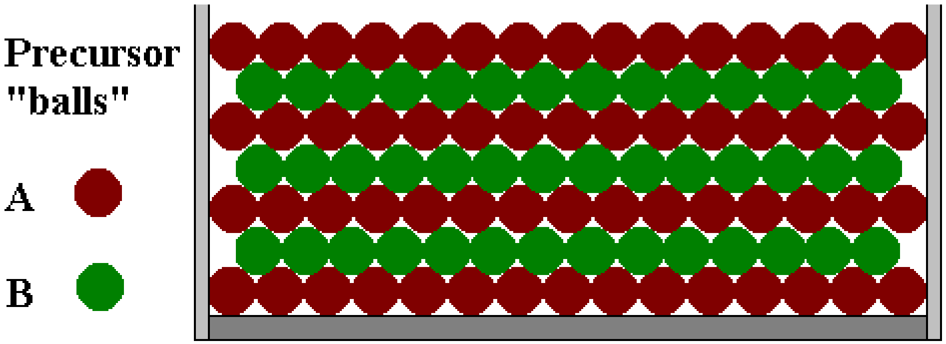
Status: 3.5.2017

3.4 Atomic Layer Deposition

History

- ALD or ALE basic works were performed in the late 60ies in Russia
- The ALCVD technique was patented by the founder of Microchemistry Tuomo Suntola, 1974
- Early 70´s: Technology was mainly used for growing Electroluminiscent (EL) thin films
- Late 70´s: The so-called Travelling Reactor concept was developed
- Mid 80´s: EL films are deposited in mass production
- 1997: Microchemistry introduced Reactor for Flat Panel Coating
- Today: ASM Microchemistry, Aixtron, Applied Materials

Atomic Layer-by-layer Growth

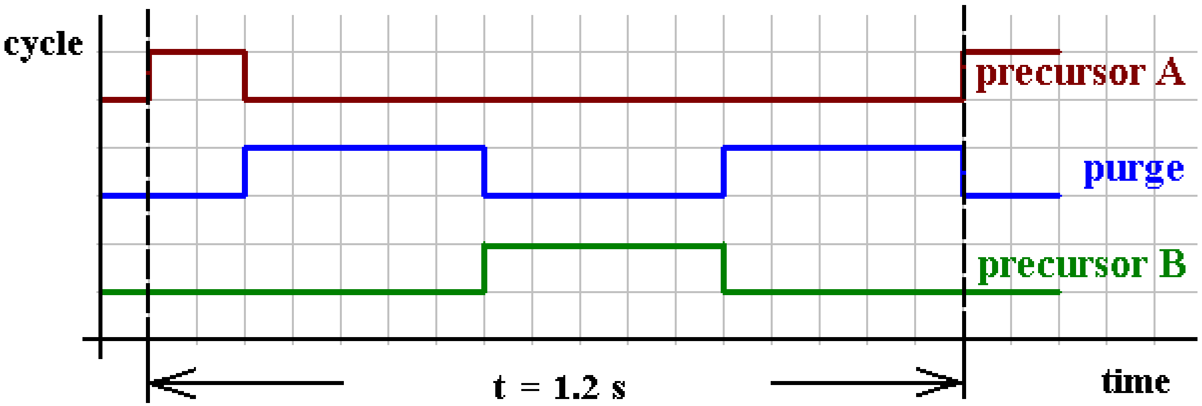


The intrinsic surface control mechanism:

Saturation of all the reaction/adsorpion sites

Purging step

ALD Cycle



Growth Requires

1. Reactive volatile precursors
   - both metal and non-metal compounds

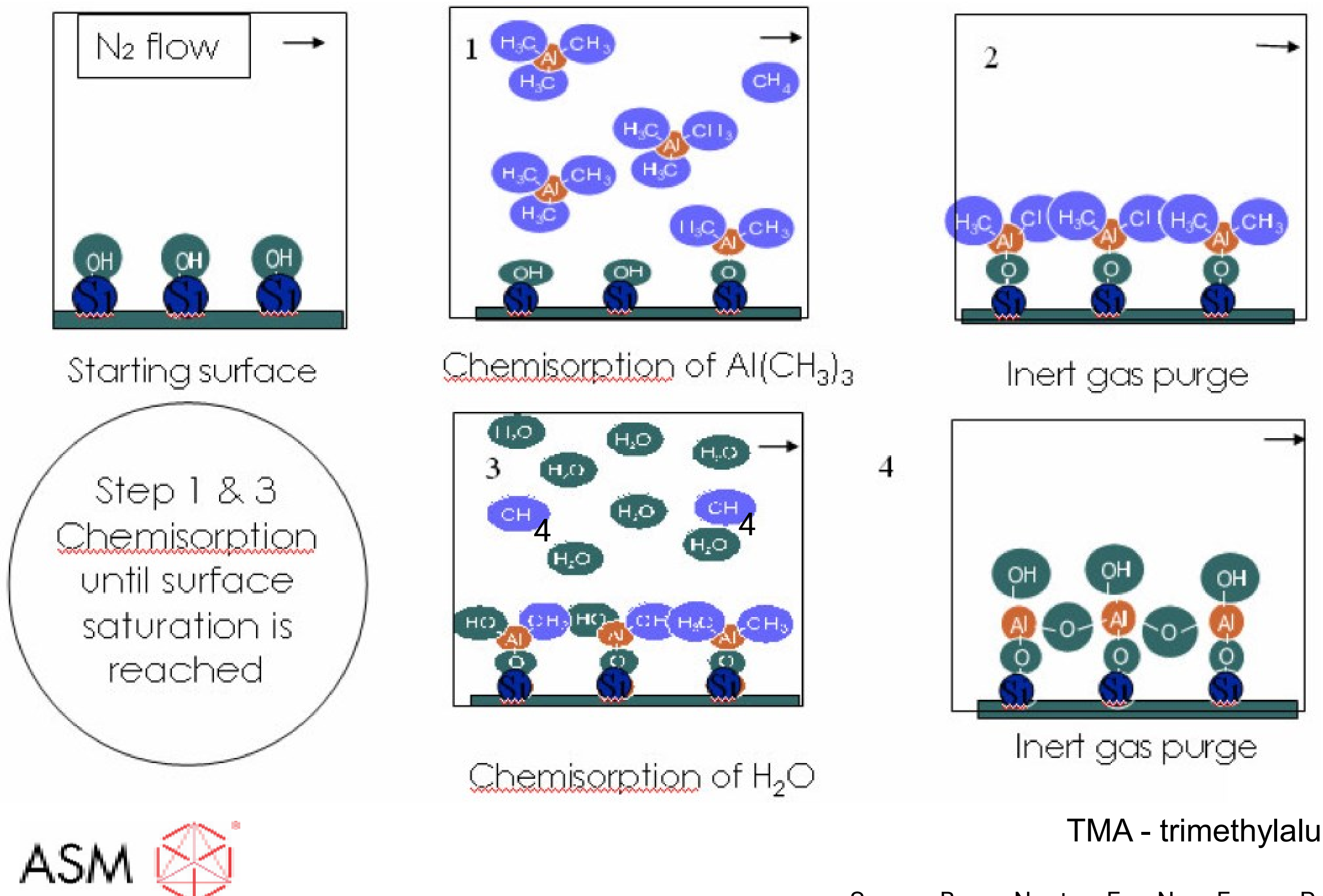
2. A substrate with well-characterized adsorption sites

3. A growth temperature that leads to the chemical reaction between the precursor and the bonding site (covalent bond formation e.g. chemisorption)
   - no condensation and decomposition allowed

