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

- 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 CVD: History

Examples of ALD Reactors Designed in Finland

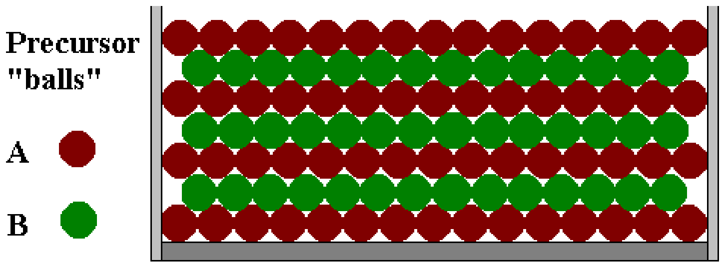
MC 120 CAT ALD reactor
Acquired by Picosun Oy
Developed in early 1990's
for R&D of heterogeneous
catalysts (e.g. US6534431)

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

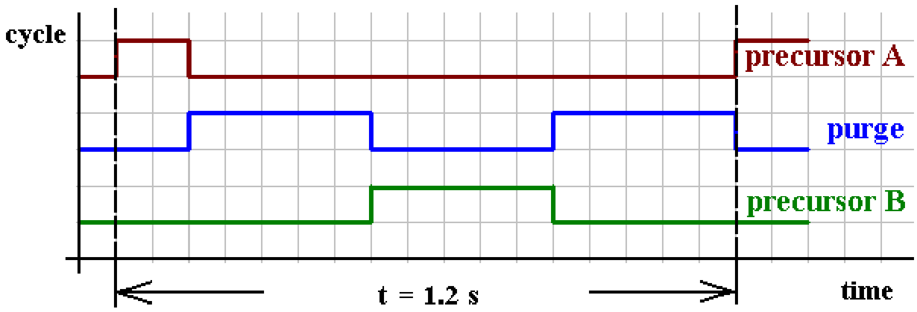
Atomic Layer-by-layer Growth



The intrinsic surface control mechanism:

- **Saturation of all the reaction**
- **Purging step**

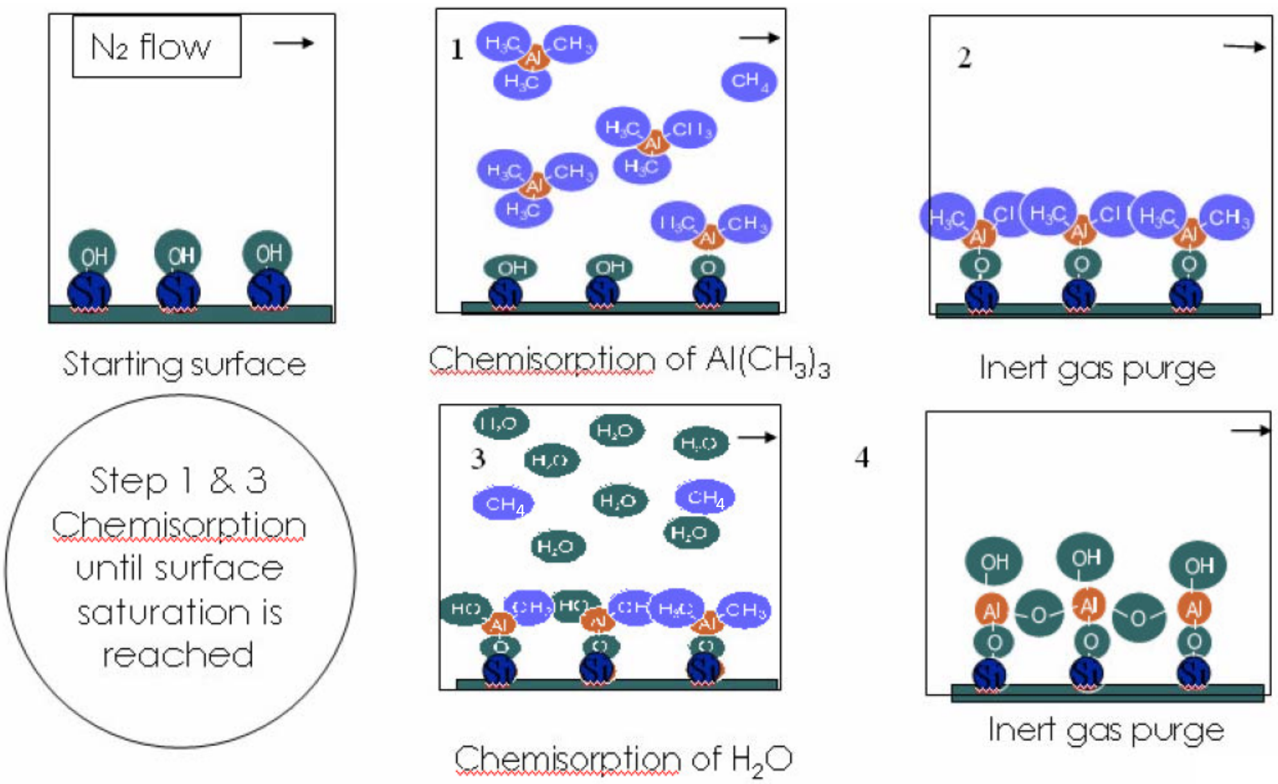
ALCVD Cycle



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

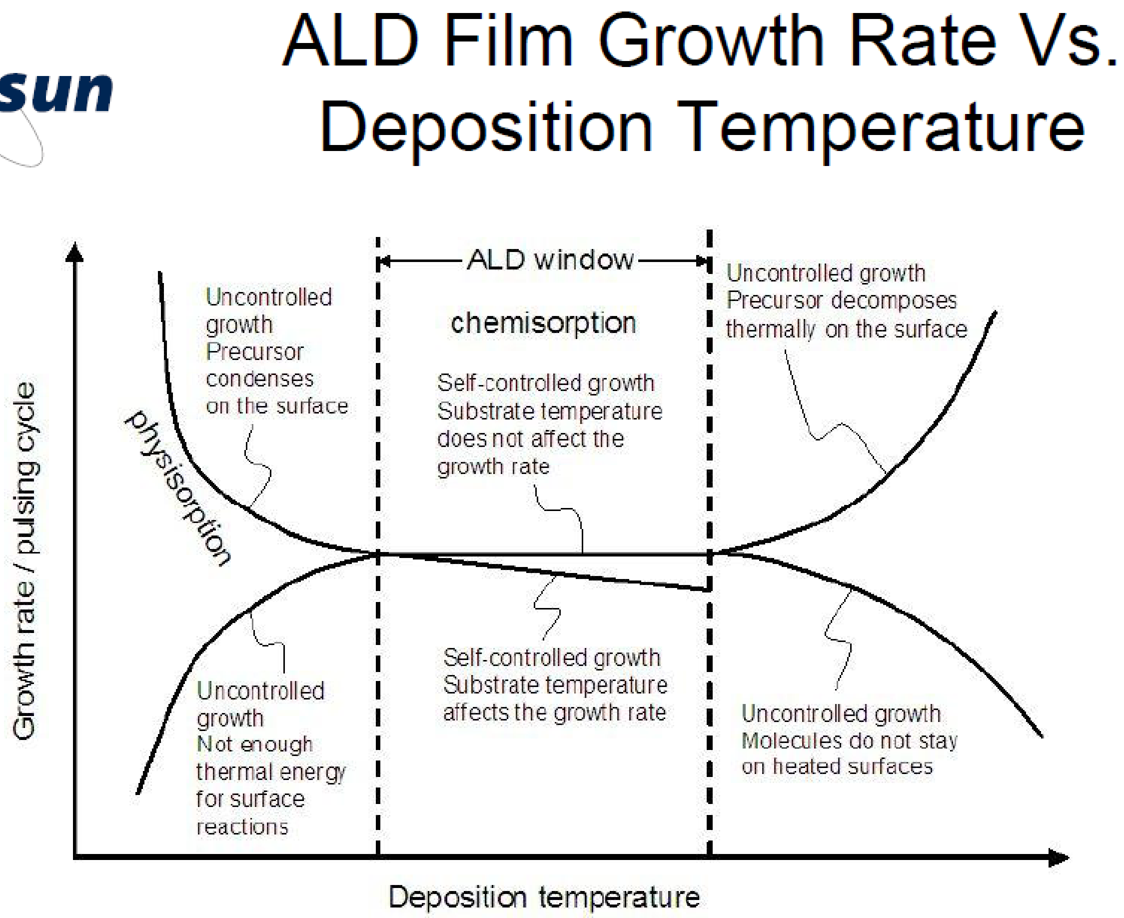
ALD of Al_2O_3 from TMA and H_2O



ASM

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

Atomic Layer CVD: Process Window



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

Atomic Layer CVD: Process Characteristics

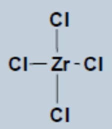
• Typical cycle time	0.5 - 5 s
- Precursor feed	0.05 - 1 s
- Purge	0.1 - 2 s
• Growth rate	0.3 - 1.5 Å / cycle
• Growth rate	10 - 100 Å / min
• Reaction temperature	150 - 500 °C
- Process window width	50 - 150 K
• Reaction pressure	1 - 10 mbar
• Purge / carrier gas	N_2, Ar
• Precursor (examples)	
- HfO_2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

