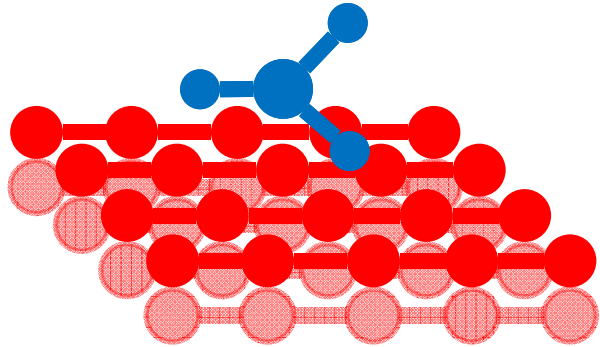$NH_{3\,(g)} + Si(Cl)(H)R_{2\,(g)} \rightarrow H_2N\text{-}Si(Cl)R_{2\,(g)} + H_{2\,(g)}$

SCHRÖDINGER®

Knowledge about ALD mechanism allows metrics for precursor design to be defined.

Large numbers of precursors can be automatically generated and screened.

SCHRÖDINGER.

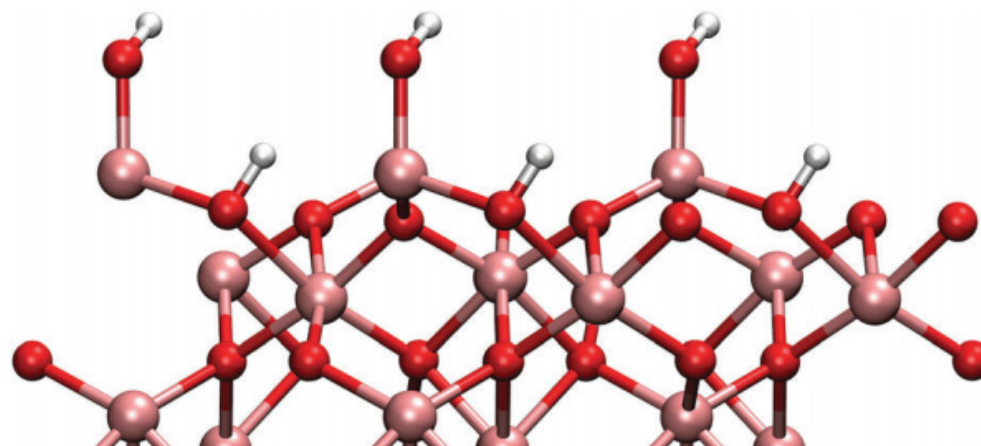**Improved models of substrates and growing surfaces**

ALD of Al_2O_3

Aalto University

PCCP

CrossMark
← click for updates

First principles study of the atomic layer deposition of alumina by TMA–H_2O-process

Timo Weckman* and Kari Laasonen

pink = Al, red = O, white = H

Fig. 1 Side-view of the hydroxylated surfaces formed from dissociatively adsorbed water. Two kinds of hydroxyl groups are present, the higher group formed from the water molecule and the lower one formed with the dissociated hydrogen and surface oxygen. A monolayer coverage is achieved when four water molecules adsorb onto a 2 × 2 cell which

ROYAL SOCIETY OF CHEMISTRY
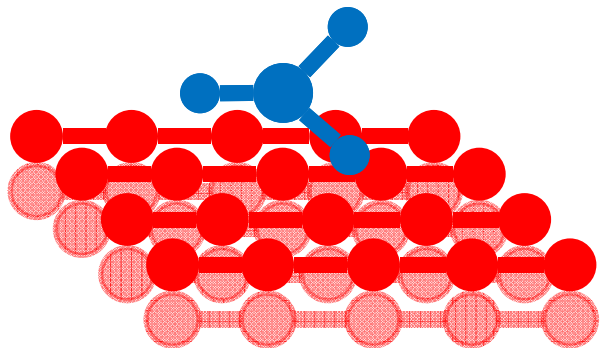
A!
Aalto University

How adsorption energy affects exposure required for saturation

ALD of Si_3N_4

C. Murray

Individual reaction steps

→ activation energies

→ kinetics of individual steps

→ kinetics of overall growth process.
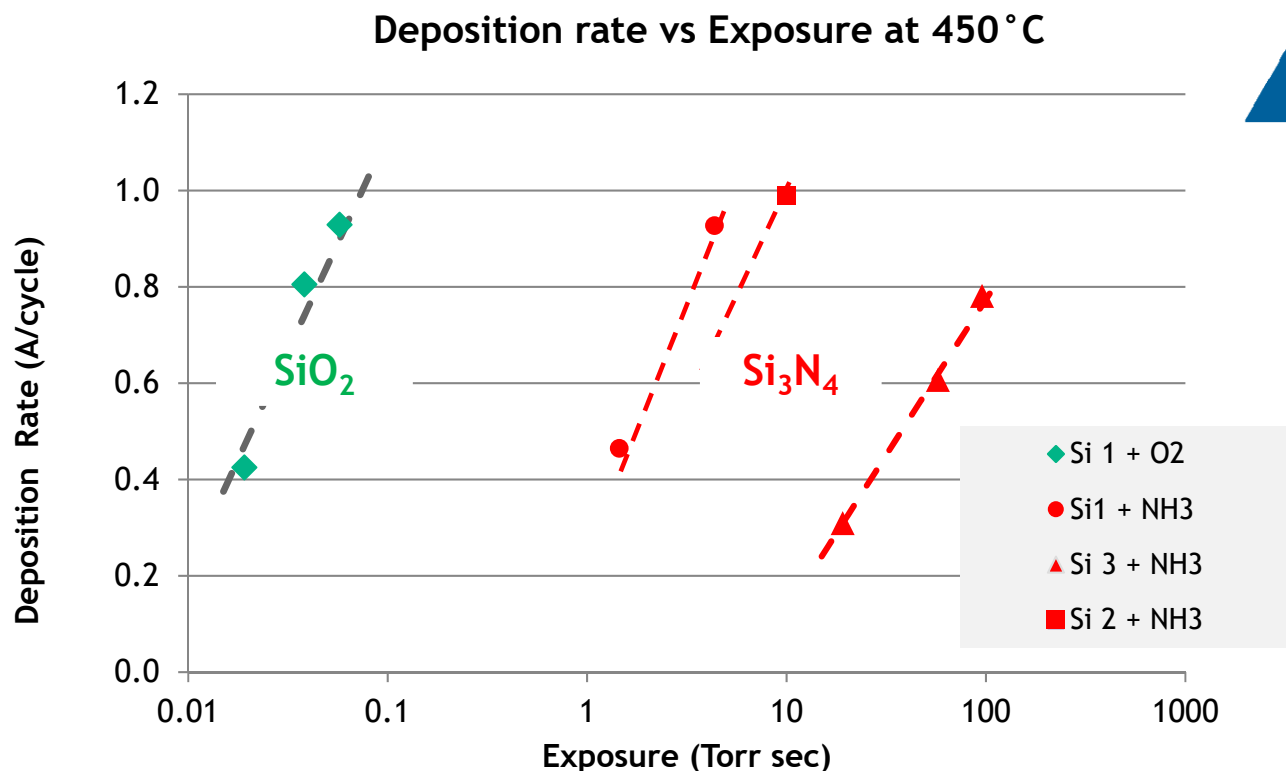
Rate at which growth process takes place

→ exposure needed

→ dependence of growth on process time

→ throughput.

