Status: 20.4.2012

3.4 Atomic Layer CVD

- History
- Basics
- Process parameters and film properties
- Applications:
  - ALD of high-k dielectrics
  - ALD of diffusion barriers
  - Copper ALD for seed layers in Cu Damascene
- Reactor types / Equipment

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- 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

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Atomic Layer CVD: History

Examples of ALD Reactors Designed in Finland

MC 120 CAT ALD reactor
Acquired by Picosun Oy
Developed in early 1990's
for R&D of heterogeneous
catalysts (e.g. US6534431)

F-950 ALD reactor
Microchemistry Ltd.
Developed in 1990's
for flat panel production

PULSAR™ 2000/3000 ALD reactors
designed by Microchemistry
owned by ASM International, Inc

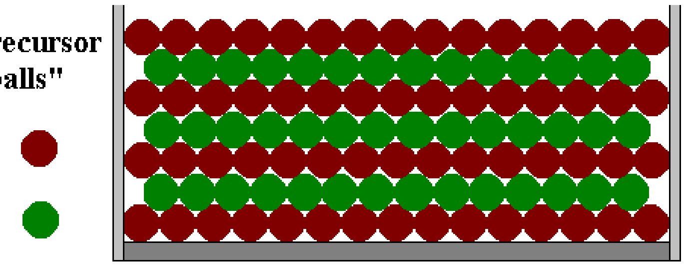
Atomic Layer CVD

Atomic Layer-by-layer Growth

Precursor "balls"

A

B



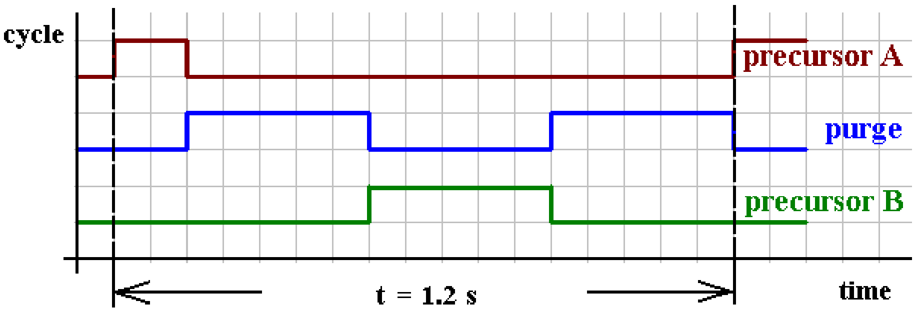
The intrinsic surface control mechanism:

- **Saturation of all the reaction**

clean something which is unclear

- **Purging step**

ALCVD Cycle



Atomic Layer CVD: 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**

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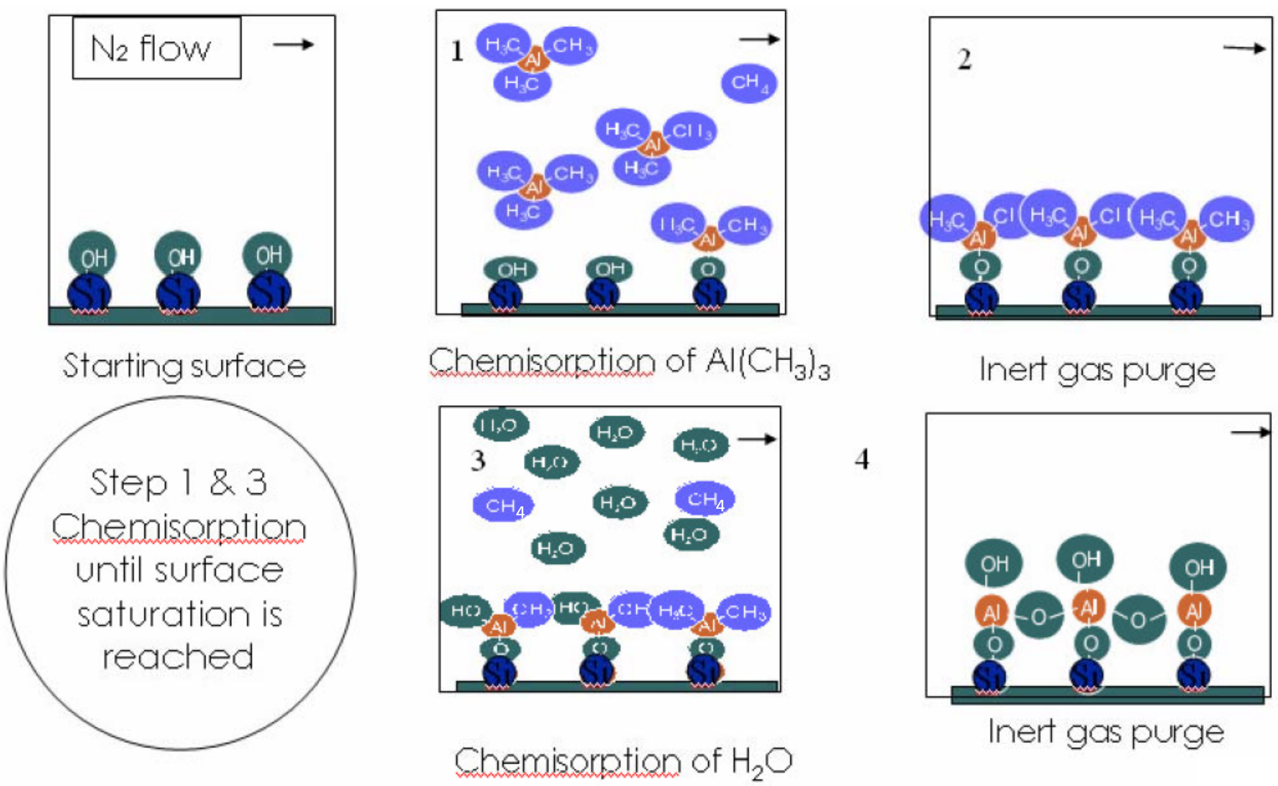
ALD of Al_2O_3 from TMA and H_2O