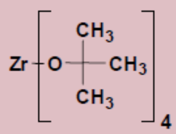


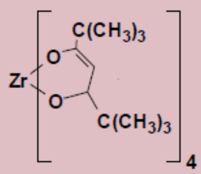
Metal Halides:
M–F, M–Cl, M–Br, M–I

Adv:
Thermal stability
Reactivity
Molecule size

Disadv:
By-products
Vapor pressure

Metalorganic



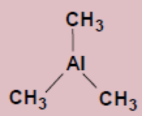


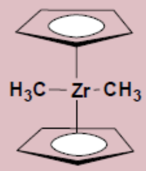
Metal alkoxides
Metal β-diketonates
Metal dialkylamidos
Metal amidinates

Adv:
Vapor pressure

Disadv:
Thermal stability
Reactivity
Molecule size

Organometallic





Metal alkyls
Metal cyclopentadienyls

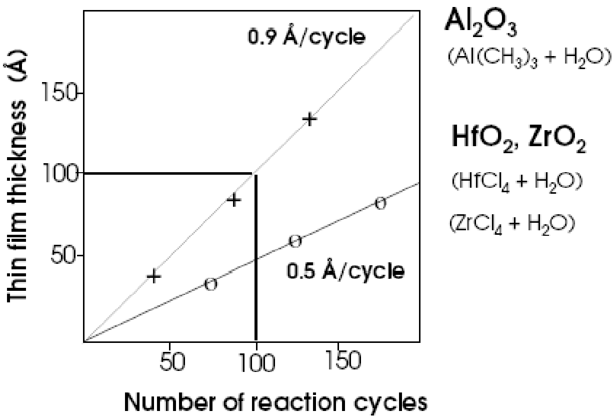
Adv:
Reactivity
Thermal stability
By-products
Vapor pressure

Disadv:
Availability

Source: Picosun Oy

ASM Front-End Operations

Overview currently available ALD Films

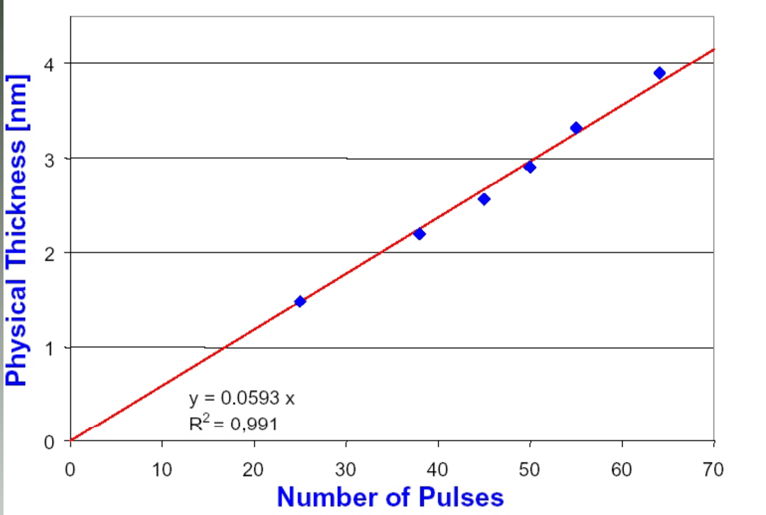


- Oxides
  - SiO2, Al2O3, HfO2, ZrO2, TiO2, Ta2O5, La2O3, Y2O3, MgO, Nb2O5, Sc2O3, CeO2, Ga2O3
  - mixed oxides like HfZrO, HfAlO, HfSiO
  - laminates like Al2O3/HfO2/Al2O3
  - SrTiO3, BaSrTiO3, BiTiO3, SrBiTaO, LaNiO3, LaCoO3
  - ZnO, ZnO:Al, In2O3, In2O3:Sn, SnO2, SnO2:Sb
- Nitrides
  - TiN, TaN, TaCN,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

