

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**

**zfm**

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 1

Atomic Layer CVD: 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 Electroluminescent (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**

**zfm**

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 2



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)



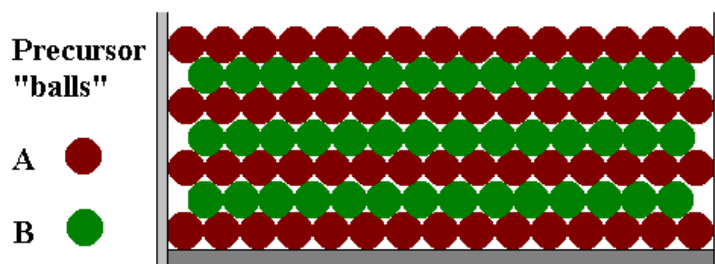
F-950 ALD reactor
Microchemistry Ltd.
Developed in 1990's
for flat panel production



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

Atomic Layer CVD

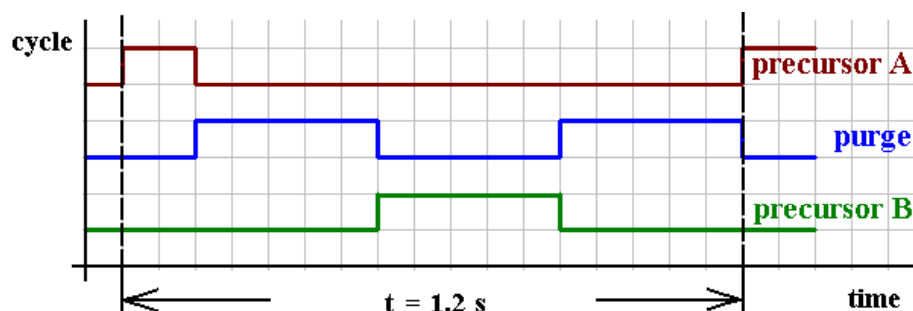
Atomic Layer-by-layer Growth



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**

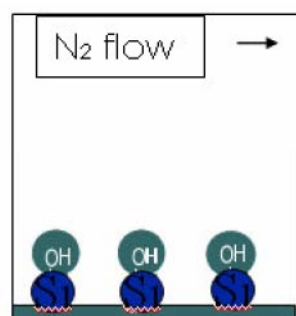


ZfM

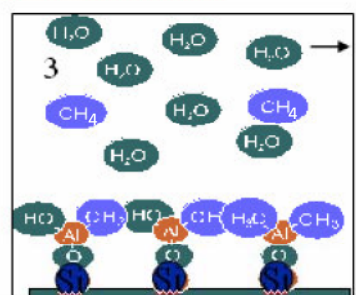
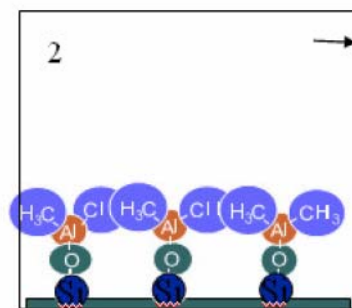
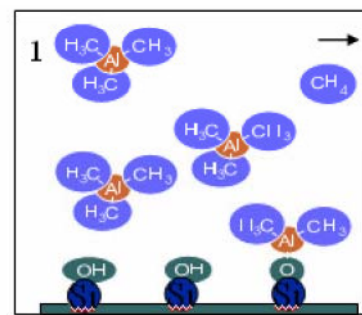
Fraunhofer
EMAS