ASM

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

ZfM Fraunhofer ENAS
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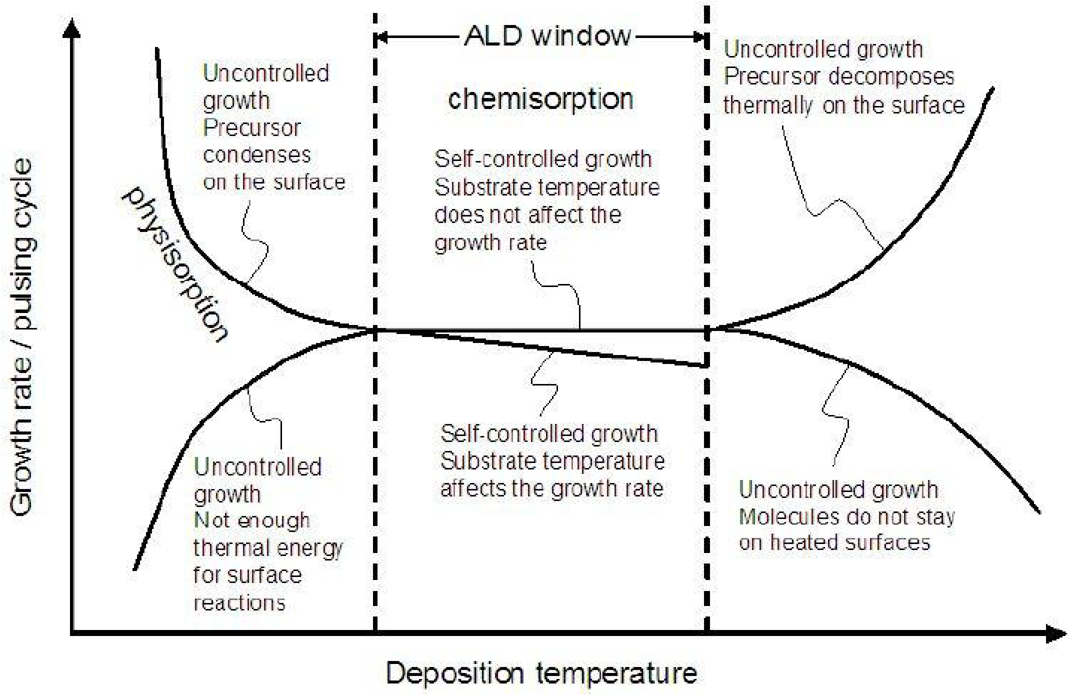
Atomic Layer CVD: Process Window

ALD Film Growth Rate Vs. Deposition Temperature



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Atomic Layer CVD: Comparison of ALCVD and CVD