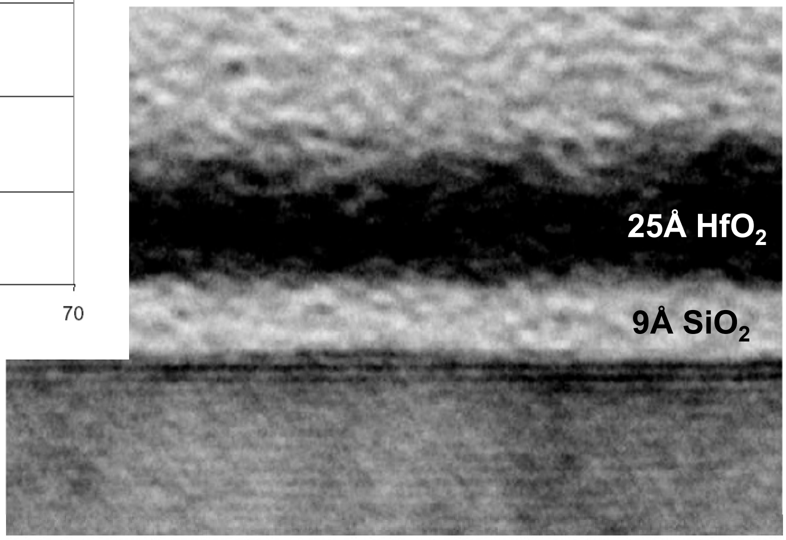
Atomic Layer CVD: Processes for IC Industry

- **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**

HfO_2 Sub-Monolayer Thickness Control



HfO_2 - TEM study



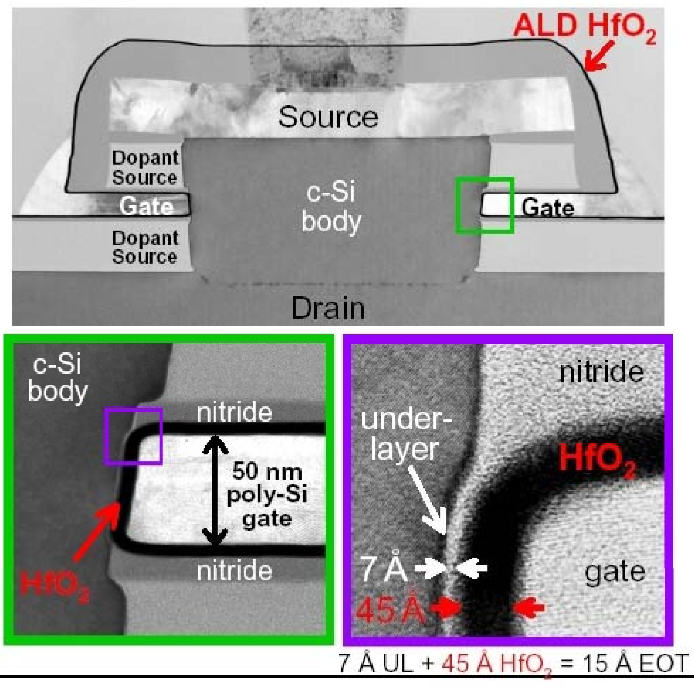
- excellent EOT < 16Å observed
- no additional SiO_2 growth