Self-limiting surface chemistry

→ saturation

→ maximum thickness increment per cycle (GPC).
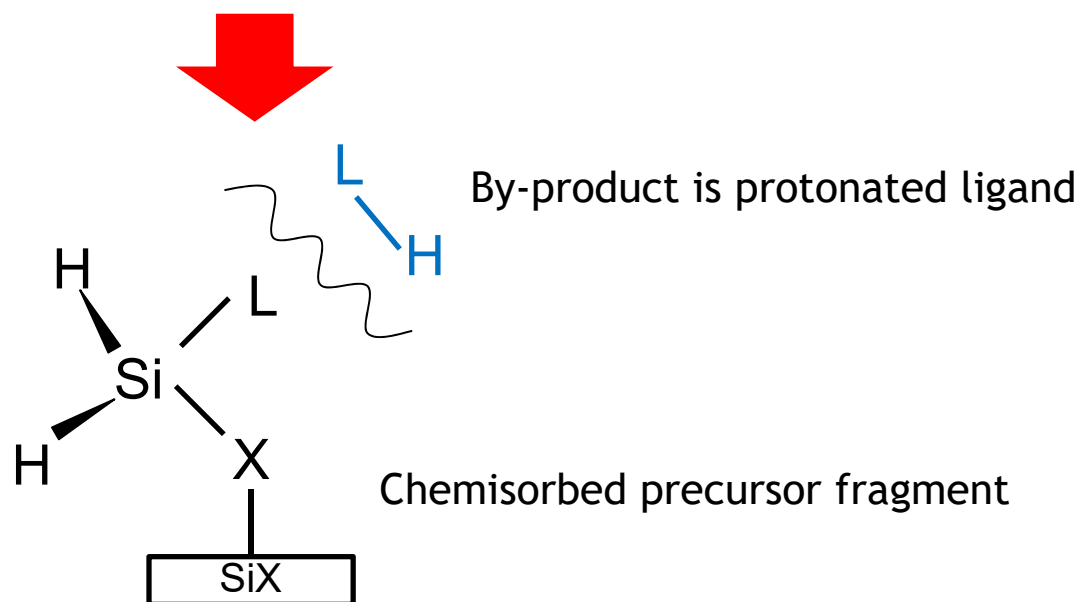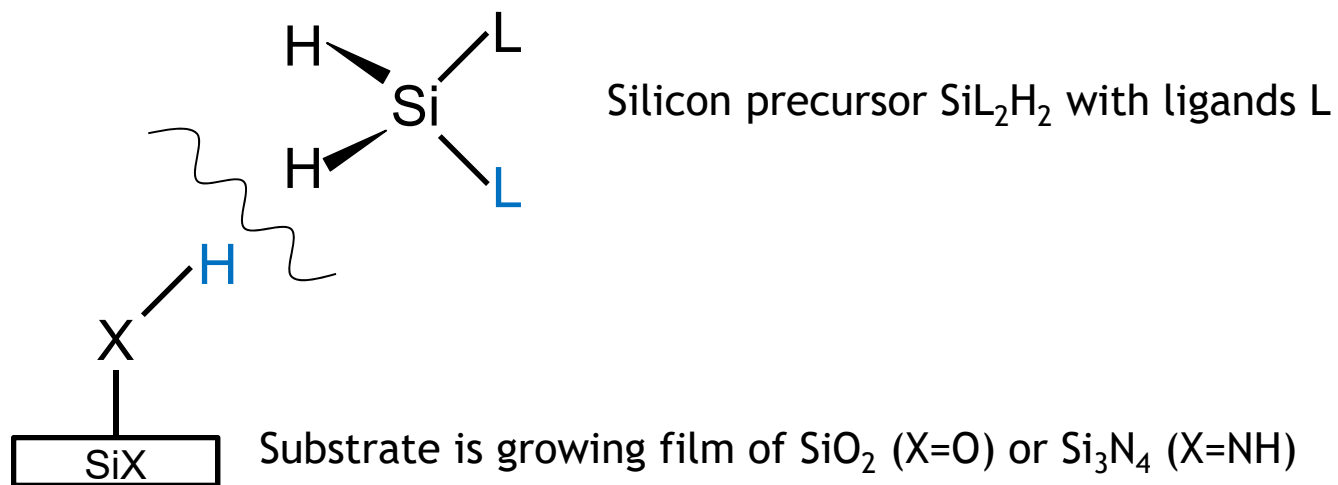
Reactivity of ALD SiO$_2$ versus Si$_3$N$_4$

Deposition rate vs Exposure at 450°C

SiO$_2$

Si$_3$N$_4$

Legend:
- Si 1 + O2
- Si1 + NH3
- Si 3 + NH3
- Si 2 + NH3

Y-axis: Deposition Rate (A/cycle), values 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2

X-axis: Exposure (Torr sec), values 0.01, 0.1, 1, 10, 100, 1000

Require 100x greater exposure of Si precursor to achieve saturation for Si$_3$N$_4$ relative to SiO$_2$
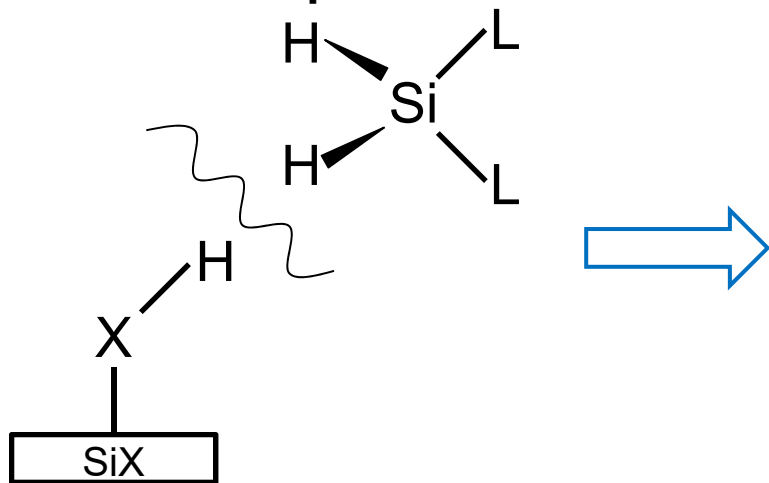
What Si precursor can solve this problem?