A L C V D	**C V D**
• Highly reactive precursors	• Less reactive precursors
• Precursors react separately on the substrate	• Precursors react at the same time on the substrate
• Precursors do not decompose at process temperature	• Precursors can decompose at process temperature
• Uniformity ensured by the saturation mechanism	• Uniformity requires uniform flux of reactants
• Thickness control by counting the number of reaction cycles	• Thickness control by precise process control and monitoring
• Surplus precursor dosing acceptable	• Precursor dosing important

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Atomic Layer CVD: Process Characteristics

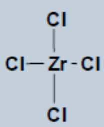
• Typical cycle time	0.5 - 5 s
- Precursor feed	0.05 - 1 s
- Purge	0.1 - 2 s
• Growth rate	0.3 - 1.5 Å / cycle
• Growth rate	10 - 100 Å / min
• Reaction temperature	150 - 500 °C
- Process window width	50 - 150 K
• Reaction pressure	1 - 10 mbar
• Purge / carrier gas	N_2, Ar
• Precursor (examples)	
- HfO_2	$HfCl_4 + H_2O$
- 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

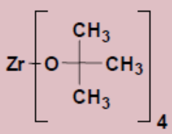


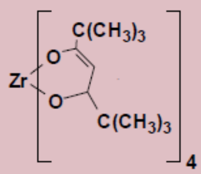
Metal Halides:
M–F, M–Cl, M–Br, M–I

Adv:
Thermal stability
Reactivity
Molecule size

Disadv:
By-products
Vapor pressure

Metalorganic



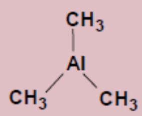


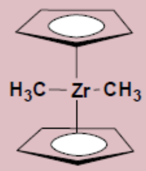
Metal alkoxides
Metal β-diketonates
Metal dialkylamidos
Metal amidinates

Adv:
Vapor pressure

Disadv:
Thermal stability
Reactivity
Molecule size

Organometallic





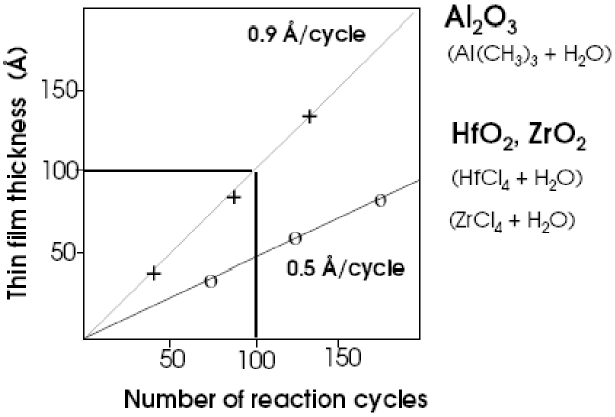
Metal alkyls
Metal cyclopentadienyls

Adv:
Reactivity
Thermal stability
By-products
Vapor pressure

Disadv:
Availability

Source: Picosun Oy

Overview currently available ALD Films



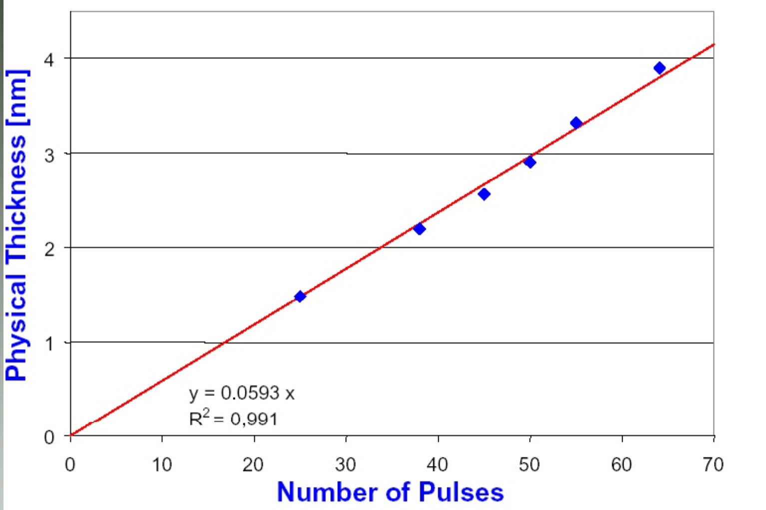
- Oxides
  - SiO2, Al2O3, HfO2, ZrO2, TiO2, Ta2O5, La2O3, Y2O3, MgO, Nb2O5, Sc2O3, CeO2, Ga2O3
  - mixed oxides like HfZrO, HfAlO, HfSiO
  - laminates like Al2O3/HfO2/Al2O3
  - SrTiO3, BaSrTiO3, BiTiO3, SrBiTaO, LaNiO3, LaCoO3
  - ZnO, ZnO:Al, In2O3, In2O3:Sn, SnO2, SnO2:Sb
- Nitrides
  - TiN, TaN, TaCN, 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 CVD: Processes for IC Industry