Ref.: M. Schumacher, GMM Workshop 2002

AIXTRON The CVD Engineering Company

Advanced Integrated Circuit Technology

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

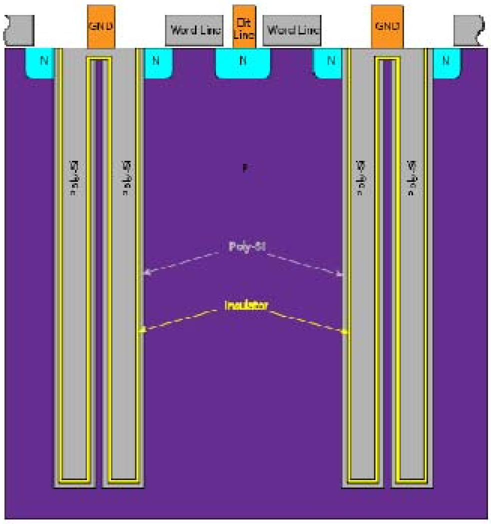
ASM

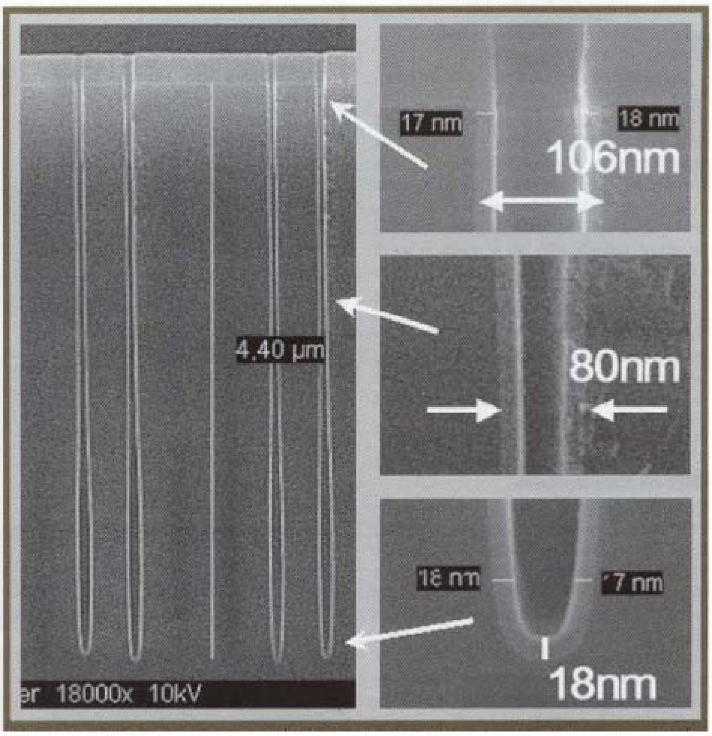
Ref.: J.W. Maes, GMM Workshop 2002

More Moore Examples - 1

DRAM Trench Capacitor

- Aspect ratio: > 60
- Al_2O_3

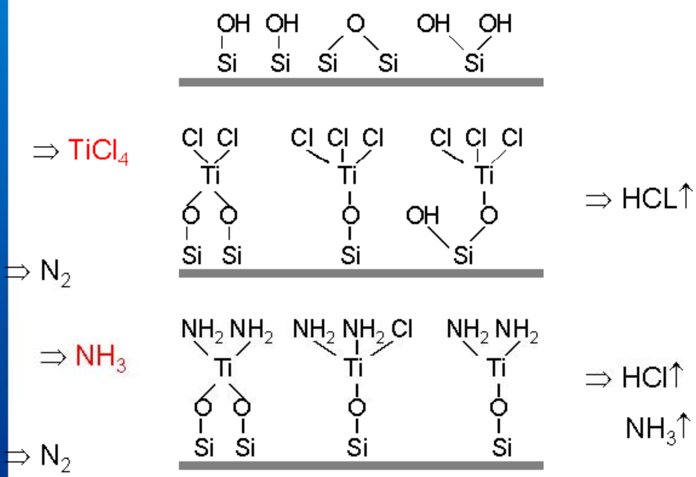


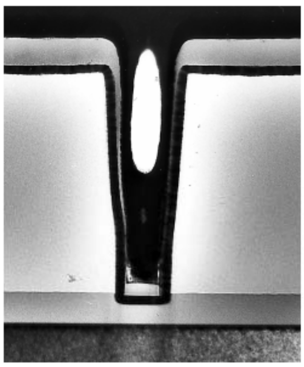


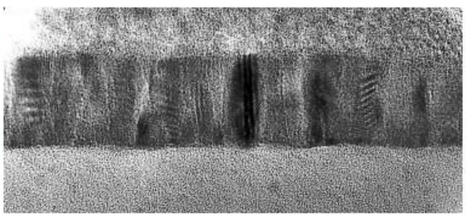
ALD of Diffusion Barrier Films