Silicon precursor SiL_2H_2 with ligands L

Substrate is growing film of SiO_2 (X=O) or Si_3N_4 (X=NH)

By-product is protonated ligand

Chemisorbed precursor fragment

Reactivity of ALD SiO₂ versus Si₃N₄

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SiH$_2$(NMe$_2$)$_2$ precursor

NH$_2$ surface model for Si$_3$N$_4$

OH surface model for SiO$_2$

BP86/SV(P) at T = 0 K

NH$_2$ Surface

OH Surface

transition state

bound by-product

desorption of by-product

E_a = 80.0 kJ/mol

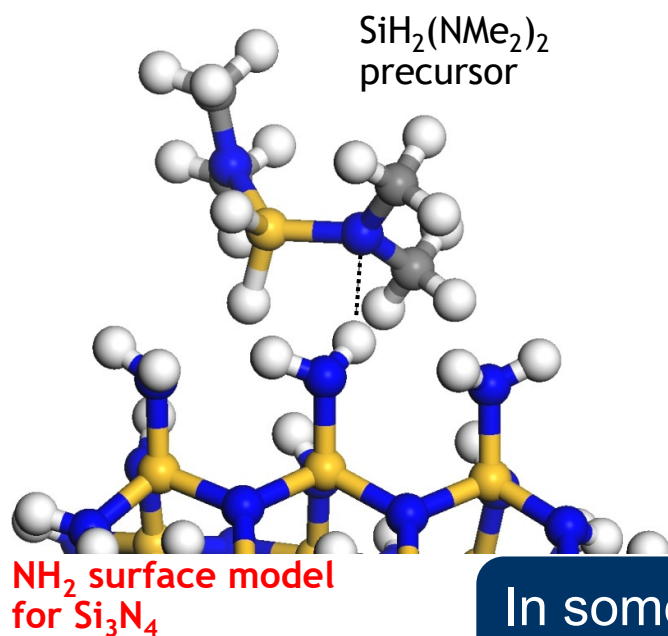unbound precursor

bound precursor

E_a = 51.7 kJ/mol
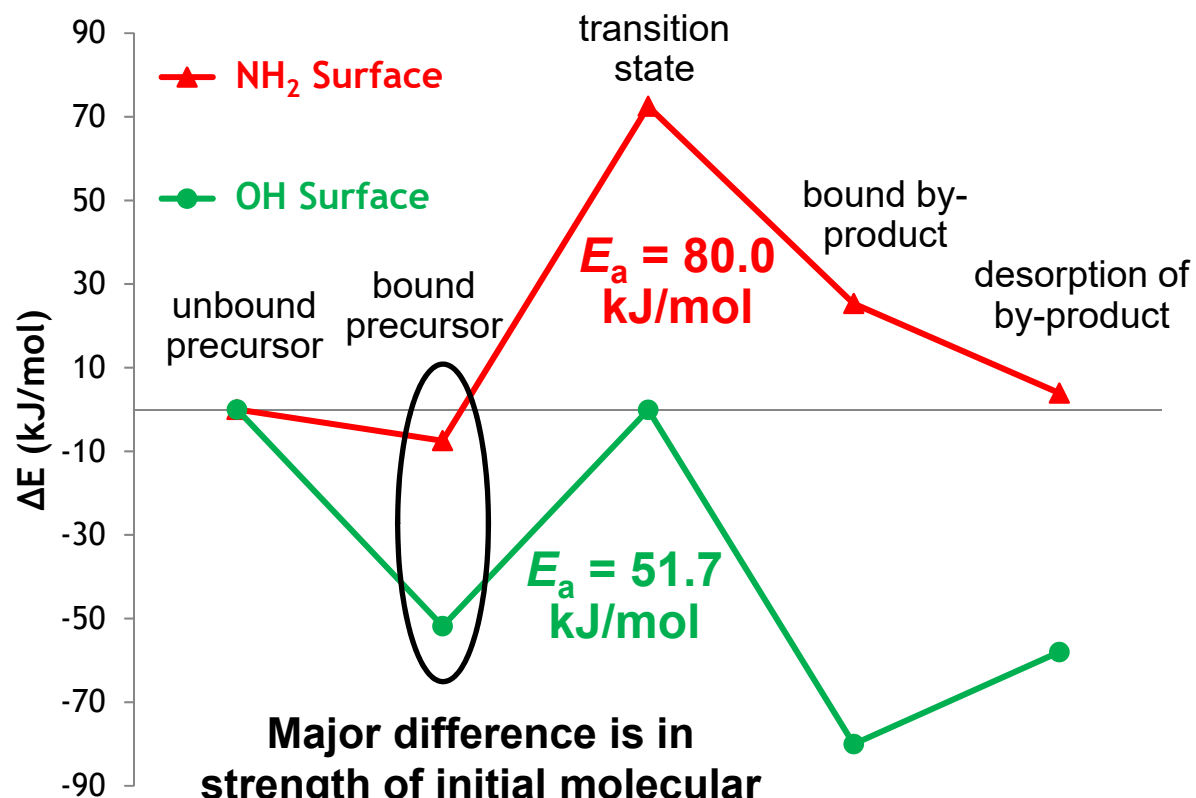
Major difference is in strength of initial molecular adsorption, not in choice of precursor

C. M. Murray *et al.*, ACS *Appl. Mater. Interf.* **6**, 10534 (2014).

$SiH_2(NMe_2)_2$ precursor

NH_2 surface model for Si_3N_4

In some cases, simple model of isolated adsorbate on surface is adequate to explain growth behaviour.
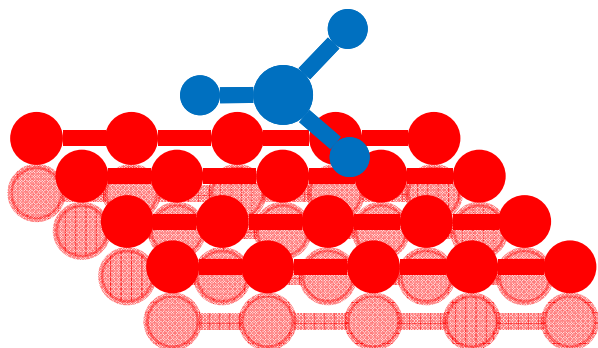
Importance of van der Waals interactions during precursor adsorption

Y. Maimaiti

ALD of Cu

How do Cu precursors adsorb onto the growing Cu surface?

Cu=pink, O=red, N=blue, C=grey, H=white
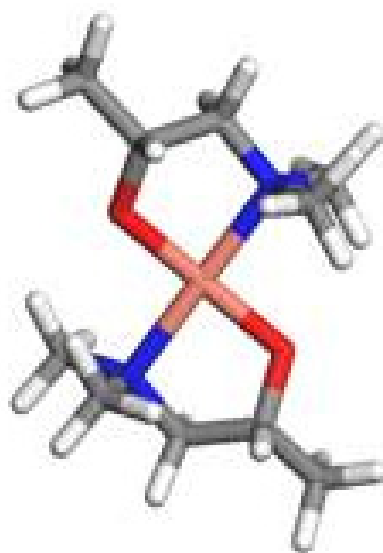
Cu-O break?
Cu-N break?