4. A precursor dose high enough to saturate the surface

5. An inert gas purge to remove the unreacted precursor molecules and reaction by-products

ALD of Al_2O_3 from TMA and H_2O

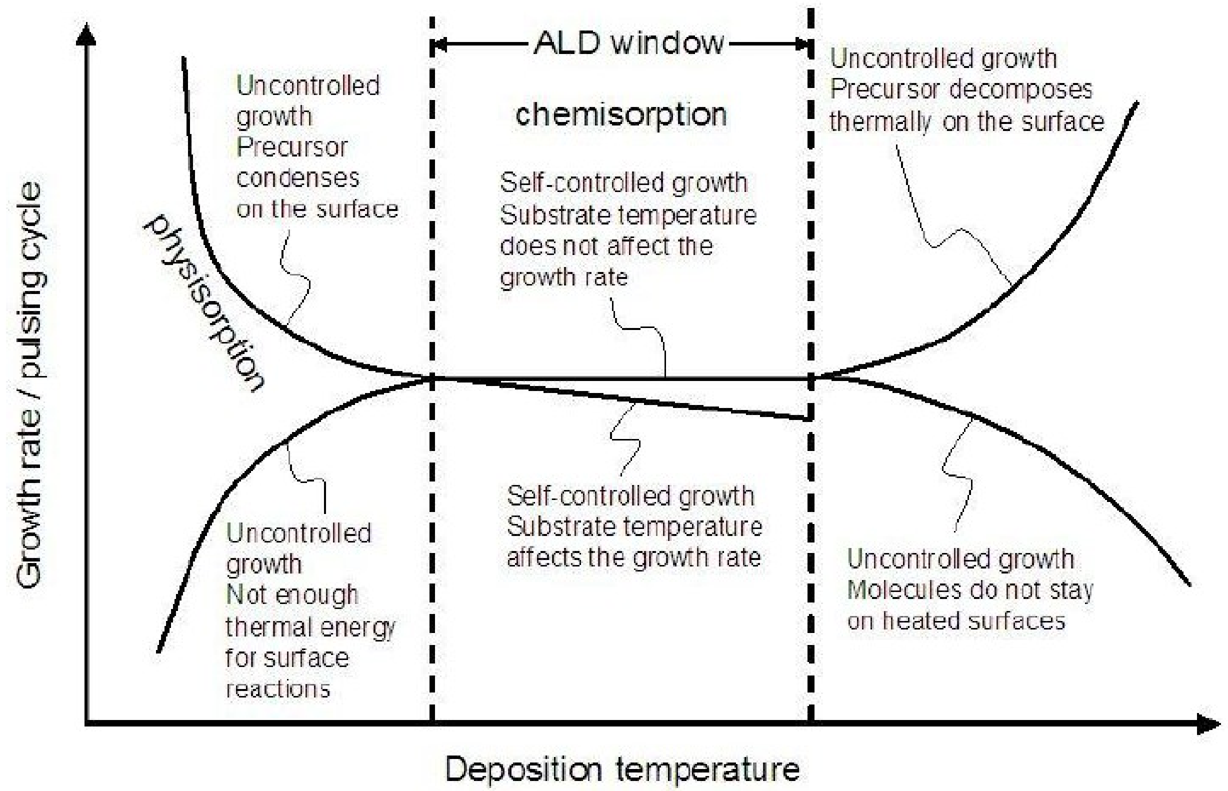


TMA - trimethylaluminium

Source: B. van Nooten, EuroNanoForum, Prague, June 2-5, 2009

Atomic Layer Deposition: Process Window

ALD Film Growth Rate Vs. Deposition Temperature



Atomic Layer Deposition: Comparison of ALD and CVD

A L D

- Highly reactive precursors
- Precursors react separately on the substrate
- Precursors do not decompose at process temperature
- Uniformity ensured by the saturation mechanism
- Thickness control by counting the number of reaction cycles
- Surplus precursor dosing acceptable

C V D

- Less reactive precursors
- Precursors react at the same time on the substrate
- Precursors can decompose at process temperature
- Uniformity requires uniform flux of reactants and temperature (in reaction rate limited case)
- Thickness control by precise process control and monitoring
- Precursor dosing important

Atomic Layer Deposition: Typical Process Characteristics

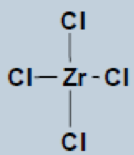
• Typical cycle time	0.5 - 5 s
- Precursor feed	0.05 - 1 s
- Purge	0.1 - 2 s
• Growth rate	0.3 - 1.5 Å / cycle
• Growth rate	10 - 100 Å / min
• Reaction temperature	150 - 500 °C
– Process window width	10…50 - 150 K
• Reaction pressure	1 - 10 mbar
• Purge / carrier gas	N_2, Ar
• Precursor (examples)	
– HfO_2	$HfCl_4 + H_2O$
– ZrO_2	$ZrCl_4 + H_2O$
– $Al2O_3$	$Al(CH_3)_3 + H_2O$
– TiN	$TiCl_4 + NH_3$ or $TiCl_4 + N_2 + H_2$
– WCN	$Et_3B + WF_6 + NH_3$
– Cu	$Cu(thd)_2 + O_3$

ALD Precursor Classes

Picosun

ALD Precursors

Inorganic

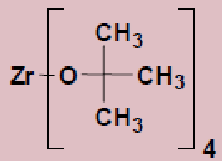


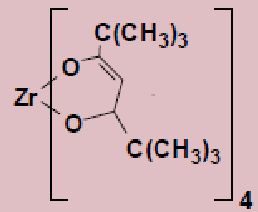
Metal Halides:
M–F, M–Cl, M–Br, M–I

Adv:
Thermal stability
Reactivity
Molecule size

Disadv:
By-products
Vapor pressure

Metalorganic



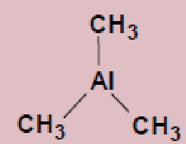


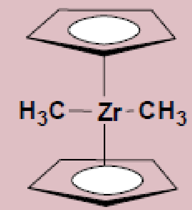
Metal alkoxides
Metal β-diketonates
Metal dialkylamidos
Metal amidinates

Adv:
Vapor pressure

Disadv:
Thermal stability
Reactivity
Molecule size

Organometallic





Metal alkyls
Metal cyclopentadienyls

Adv:
Reactivity
Thermal stability
By-products
Vapor pressure

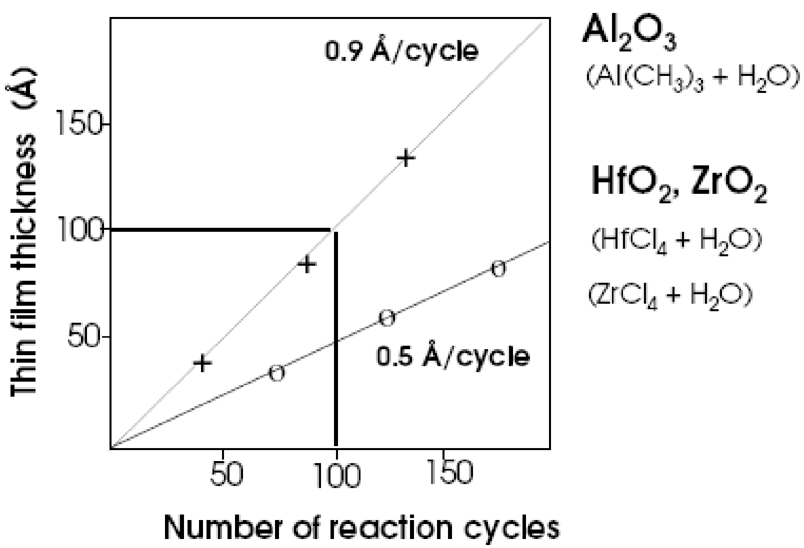
Disadv:
Availability

Source: Picosun Oy

ASM

Overview currently available ALD Films

Front-End Operations



- Oxides
  - SiO2, Al2O3, HfO2, ZrO2, TiO2, Ta2O5, La2O3, Y2O3, MgO, Nb2O5, Sc2O3, CeO2, Ga2O3
  - mixed oxides like HfZrO, HfAlO, HfSiO
  - laminates like Al2O3/HfO2/Al2O3
  - SrTiO3, BaSrTiO3, BiTiO3, SrBiTaO, LaNiO3, LaCoO3
  - ZnO, ZnO:Al, In2O3, In2O3:Sn, SnO2, SnO2:Sb
- Nitrides
  - TiN, TaN, TaCN, WN, WCN, NbN, MoN, HfN, AlN, mixed nitrides like TiAlN, TaSiN
- Carbides
  - TaC, WC
- II-VI Compounds
  - ZnS, ZnSe, ZnTe, ZnSSe , CaS, SrS, BaS, CdS, CdTe,
  - MnTe, HgTe, HgCdTe, CdMnTe, ZnS:M (M= Mn, Tb, Tm),
  - CaS:M (M= Eu ,Ce, Tb, Pb), SrS:M (M= Ce, Tb, Pb)
- Others:
  - W, Ta, Ti, Cu, Ru, RuO2, Pt, Ir, CuO
  - La2S3, PbS, In2S3, CaF2, SrF2, ZnF2