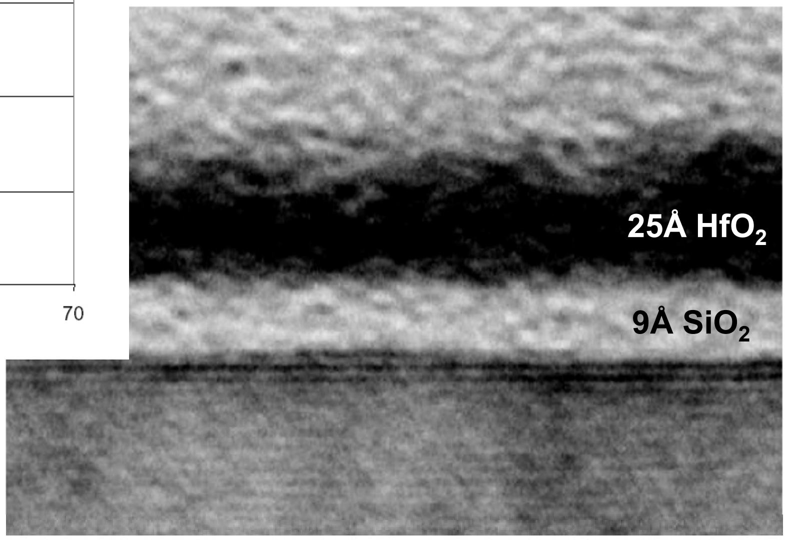
- **High-k gate dielectrics**
  - Replacement of current SiO_2/Si_3N_4 films
  - Processes available for ZrO_2, HfO_2, mixed materials
  - Targeted (equivalent) oxide thickness - EOT: ~ 1.0 nm
- **High-k capacitor dielectrics**
  - Replacement of current SiO_2/Si_3N_4, Ta_2O_5 films
  - ALCVD processes 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

High-k Dielectrics for MOS Gates

HfO_2 Sub-Monolayer Thickness Control



HfO_2 - TEM study



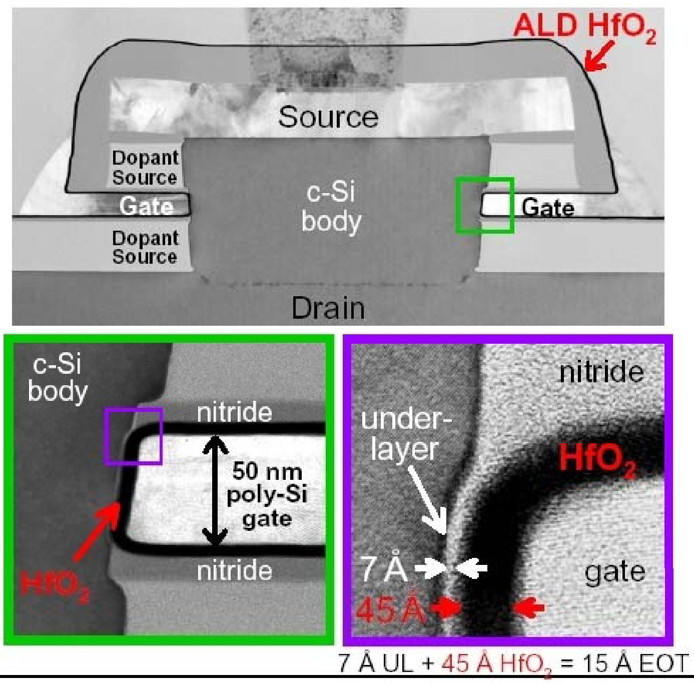
- excellent EOT < 16Å observed
- no additional SiO_2 growth