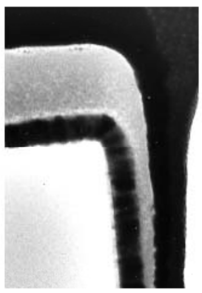
imec

ALCVD™





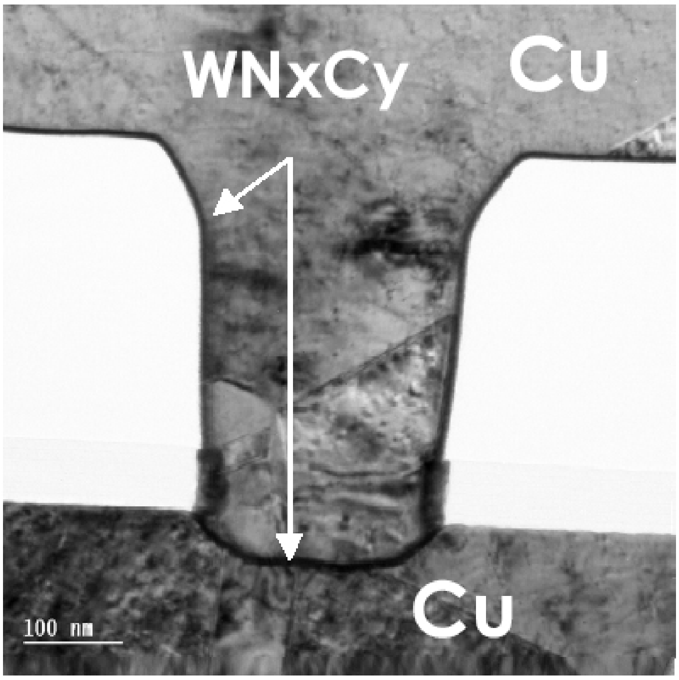




KM © imec 2001

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

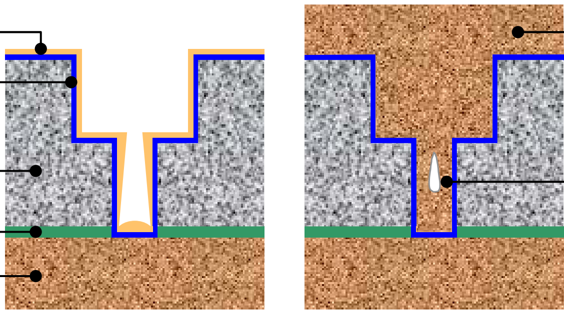
Advantages:

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

Disadvantages/Challenges:

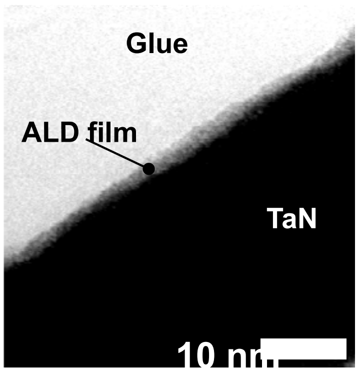
- Surface sensitivity
- Cost-effective only for very thin films
- For porous and part of low-density low-k materials only applicable at sealed surfaces