Atomic Layer Deposition: Processes for IC Industry

High-k gate dielectrics

- Replacement of current SiO_2/Si_3N_4 films
- Processes available for ZrO_2, HfO_2, mixed materials
- Targeted (equivalent) oxide thickness - EOT: ~ 1.0 nm

High-k capacitor dielectrics

- Replacement of current SiO_2/Si_3N_4, Ta_2O_5 films
- ALCVD processes for Al_2O_3, Ta_2O_5

Diffusion barriers (to avoid Cu diffusion)

- Replacement current sputtered diffusion barriers
- ALCVD processes for TiN, W(C)N, Ta(C)N, mixed nitrides

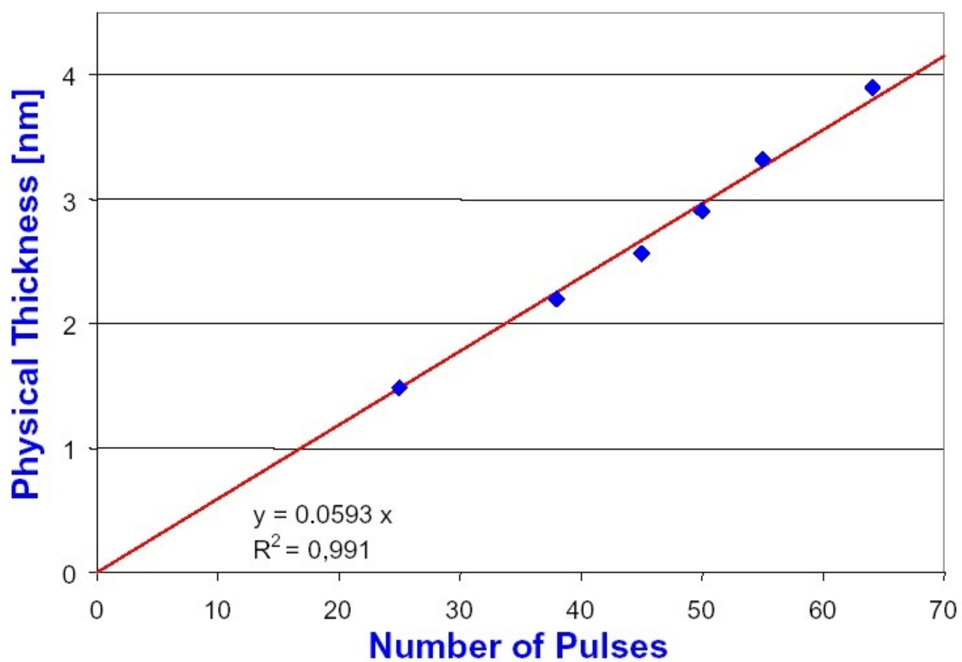
Metal films

- ALD Cu seed layers for Cu electroplating
- Electrodes for high k gate and capacitor applications

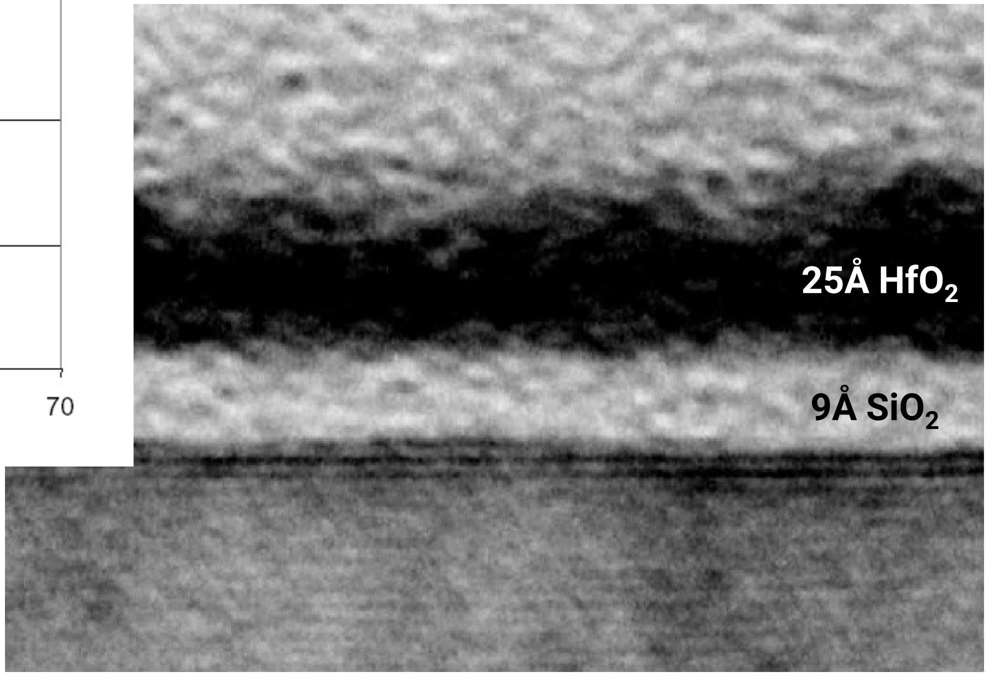
EOT – equivalent oxide thickness

High-k Dielectrics for MOS Gates

HfO_2 Sub-Monolayer Thickness Control



HfO_2 - TEM study



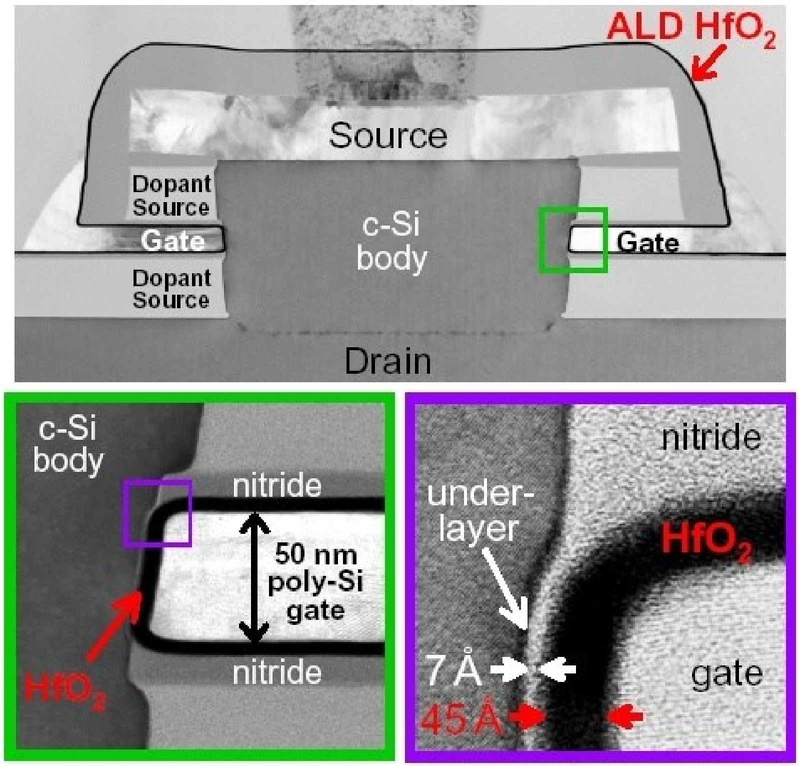
- excellent EOT < 16Å observed
- no additional SiO_2 growth