Ref.: M. Schumacher, GMM Workshop 2002

AIXTRON The CVD Engineering Company

High-k Dielectrics for MOS Gates

Surface saturation results in excellent step coverage



- 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

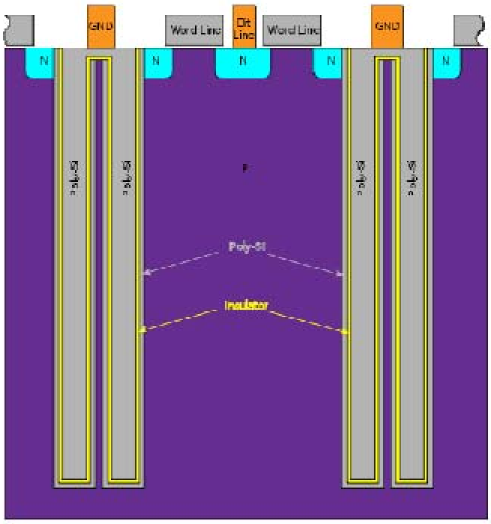
ASM

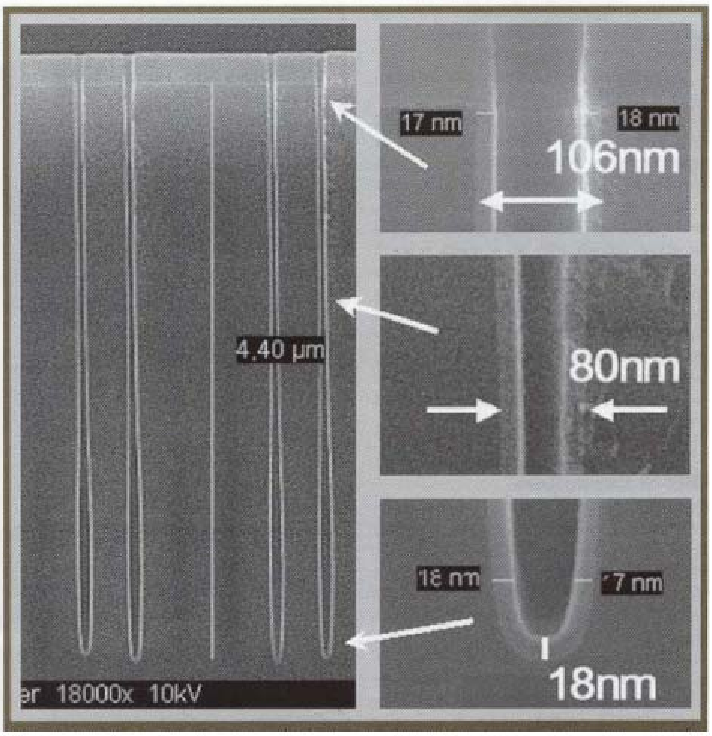
Ref.: J.W. Maes, GMM Workshop 2002

More Moore Examples - 1

DRAM Trench Capacitor

- Aspect ratio: > 60
- Al_2O_3





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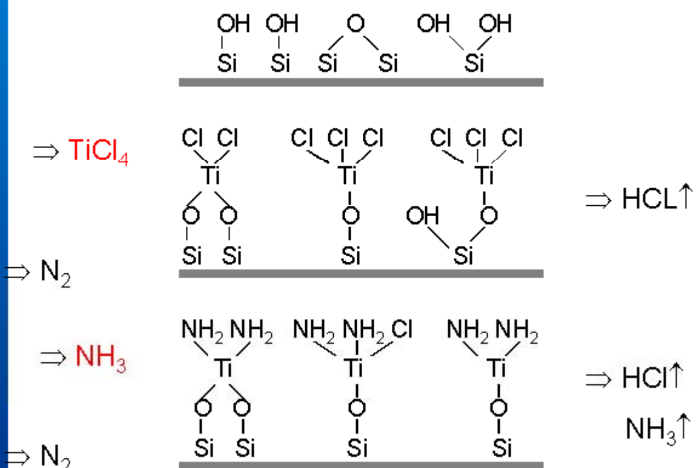
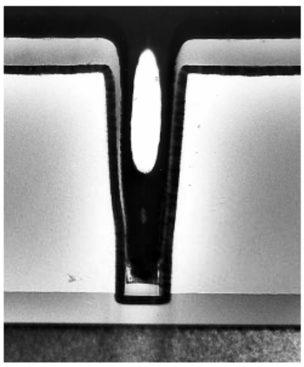
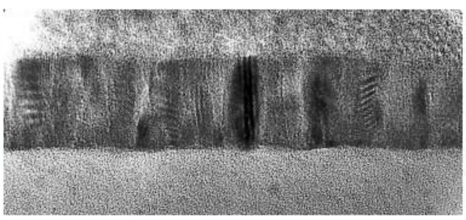
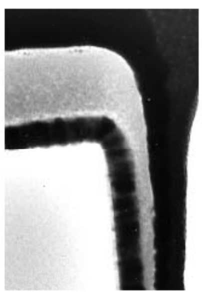
ALD of Diffusion Barrier Films