→ form **Cu-Cu**

Cu-O break?
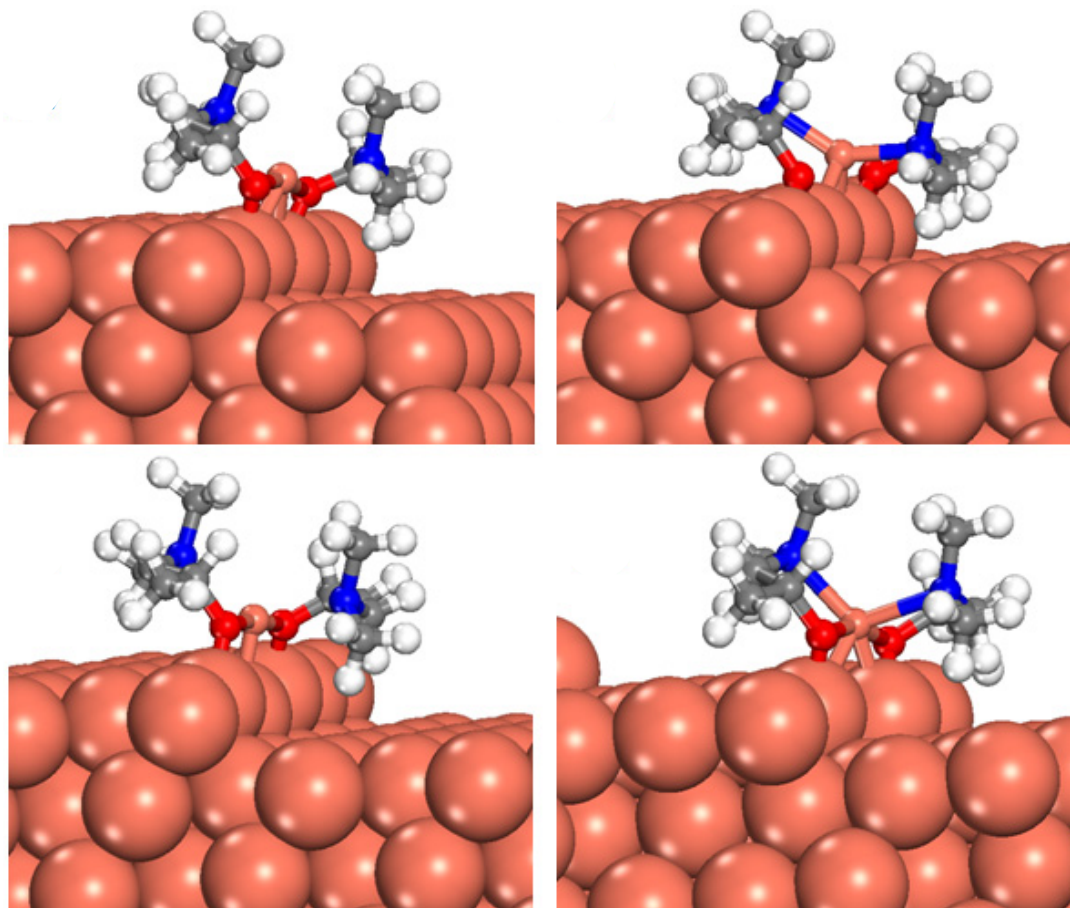**Cu-N** break?

…and **vdW interactions?**

Cu(dmap)₂
dmap=dimethyl-amino-propoxide

Chemisorption onto edge or kink for all functionals, regardless of vdW treatment:

Y. Maimaiti *et al.*, *J. Phys. Chem. C* **119**, 9375–9385 (2015).

Adsorption onto flat Cu(111) is sensitive to van der Waals forces, alignment of Cu-O and cleavage of Cu-N:

(b)
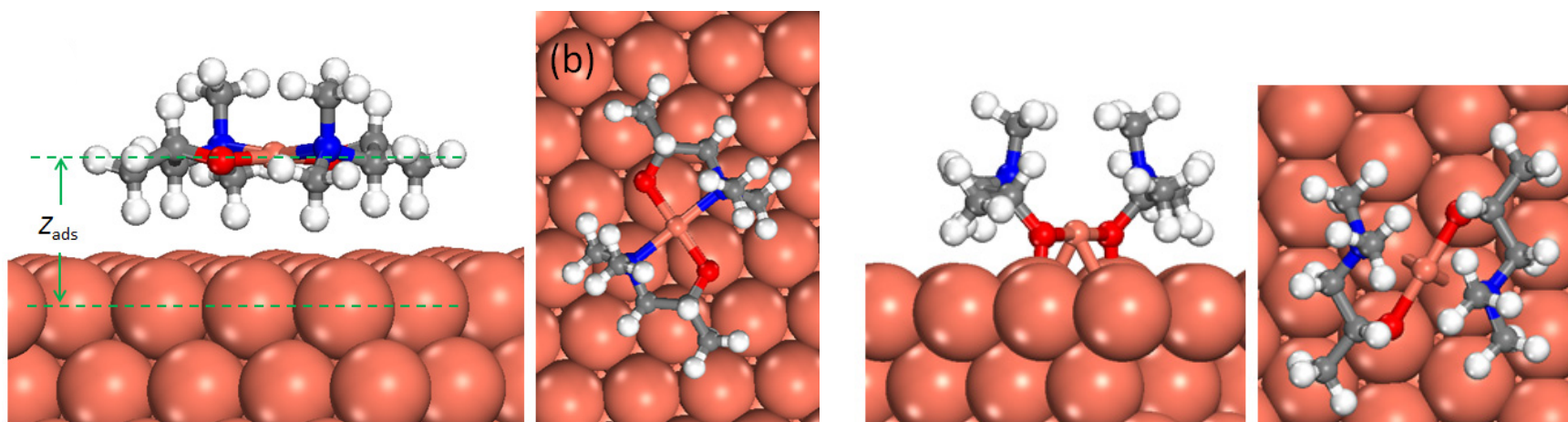
	ΔE(physisorbed)	ΔE(chemisorbed)
PBE	-0.4 eV (3 sites)	-1.5 eV (1 site)
vdW-DF2	-1.0 eV (3 sites)	-2.0 eV (1 site)
optB88-vdW	-1.6 eV (1 site)	-3.2 eV (3 sites)
PBE-D3	no sites	-3.5 eV (4 sites)