Ref.: M. Schumacher, GMM Workshop 2002

AIXTRON The CVD Engineering Company

High-k Dielectrics for MOS Gates

Surface saturation results in excellent step coverage



7 Å UL + 45 Å HfO_2 = 15 Å EOT

- High-k & ALCVD also enable non-planar device structures
- 50nm VRG-nMOSFET using ALCVD deposited HfO2 as gate dielectric

Source: Agere / J.M. Hergenrother et al., 2001 IEDM

ASM

Ref.: J.W. Maes, GMM Workshop 2002

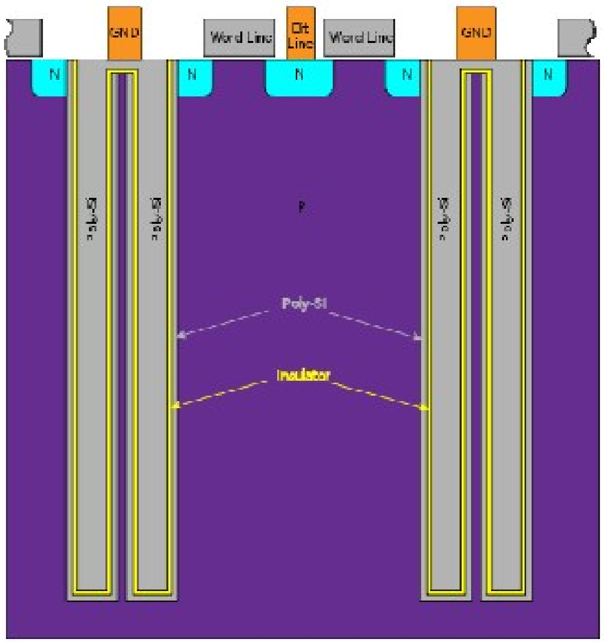
ASM

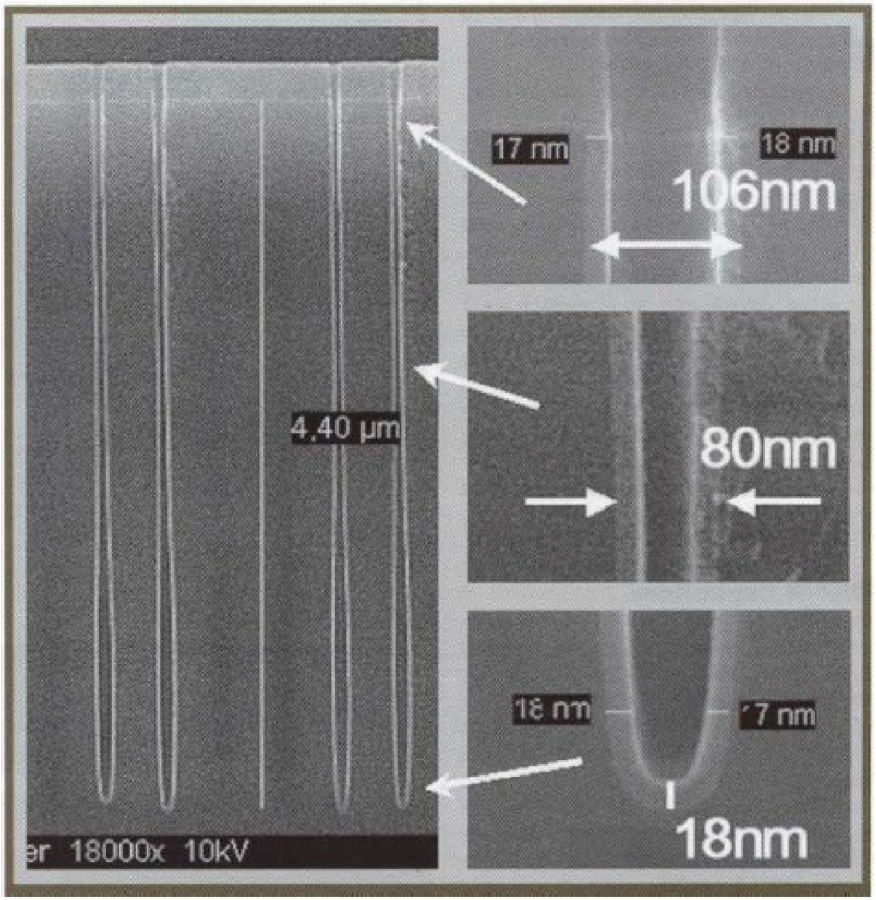
Front-End Operations

More Moore Examples - 1

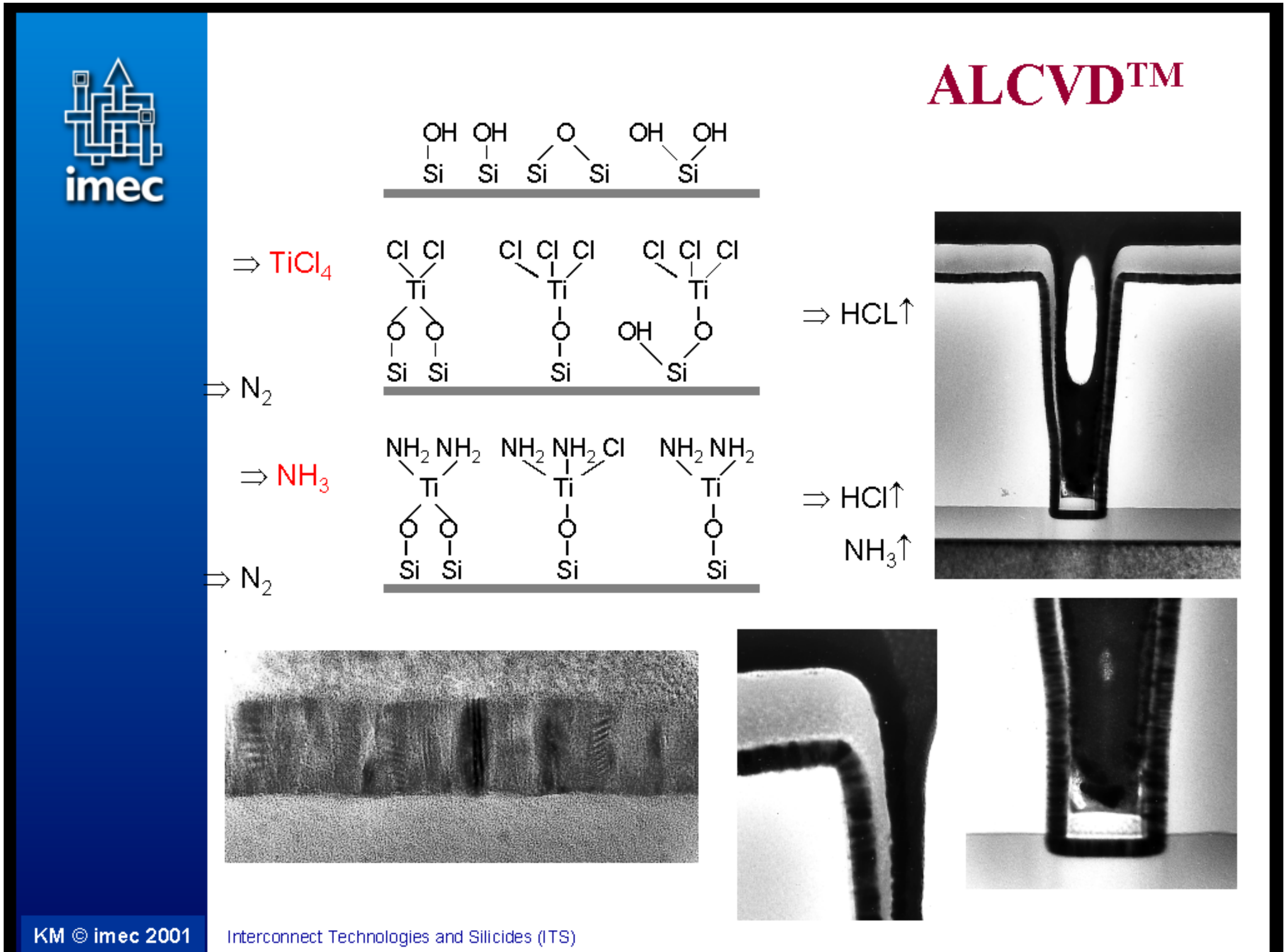
DRAM Trench Capacitor