ALCVD™





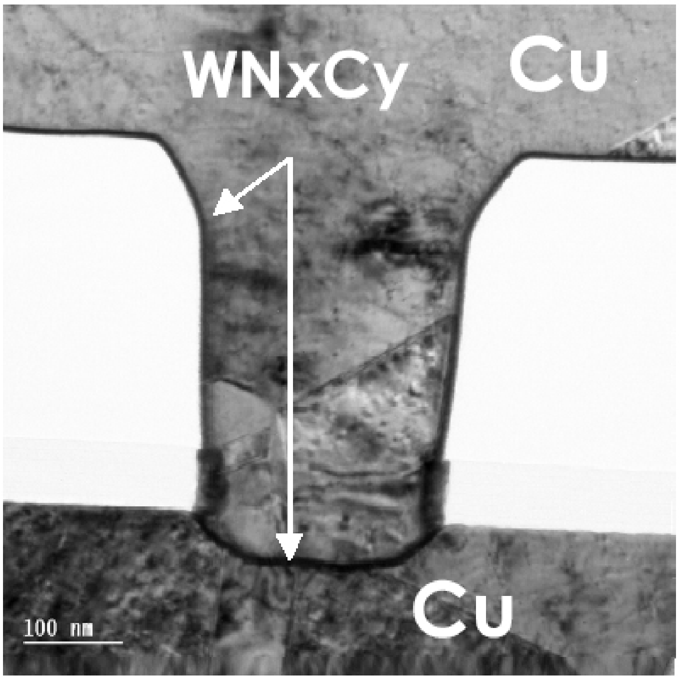




KM © imec 2001

Interconnect Technologies and Silicides (ITS)

Atomic Layer Deposition of WCN barrier films



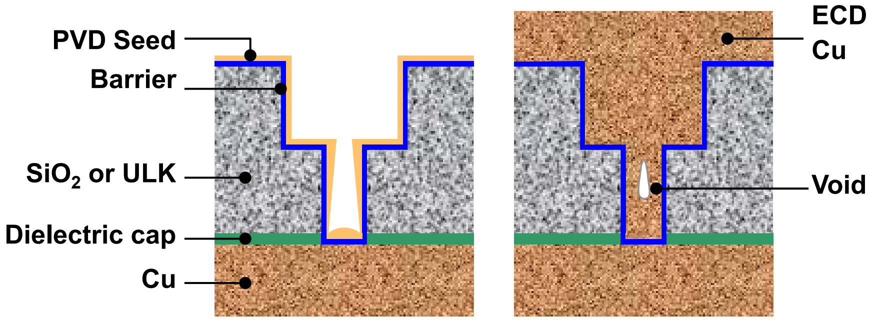
Li et al. (ASM, Philips), IITC 2002

Application of ALD to barrier films

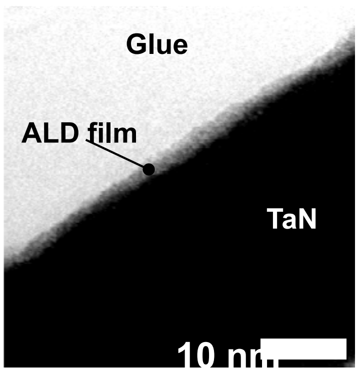
Advantages:
- Highly conformal deposition
- Controlled thickness
- Extremely thin films
- Excellent thickness uniformity