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

Advanced Integrated Circuit Technology

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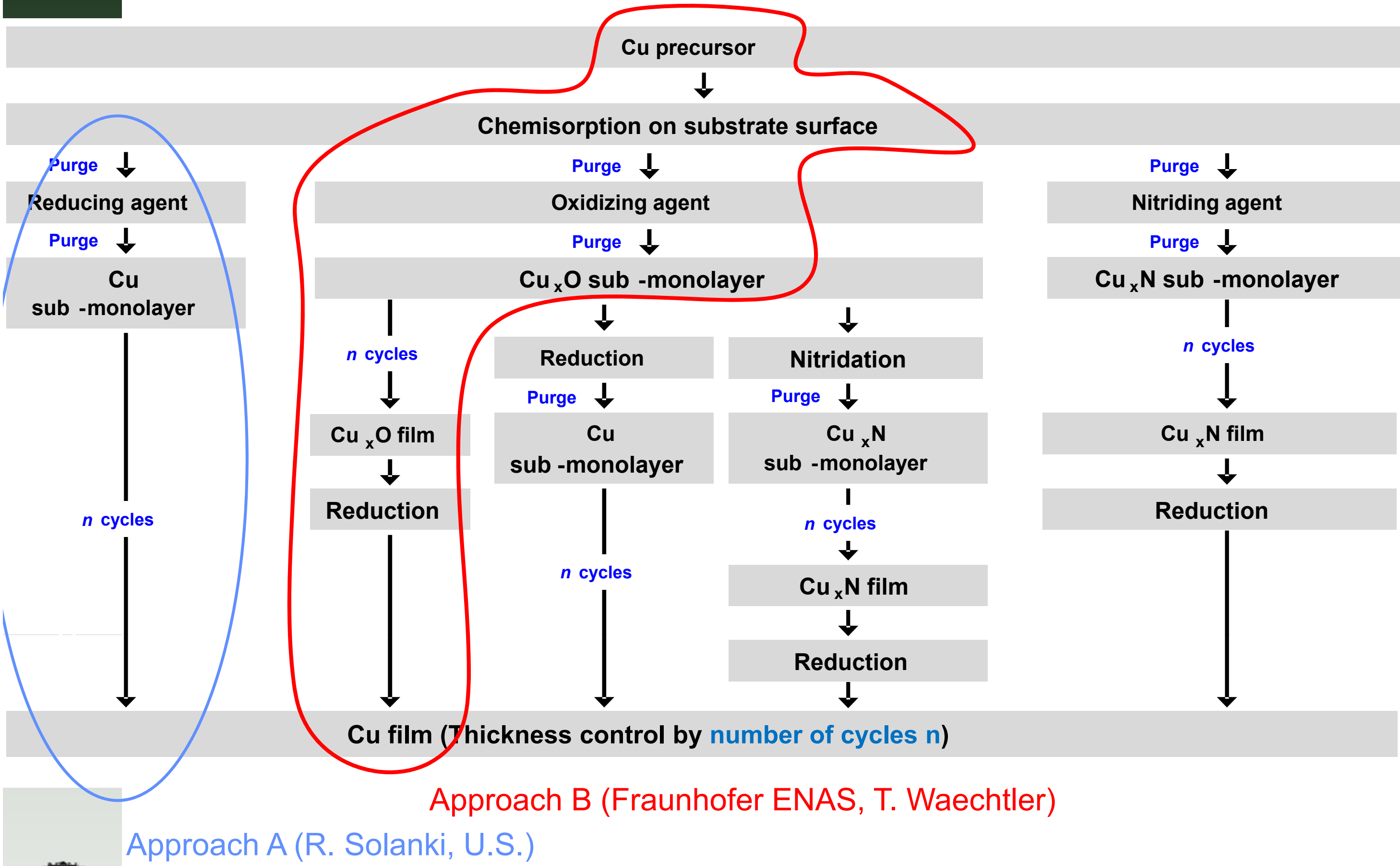
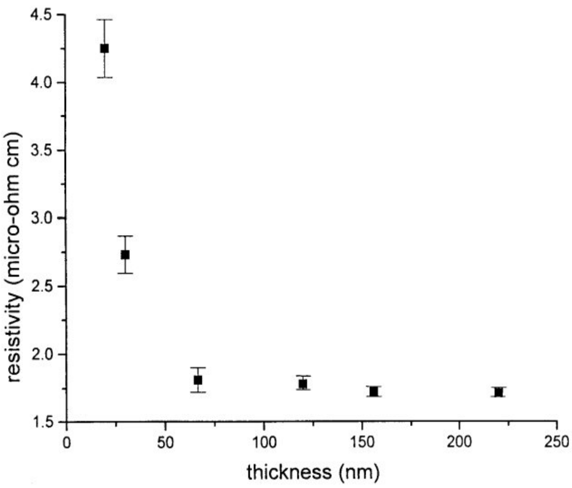
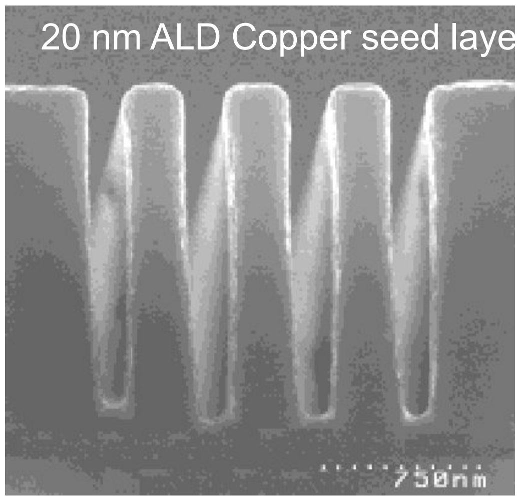
Known Approaches for Cu ALD



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

<u>First reaction step (alhohol pulse):</u> ROH $\longrightarrow$ R• (ad) + OH• (ad)   R.. Alkyl group

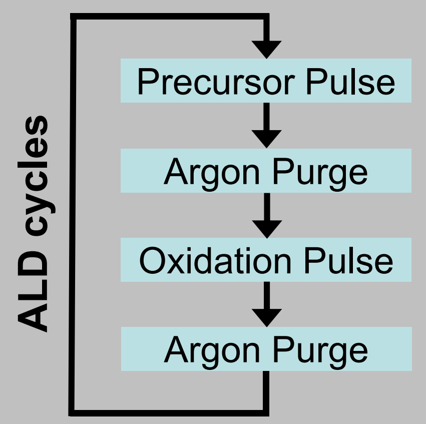
<u>Second reaction step ($Cu(hfac)_2$ pulse):</u>