- Aspect ratio: > 60
- Al_2O_3

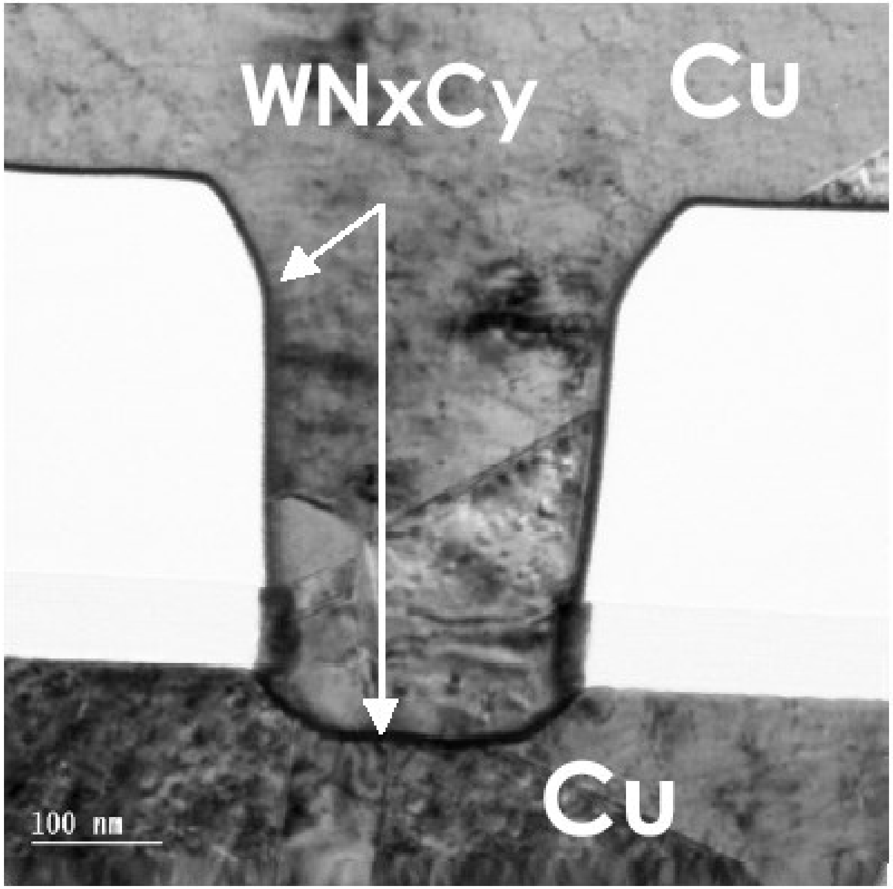




ALD of Diffusion Barrier Films



Atomic Layer Deposition of WCN barrier films



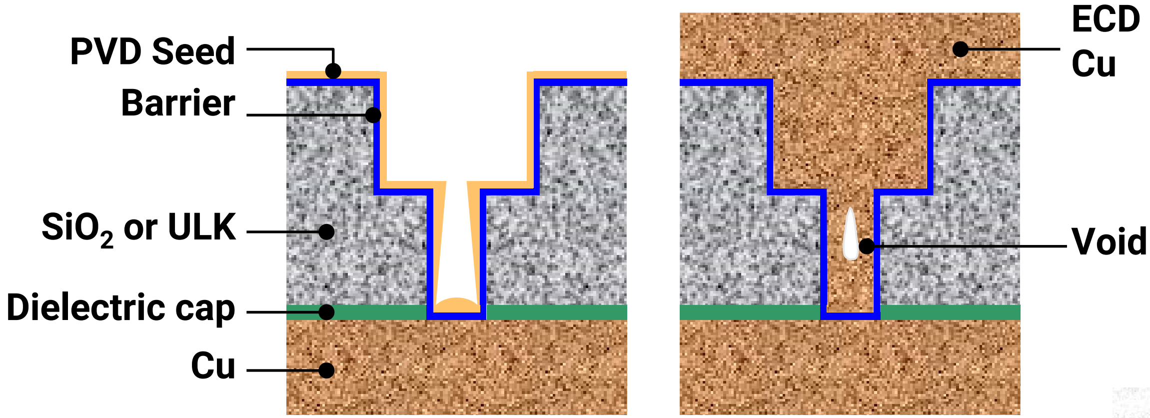
Li et al. (ASM, Philips), IITC 2002

Application of ALD to barrier films

Advantages:
Highly conformal deposition
Controlled thickness
Extremely thin films
Excellent thickness uniformity

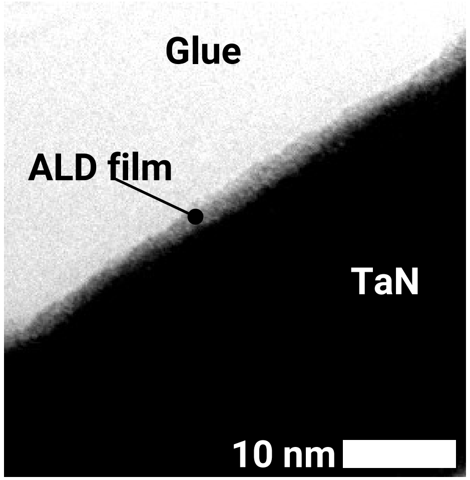
Disadvantages/Challenges:
Surface sensitivity
Cost-effective only for very thin films
For porous and part of low-density low-k materials only applicable at sealed surfaces