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

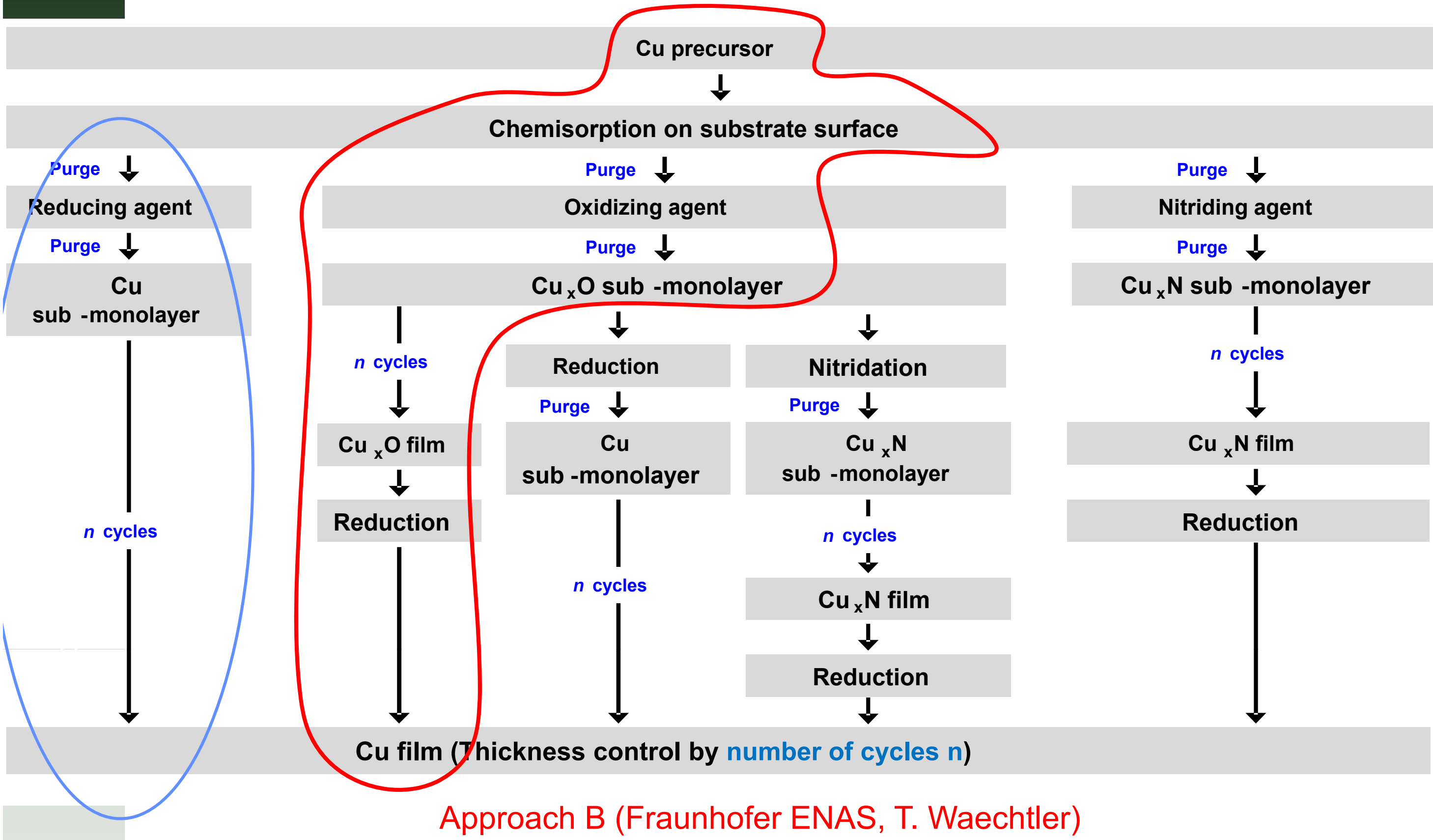


Why copper ALD?
- Seed layer for Cu damascene process
- Metallization of narrow holes and trenches, e.g. through-silicon vias (TSV)
- Conformally coating 3D nano-structures (porous materials, nanowires, CNTs, ...)



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

Known Approaches for Cu ALD

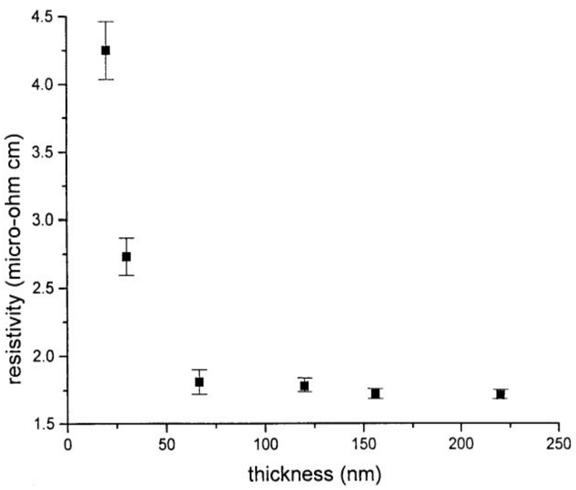


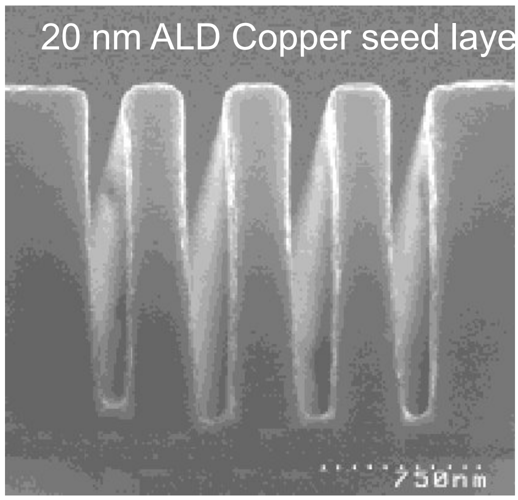
Approach B (Fraunhofer ENAS, T. Waechtler)