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

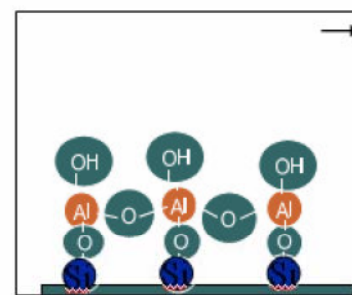
Chapter 3.4 - 5

ALD of Al_2O_3 from TMA and H_2O 

Step 1 & 3
Chemisorption
until surface
saturation is
reached



4



ASM



ZfM

Fraunhofer
EMAS

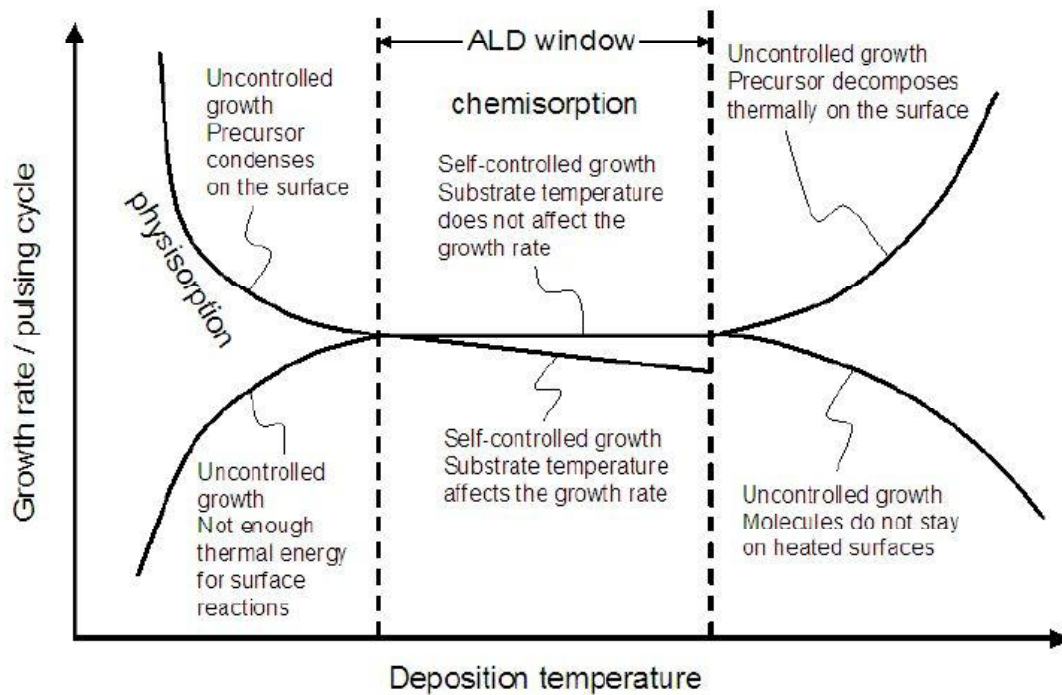
Source: B. van Nooten, EuroNanoForum, Prague, June 2-5, 2009

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 6



ALD Film Growth Rate Vs. Deposition Temperature



ZfM

Fraunhofer
EMAS

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 7

Atomic Layer CVD: Comparison of ALCVD and CVD

ALCVD

- 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

CVD

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



ZfM

Fraunhofer
EMAS

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 8

Atomic Layer CVD: Process Characteristics

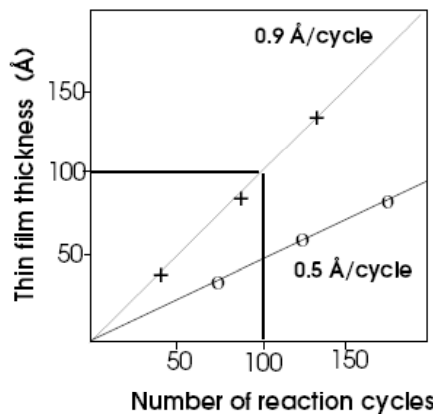
• Typical cycle time	0.5 - 5 s
- Precursor feed	0.05 - 1 s
- Purge	0.1 - 2 s
• Growth rate	0.3 - 1.5 Å / cycle
• Growth rate	10 - 100 Å / min
• Reaction temperature	150 - 500 °C
- Process window width	50 - 150 K
• Reaction pressure	1 - 10 mbar
• Purge / carrier gas	N ₂ , Ar
• Precursor (examples)	
- HfO ₂	HfCl ₄ + H ₂ O
- ZrO ₂	ZrCl ₄ + H ₂ O
- Al ₂ O ₃	Al(CH ₃) ₃ + H ₂ O
- TiN	TiCl ₄ + NH ₃ or TiCl ₄ + N ₂ + H ₂
- WCN	Et ₃ B + WF ₆ + NH ₃
- Cu	Cu(thd) ₂ + O ₃