Atomic Layer Deposition of Copper



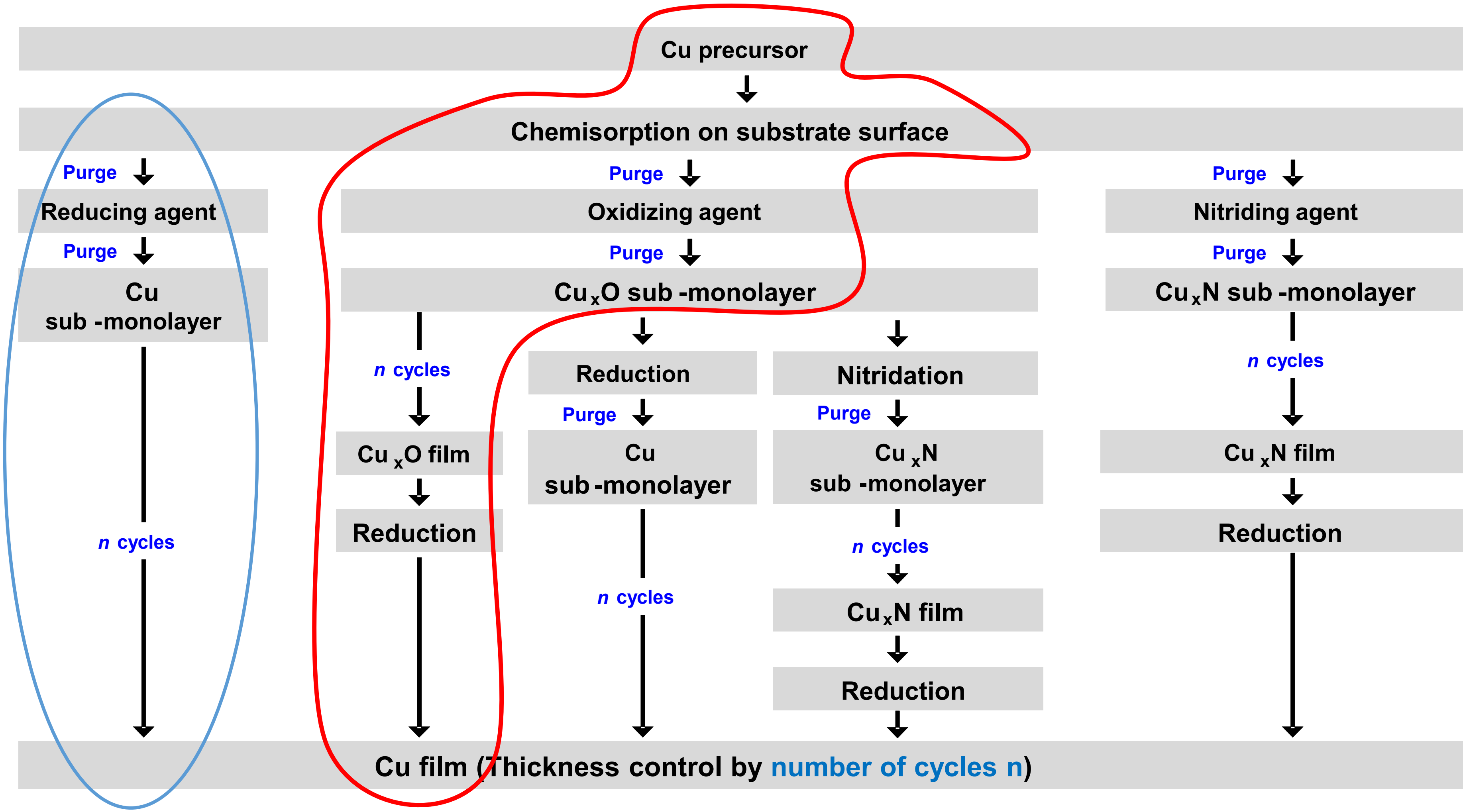
Why copper ALD?

- Seed layer for Cu damascene process
- Metallization of narrow holes and trenches, e.g. through-silicon vias (TSV)
- Conformally coating 3D nano-structures (porous materials, nanowires, CNTs, ...)



TEM cross section of ALD film on TaN
Ellipsometric thickness: 3.6 nm

Known Approaches for Cu ALD

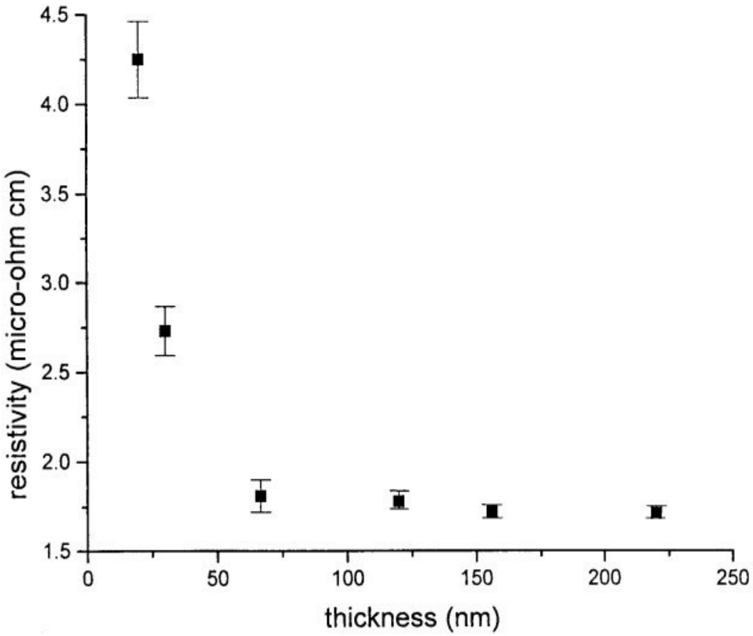


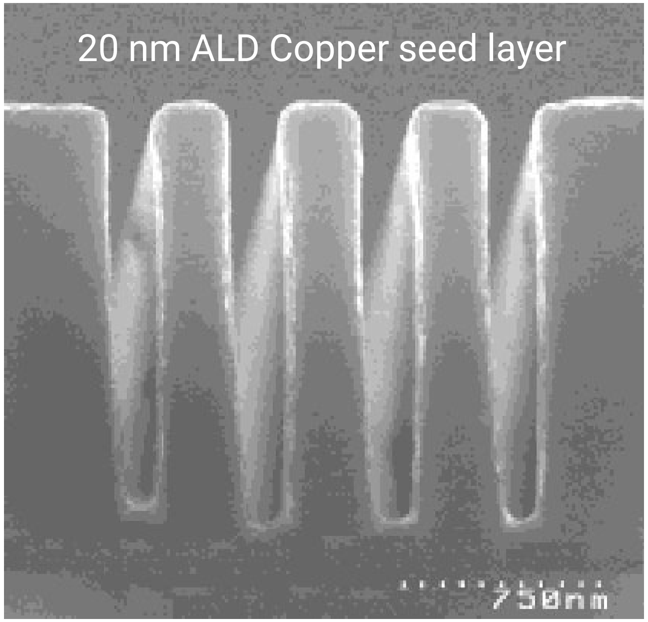
Approach A (R. Solanki, U.S.)

Approach B (Fraunhofer ENAS, T. Waechtler)

Approach A: ALD of Copper with n cycles of reducing agent and Cu prec.

Cu source: Cu(II) hexafluoroacetylacetonate ($Cu(hfac)_2$)
Reducing agents: Methanol, Ethanol, Isopropyl alcohol (IPA), Formalin
Typical deposition temperature: 300°C



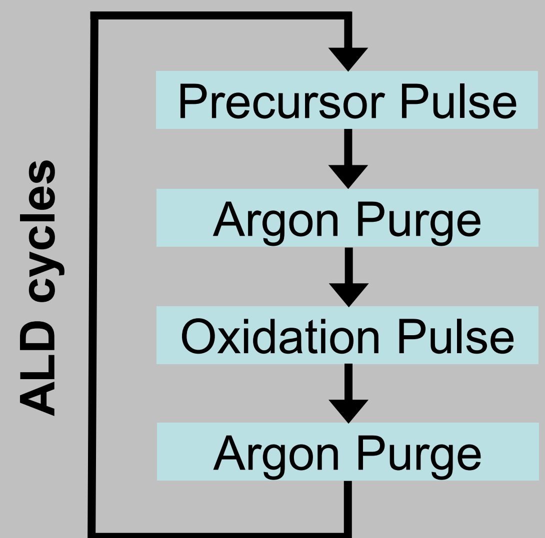


Possible ALD reaction mechanism
First reaction step (alhohol pulse): ROH $\longrightarrow$ R• (ad) + OH• (ad)   R.. Alkyl group
Second reaction step ($Cu(hfac)_2$ pulse):
$Cu(hfac)_2 \cdot X\ H_2O + H_2 + R\bullet\,(ad) + OH\bullet\,(ad) \longrightarrow Cu + RH + (CF_3)_2CH\bullet + (COOH)_2$

Ref.: R. Solanki, ALD Conference 2001

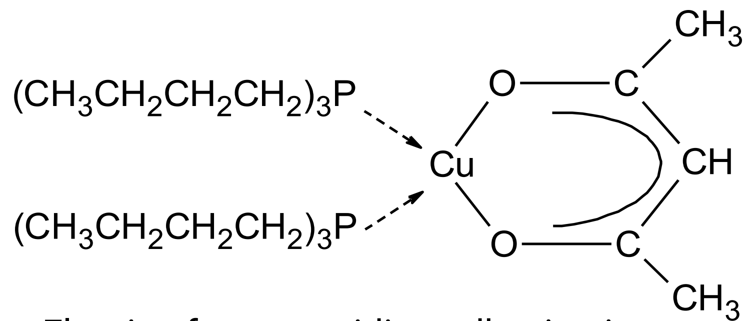
Approach B: Copper oxide ALD with n cycles of Cu prec. and oxidizing agent & subsequent reduction of complete film