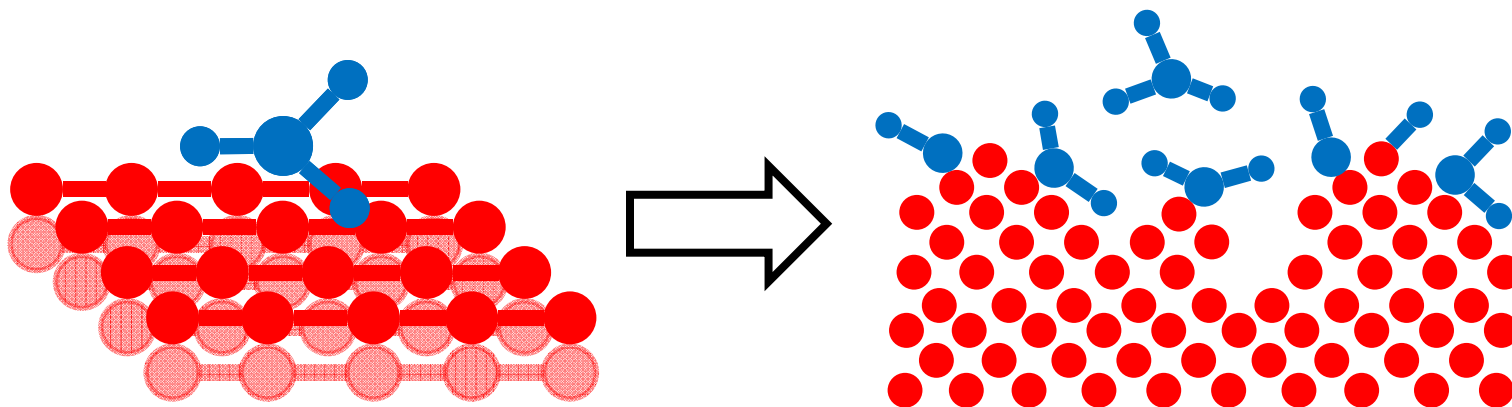Adsorption onto flat Cu(111) is sensitive to van der Waals forces, alignment of Cu-O and cleavage of Cu-N:
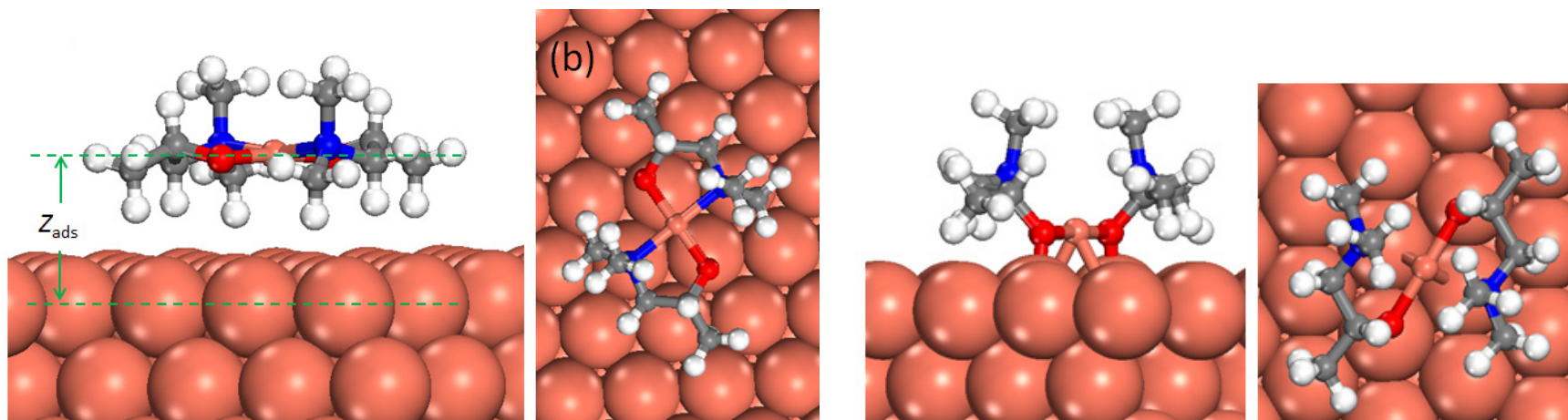
No consensus yet on how best to incorporate vdW contribution to adsorption.

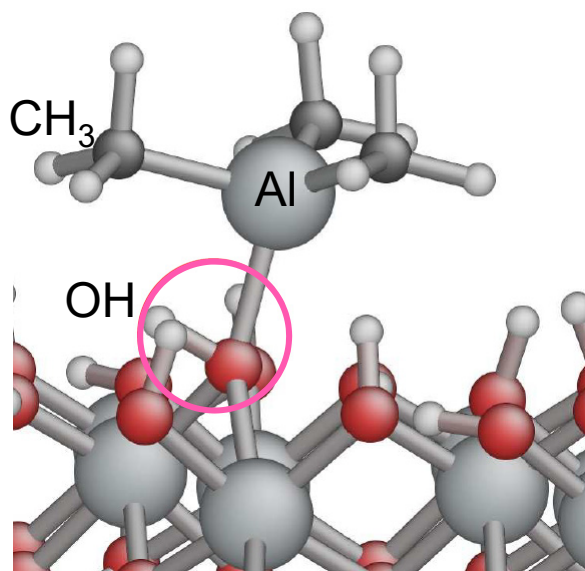**Isolated ligands can persist on surface for entire cycle**

ALD of Al_2O_3

M. Shirazi

TMA pulse: Computed activation energies for transfer of H^+ from surface-OH to adsorbate-CH_3, resulting in desorption of CH_4:
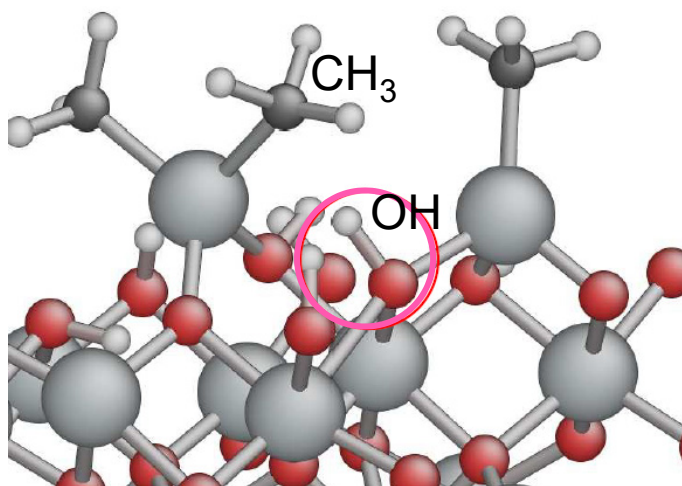

E_a=0.28 eV
from 3-coordinate OH
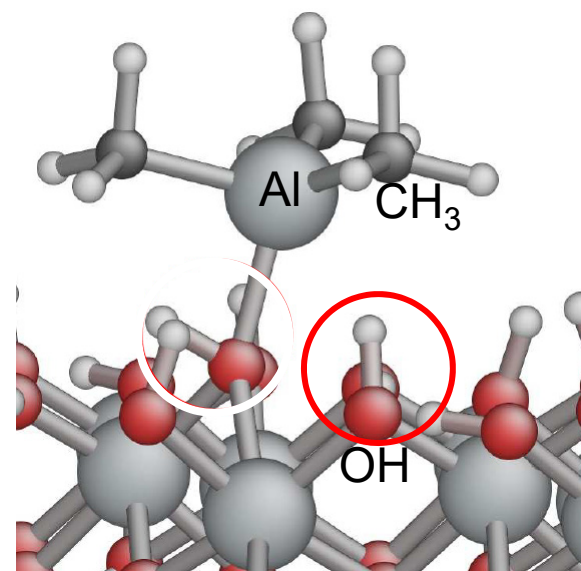
E_a=0.74 eV
from 2-coordinate OH