ALD Precursor Classes



ALD Precursors

Inorganic	Metalorganic	Organometallic
$\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{Zr}-\text{Cl} \\ \\ \text{Cl} \end{array}$ <p>Metal Halides: M-F, M-Cl, M-Br, M-I</p> <p>Adv: Thermal stability Reactivity Molecule size</p> <p>Disadv: By-products Vapor pressure</p>	<div style="display: flex; justify-content: space-around;"> <div> $\text{Zr} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{O}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right]_4$ </div> <div> $\text{Zr} \left[\begin{array}{c} \text{O} \\ \\ \text{C}(\text{CH}_3)_3 \\ \\ \text{O} \\ \\ \text{C}(\text{CH}_3)_3 \end{array} \right]_4$ </div> </div> <p>Metal alkoxides Metal β-diketonates Metal dialkylamidates Metal amidinates</p> <p>Adv: Vapor pressure</p> <p>Disadv: Thermal stability Reactivity Molecule size</p>	<div style="display: flex; justify-content: space-around;"> <div> $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{Al}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ </div> <div> $\begin{array}{c} \text{Cyclopentadienyl} \\ \\ \text{H}_3\text{C}-\text{Zr}-\text{CH}_3 \\ \\ \text{Cyclopentadienyl} \end{array}$ </div> </div> <p>Metal alkyls Metal cyclopentadienyls</p> <p>Adv: Reactivity Thermal stability By-products Vapor pressure</p> <p>Disadv: Availability</p>



Al₂O₃
(Al(CH₃)₃ + H₂O)

HfO₂, ZrO₂
(HfCl₄ + H₂O)
(ZrCl₄ + H₂O)

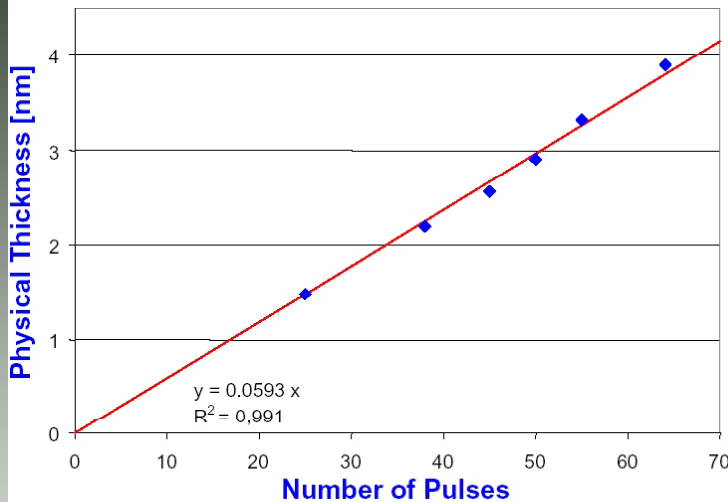
- **Oxides**
 - SiO₂, Al₂O₃, HfO₂, ZrO₂, TiO₂, Ta₂O₅, La₂O₃, Y₂O₃, MgO, Nb₂O₅, Sc₂O₃, CeO₂, Ga₂O₃
 - mixed oxides like HfZrO, HfAlO, HfSiO
 - laminates like Al₂O₃/HfO₂/Al₂O₃
 - SrTiO₃, BaSrTiO₃, BiTiO₃, SrBiTaO, LaNiO₃, LaCoO₃
 - ZnO, ZnO:Al, In₂O₃, In₂O₃:Sn, SnO₂, SnO₂:Sb
- **Nitrides**
 - TiN, TaN,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