1st step: Copper oxide ALD



2nd step: Vapor phase reduction

- **Cu(I) β-diketonate precursor**



  - Fluorine free – avoiding adhesion issues
  - Liquid under standard conditions – liquid precursor delivery during ALD

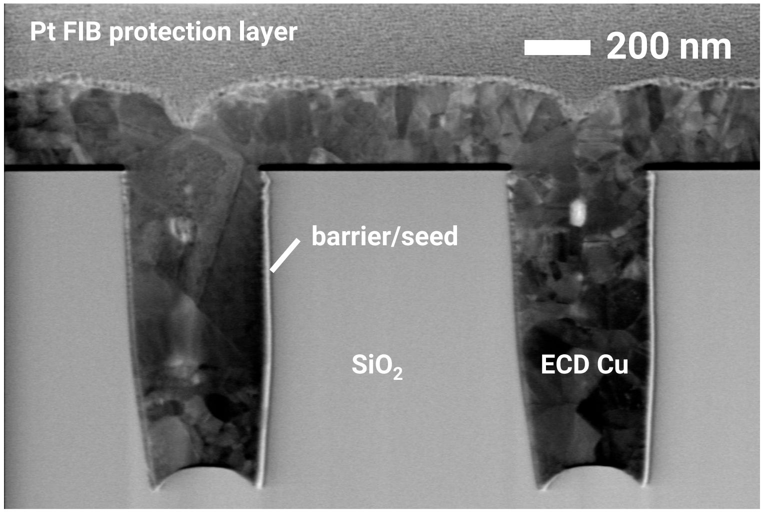
- **Oxidation by a mixture of water vapor and O_2 (“wet O_2“)**

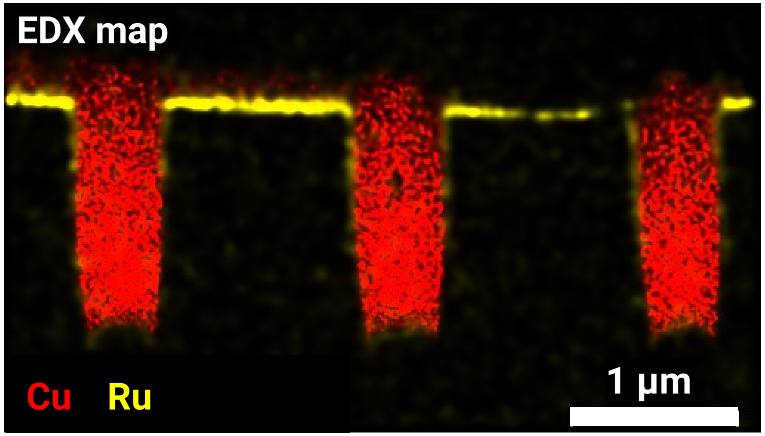
Well established process for Cu_xO ALD

T. Waechtler, et al., *J. Electrochem. Soc.* **156**, H453 (2009)
T. Waechtler, et al., DE 10 2007 058 571, international patents pending

ECD Experiments on ALD Copper

FIB lamella preparation and STEM investigation of filled interconnect





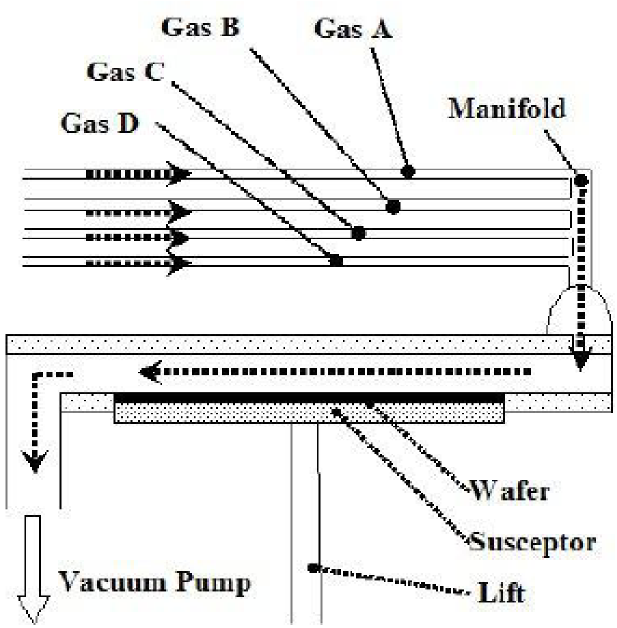
- Good filling behavior when combining ALD Cu and Ru already under unoptimized ECD conditions (note: conformal ECD, no buttom up fill !)
- PVD TaN/Ru stack showing strong thickness inhomogeneity within features
- Good conformality and step coverage of ALD copper seed