$Cu(hfac)_2 \cdot X\, H_2O + H_2 + R\bullet\,(ad) + OH\bullet\,(ad) \longrightarrow Cu + RH + (CF_3)_2CH\bullet + (COOH)_2$

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

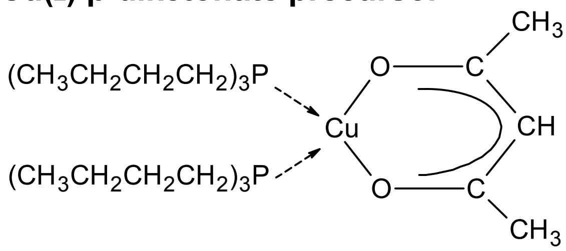
1st step: Copper oxide ALD



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

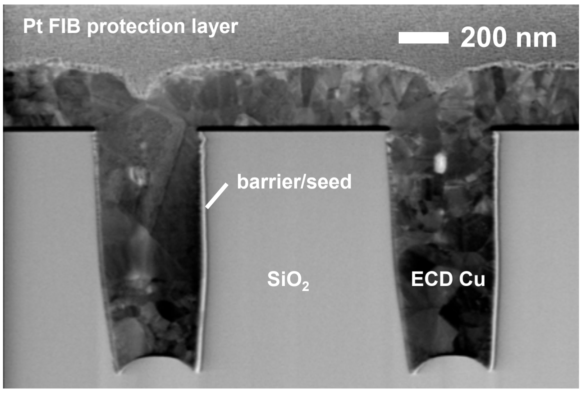
- **Oxidation by a mixture of water vapor and O_2 ("wet O_2")**

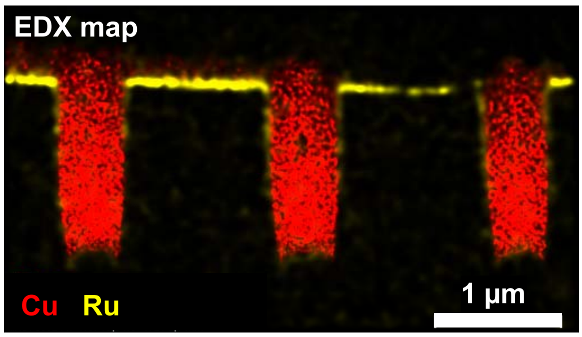
Well established process for Cu_xO ALD

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





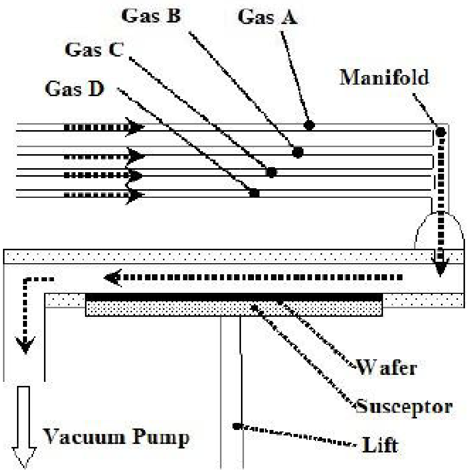
- Good filling behavior when combining ALD Cu and Ru already under unoptimized ECD conditions (note: conformal ECD, no buttom up fill !)
- PVD TaN/Ru stack showing strong thickness inhomogeneity within features
- Good conformality and step coverage of ALD copper seed

Combination Ru/ALD Cu could enable nanoscale interconnect metallization

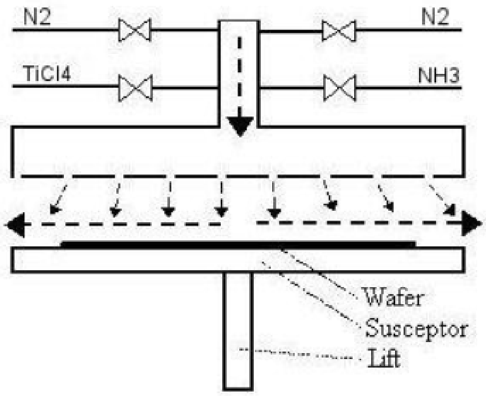
Equipment: Reactor Types

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)