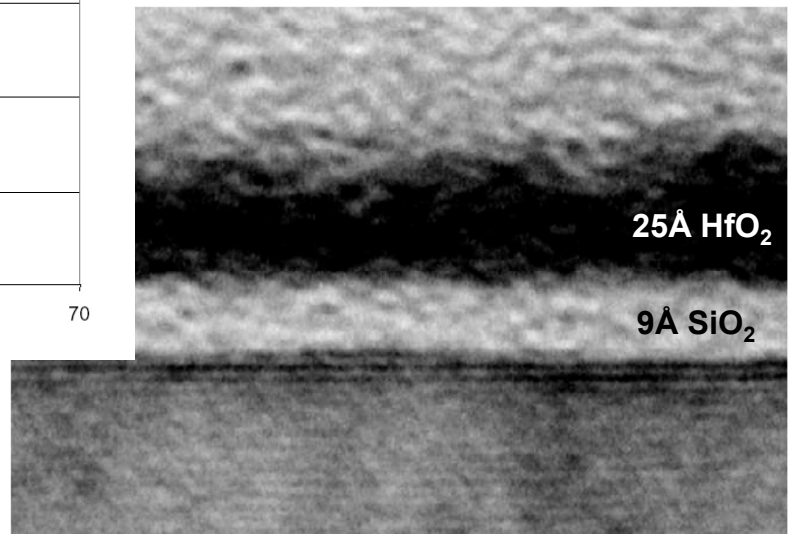
- **High-k gate dielectrics**
 - Replacement of current SiO₂/Si₃N₄ films
 - Processes available for ZrO₂, HfO₂, mixed materials
 - Targeted (equivalent) oxide thickness - EOT: ~ 1.0 nm
- **High-k capacitor dielectrics**
 - Replacement of current SiO₂/Si₃N₄, Ta₂O₅ films
 - ALCVD processes for Al₂O₃, Ta₂O₅
- **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

HfO₂ Sub-Monolayer Thickness Control



HfO₂ - TEM study



- excellent EOT < 16Å observed
- no additional SiO₂ growth

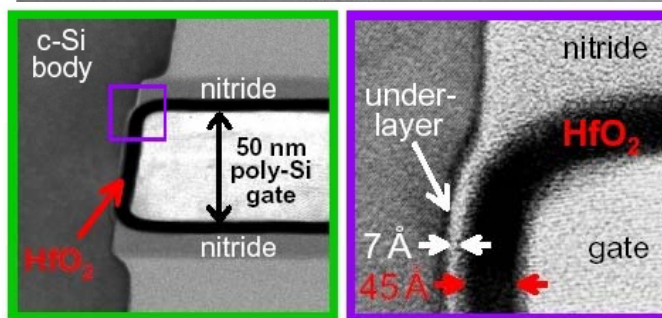
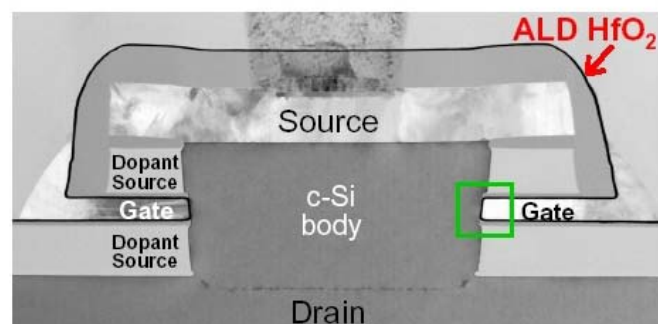
Ref.: M. Schumacher, GMM Workshop 2002