Combination Ru/ALD Cu could enable nanoscale interconnect metallization

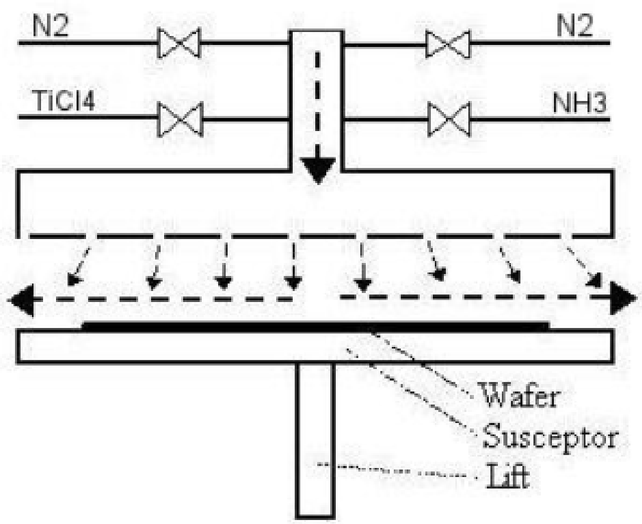
Equipment: Reactor Types

Source: Picosun

Reactor Flow-type



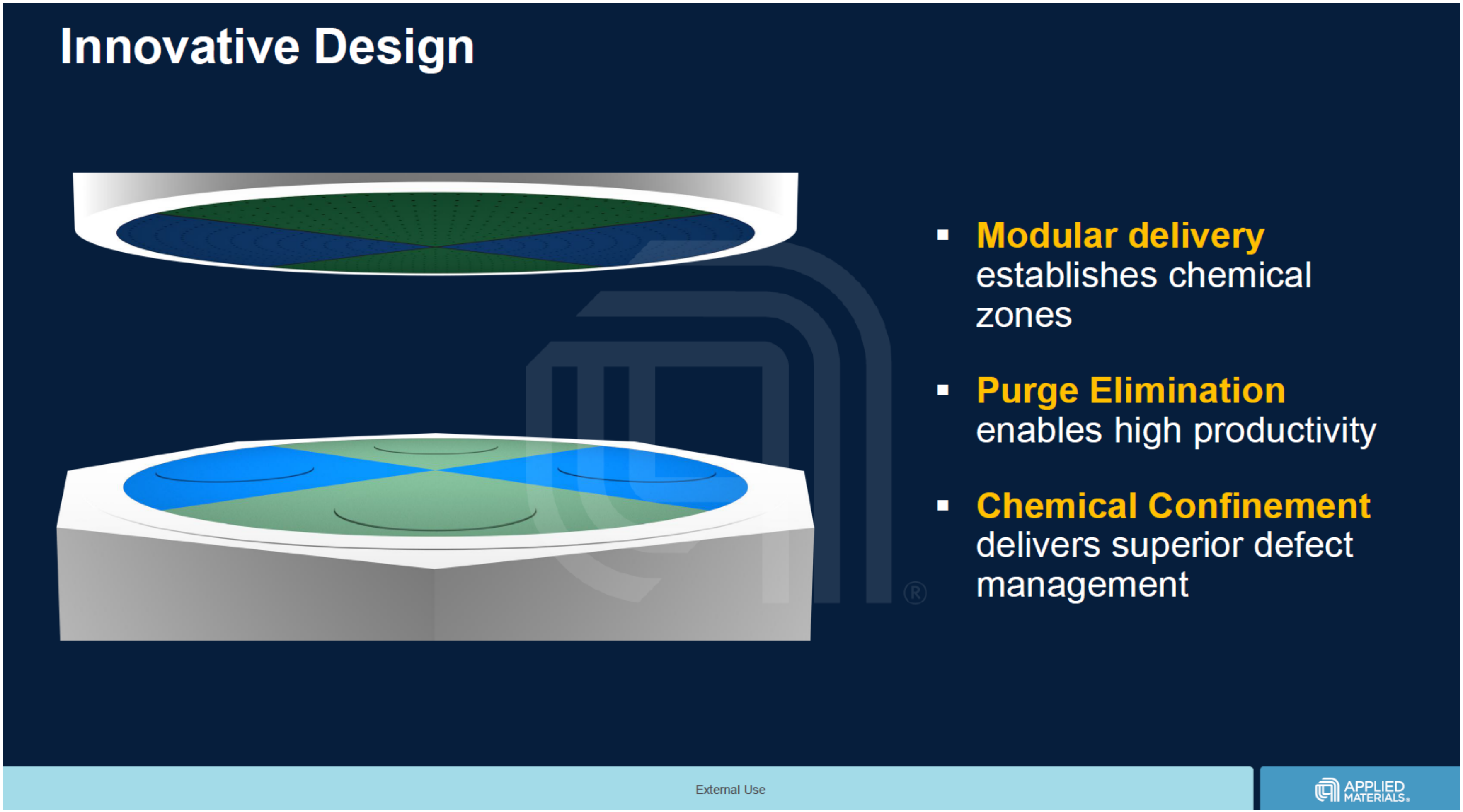
Cross-flow Reactor



Perpendicular flow Reactor
“showerhead“

Equipment: Reactor Types – Spatial ALD

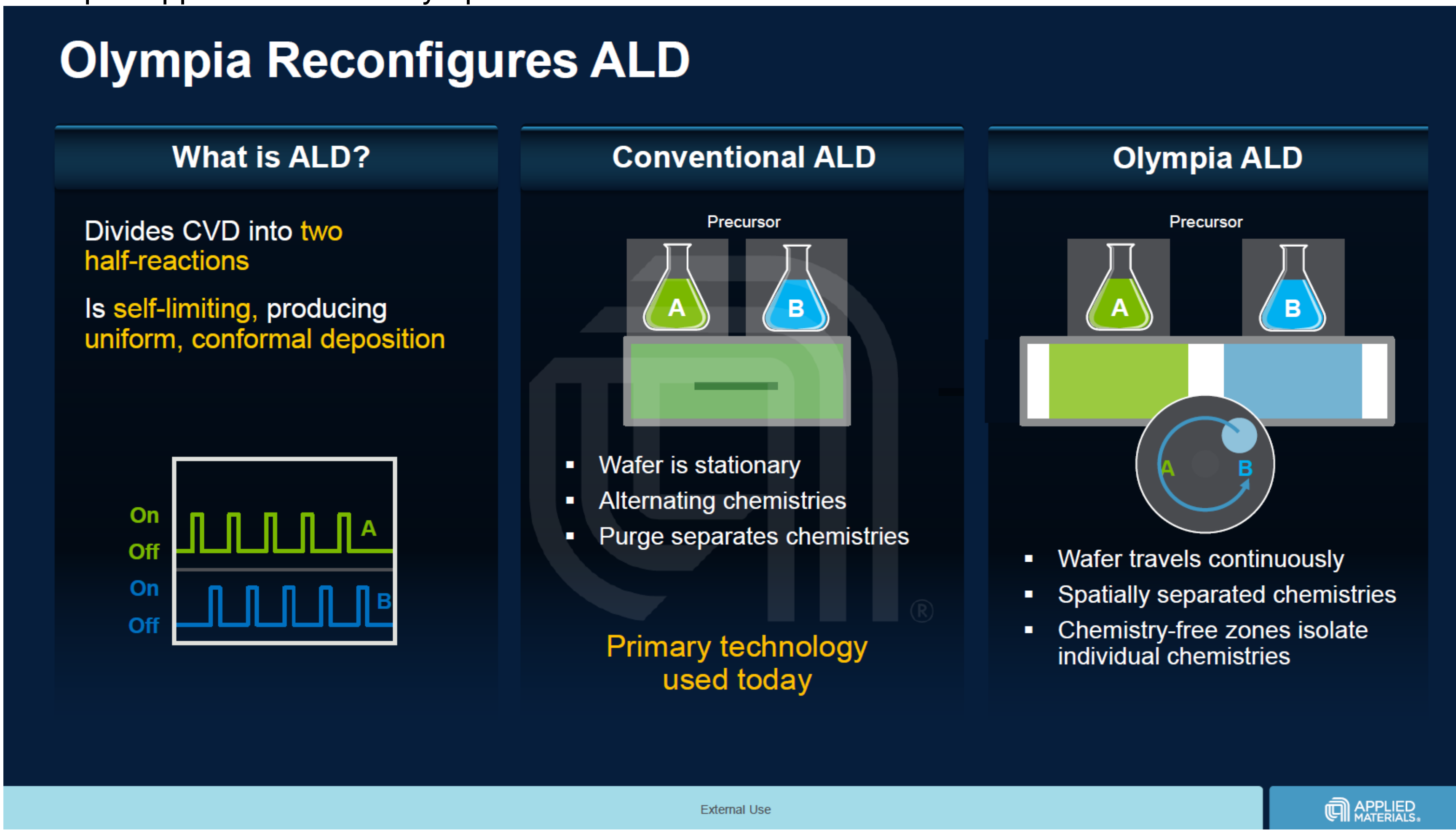
Example: Applied Materials Olympia™ ALD



Source: Technical Briefing, Applied Materials, 2015-07-13

Equipment: Reactor Types – Spatial ALD

Example: Applied Materials Olympia™ ALD

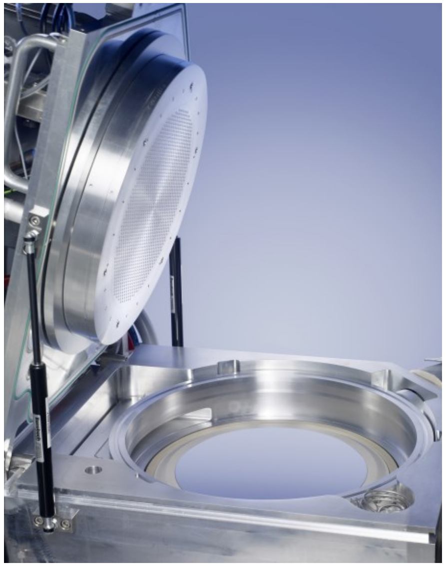


Source: Technical Briefing, Applied Materials, 2015-07-13

Equipment example: AIXTRON Tricent ALD

Results:

- >95% step coverage in a 50:1 AR structures with Al_2O_3, HfO_2, HfSiOx and ZrO_2 film
- >90% step coverage in a 50:1 AR structures with TiN film
- WiW and WtW uniformity <1.0%, 1 sigma
- >10 wph for 60Å ZrO_2 film with >95% step coverage in 50:1 AR
- <20 adders with particle size >0.16µm in high volume manufacturing
- >90% Availability in high volume manufacturing
- Good thickness and interface control for nanolaminate and alloy films
- Low leakage for DRAM and Gate Dielectrics high-k films



Source: www.aixtron.com (2010)