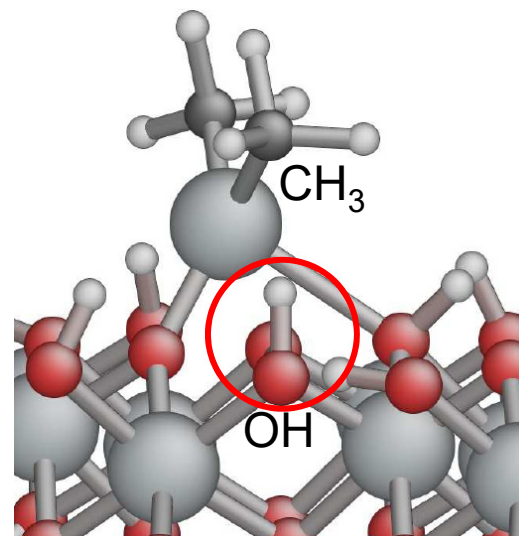**TMA pulse:** Computed activation energies for transfer of H^+ from surface-OH to adsorbate-CH_3, resulting in desorption of CH_4:

E_a=0.26 eV
from 3-coordinate OH

no reaction
from 2-coordinate OH

TMA pulse: Computed activation energies for transfer of H^+ from surface-OH to adsorbate-CH_3, resulting in desorption of CH_4:
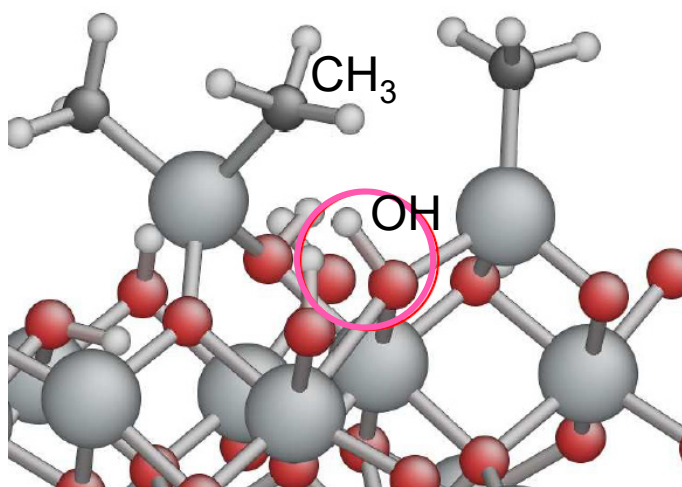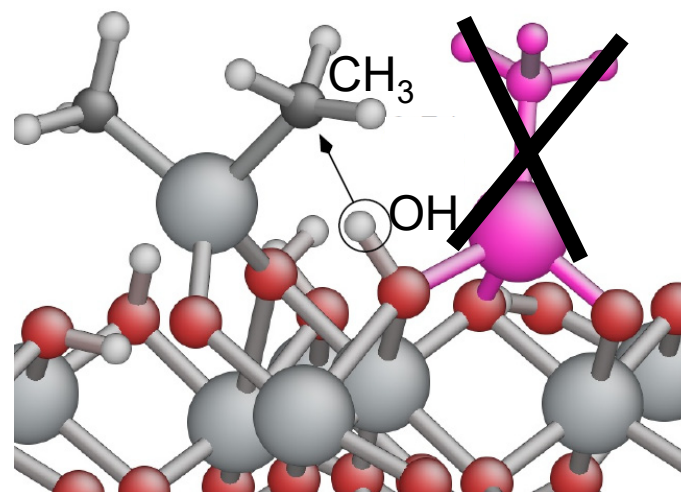

E_a=0.26 eV
from 3-coordinate OH
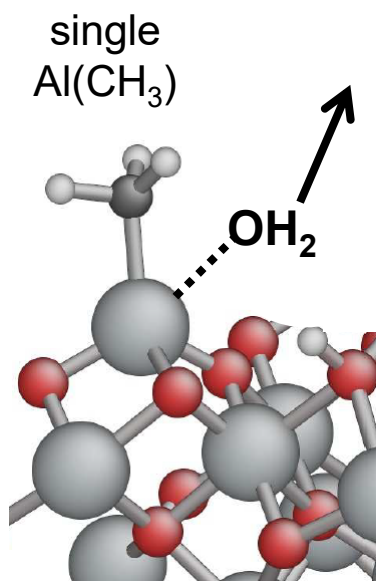
E_a=0.74 eV
from 2-coordinate OH
when neighbouring $AlCH_3$ is missing

Cooperative effect: neighbouring adsorbate increases coordination number of O and thus increases Brønsted acidity of OH.

H$_2$O pulse

single
Al(CH$_3$)

...OH$_2$

No chemisorption
of single H$_2$O
to single Al(CH$_3$)

large grey=Al, red=O, white=H, small grey=C

H$_2$O pulse

single
Al(CH$_3$)

H$_2$O

3.Al(CH$_3$)
cluster

···**OH$_2$**

Al

E_a=0.52 eV

No chemisorption
of single H$_2$O
to single Al(CH$_3$)

large grey=Al, red=O, white=H, small grey=C

H$_2$O pulse

single Al(CH$_3$)

OH$_2$

No chemisorption
of single H$_2$O
to single Al(CH$_3$)