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

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 ⟶ 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

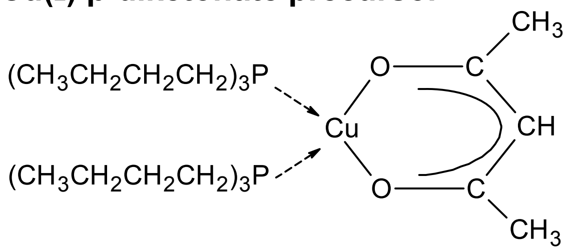
ALD cycles

Precursor Pulse
↓
Argon Purge
↓
Oxidation Pulse
↓
Argon Purge

Process temperature < 140°C

2nd step: Vapor phase reduction

- **Cu(I) β-diketonate precursor**



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

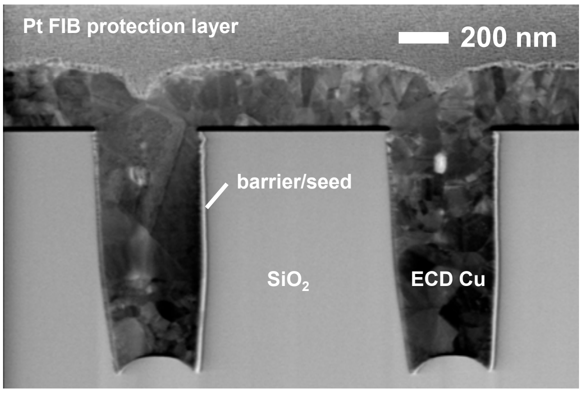
- **Oxidation by a mixture of water vapor and O_2 (“wet O_2“)**

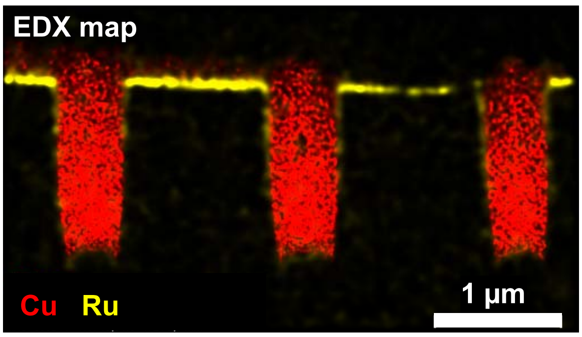
Well established process for Cu_xO ALD

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

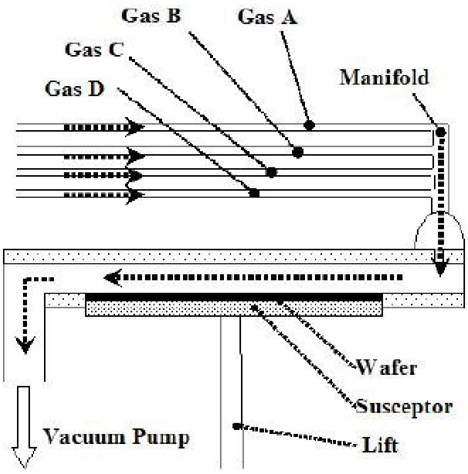
Combination Ru/ALD Cu could enable nanoscale interconnect metallization

Equipment: Reactor Types

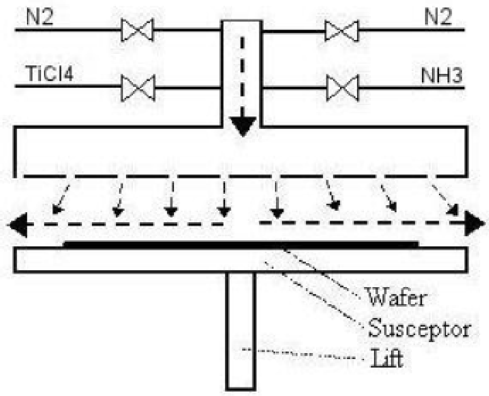
Source:

Picosun

Reactor Flow-type



Cross-flow Reactor



Perpendicular flow Reactor
“showerhead“

Equipment 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)