H$_2$O

3.Al(CH$_3$) cluster

Al

E_a=0.52 eV

2H$_2$O

E_a=0

large grey=Al, red=O, white=H, small grey=C

2H$_2$O

3.Al(CH$_3$) cluster

E_a=0
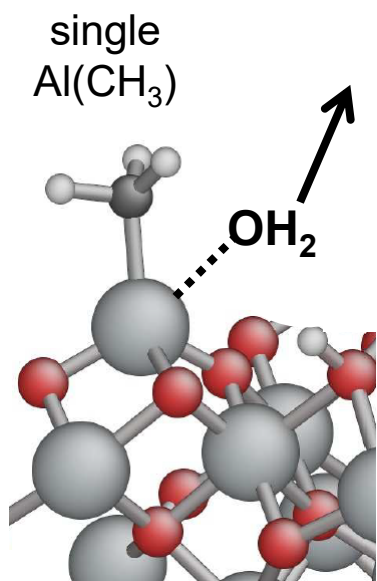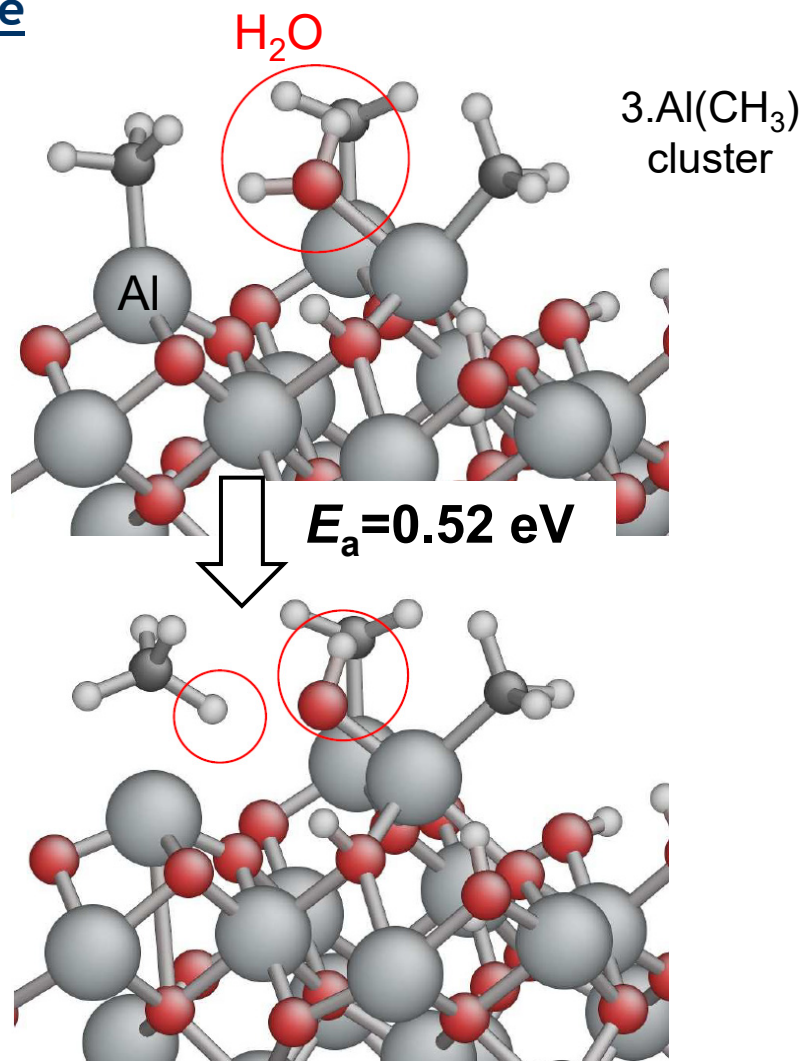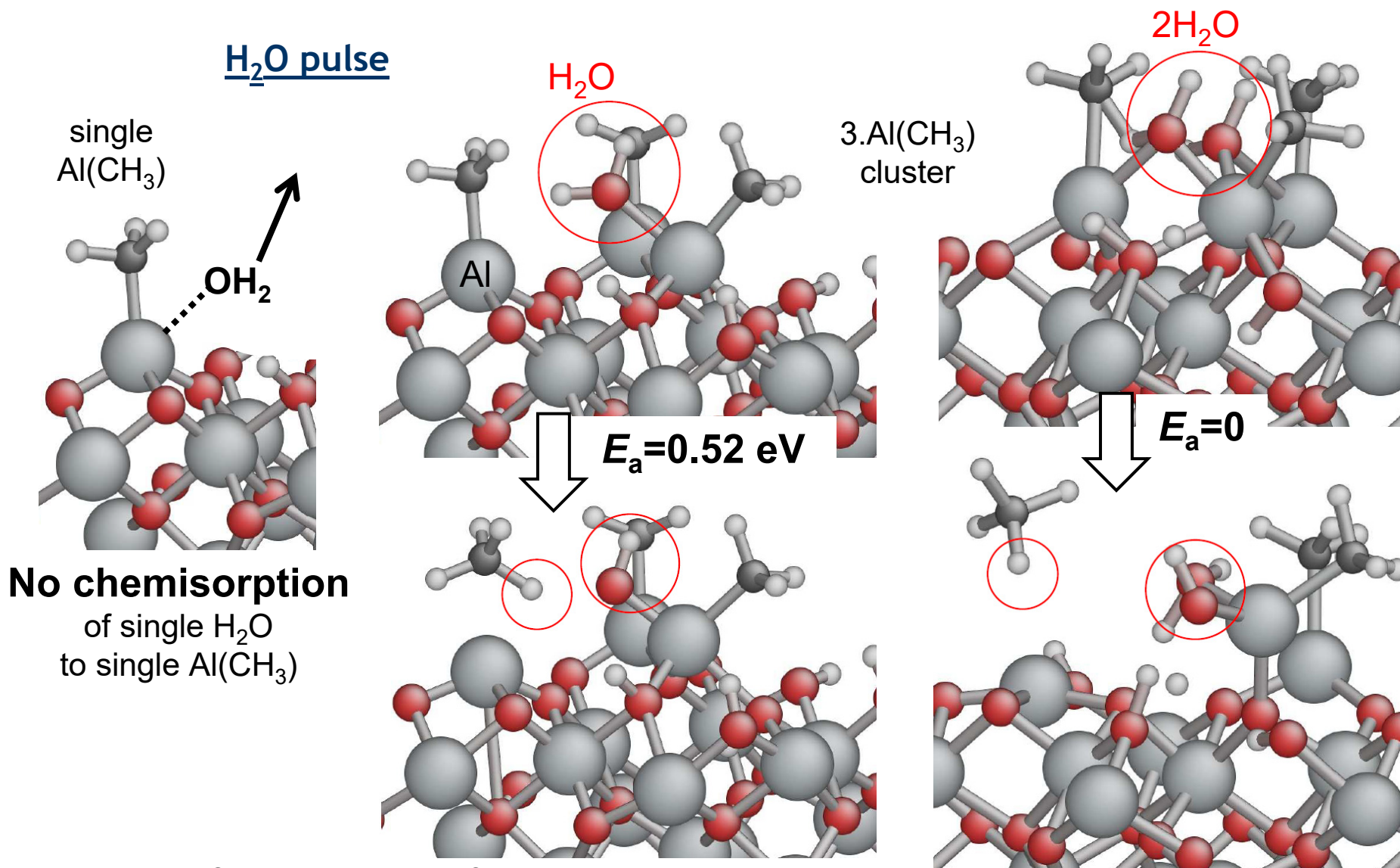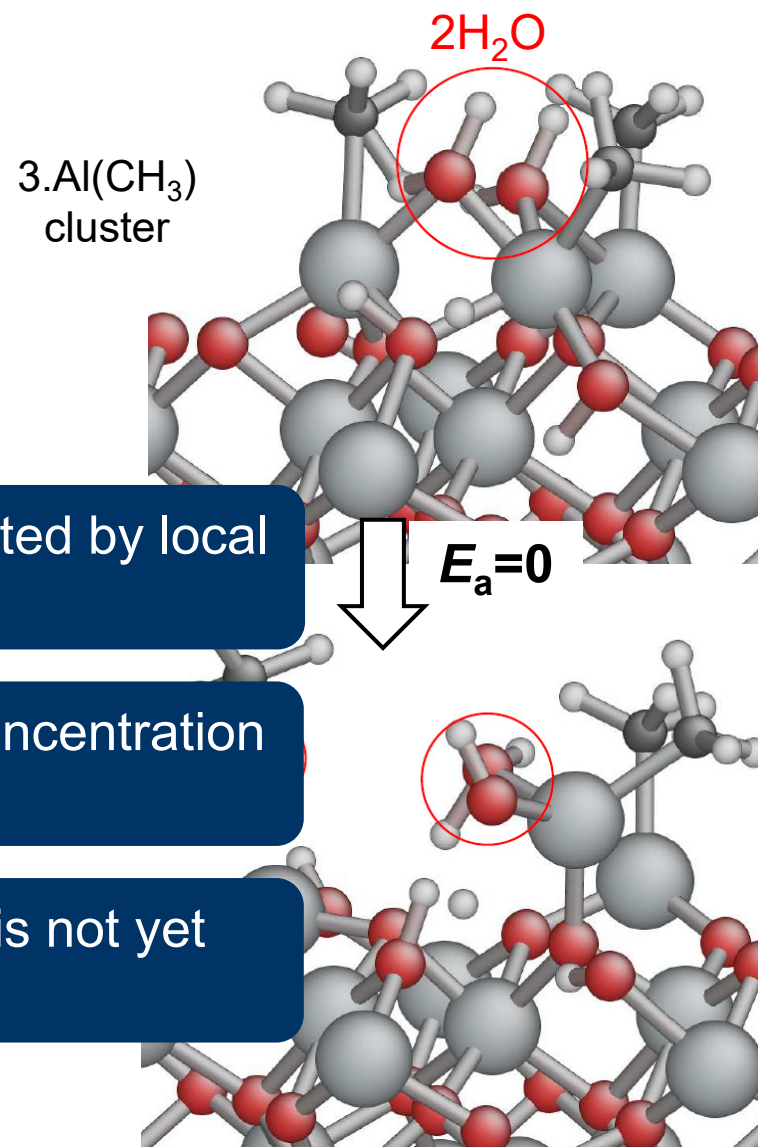
Kinetics of surface reactions strongly affected by local environment.

Reactions are accelerated by high local concentration of ligands.

Effect of local film morphology on kinetics is not yet known.

large grey=Al, red=O, white=H, small grey=C

Check for updates

What is limiting low-temperature atomic layer deposition of Al$_2$O$_3$? A vibrational sum-frequency generation study

V. Vandalon[a)] and W. M. M. Kessels[a)]

PDF   ABSTRACT   FULL TEXT   FIGURES   SUPPLEM

Atomic layer deposition   .   Chemical reaction cross sections   .   Hydrogen reactions

ABSTRACT

The surface reactions during atomic lay
Al(CH$_3$)$_3$ and H$_2$O have been studied wit
to reveal what is limiting the growth at
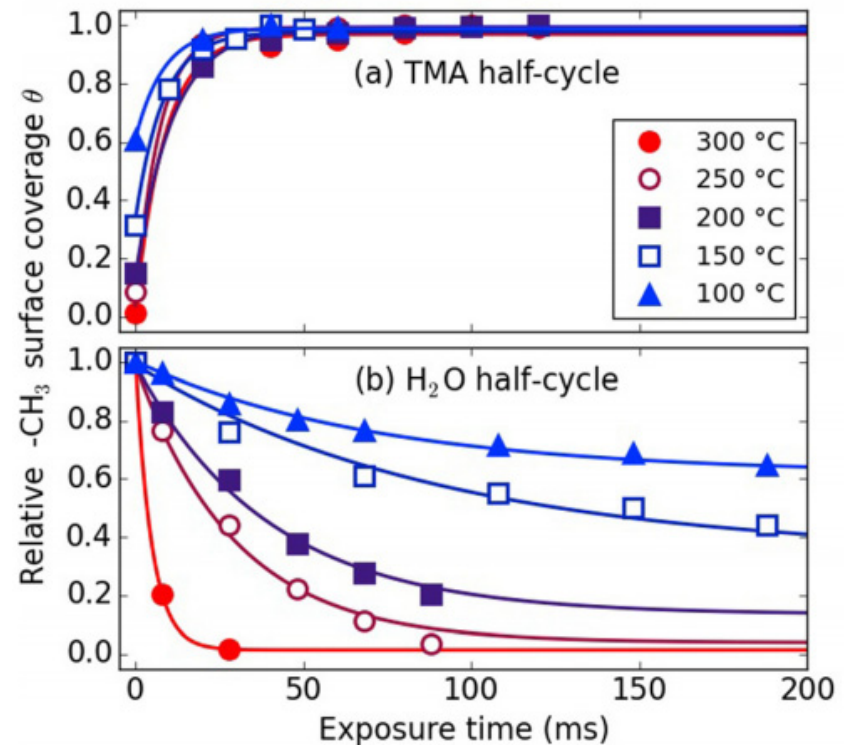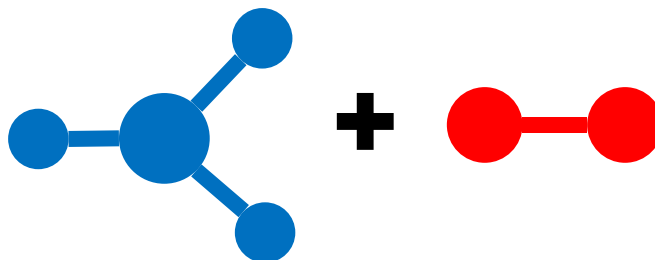
FIG. 3. Relative –CH$_3$ surface coverage θ, extracted from the BB-SFG spectra as a function of TMA and H$_2$O exposure for various temperatures. The solid lines represent fits to the data in order to extract information about the reaction kinetics.

TU/e
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Eindhoven
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Where innovation starts

SUCCESSES:

Screening based on intrinsic chemistry;
Oligomer formation during MLD
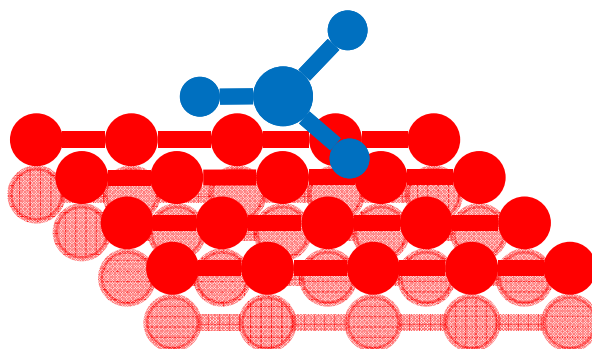
CHALLENGES:

Volatility?
Thermal stability?

Simon Elliott
simon.elliott@tyndall.ie

www.tyndall.ie

SUCCESSES:

Sketch out reaction mechanism;

Account for many experimental anomalies

CHALLENGES:

Accuracy of weak interactions;
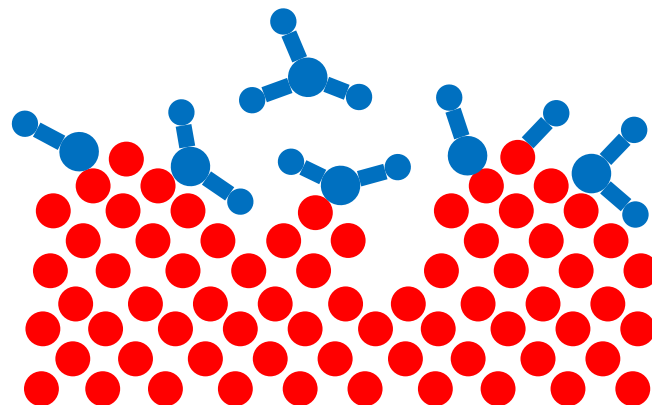
Need more realistic surface geometries for kinetics

Simon Elliott
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www.tyndall.ie

SUCCESSES:

More accurate activation energies;
Indications of how morphology evolves

CHALLENGES:

Automatic search?

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www.tyndall.ie