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 13

High-k Dielectrics for MOS Gates

Surface saturation results in excellent step coverage



$$7 \text{ Å UL} + 45 \text{ Å HfO}_2 = 15 \text{ Å EOT}$$

- 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

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

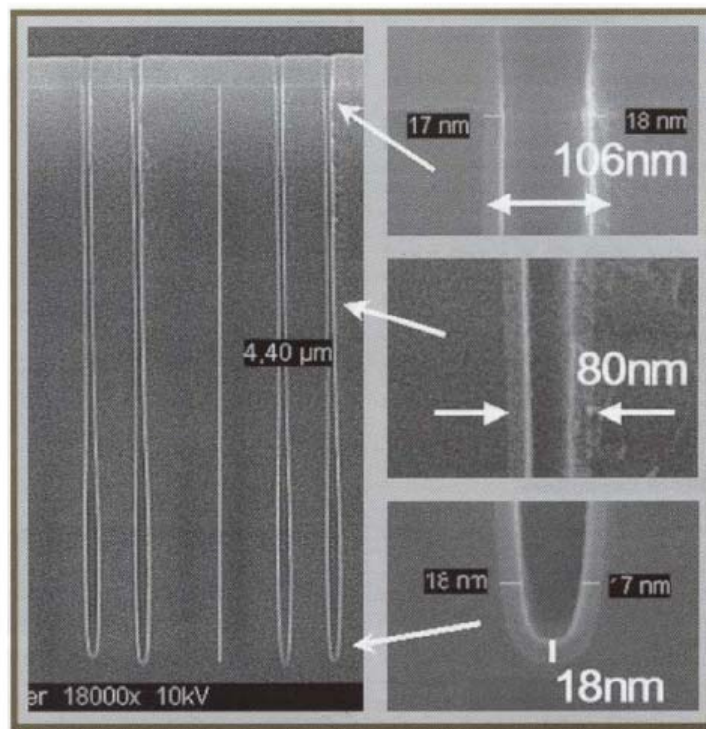
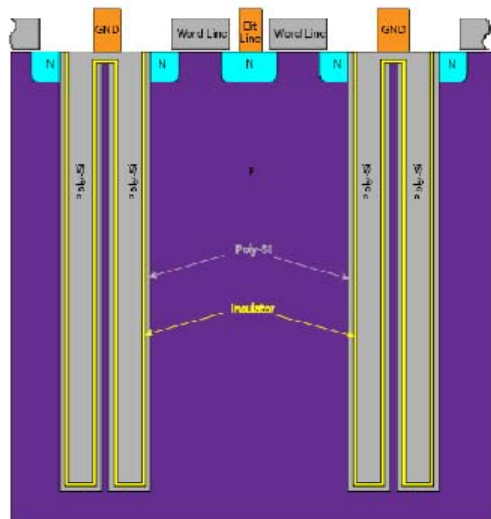


Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 14

DRAM Trench Capacitor

- Aspect ratio: > 60
- Al_2O_3



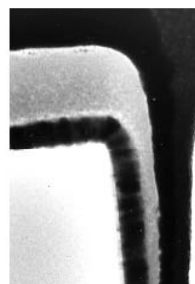
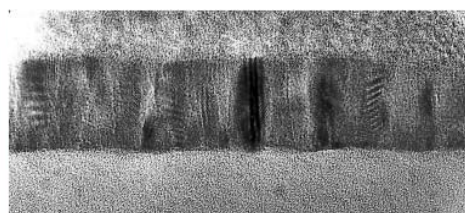
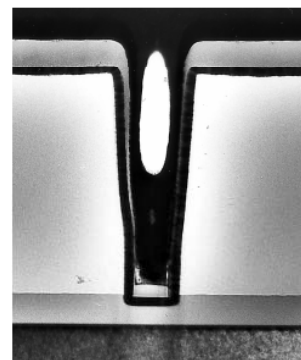
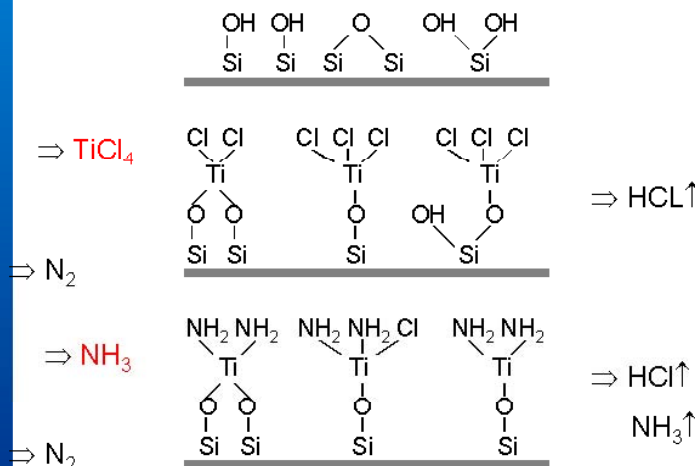
Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 15

ALD of Diffusion Barrier Films



ALCVD™



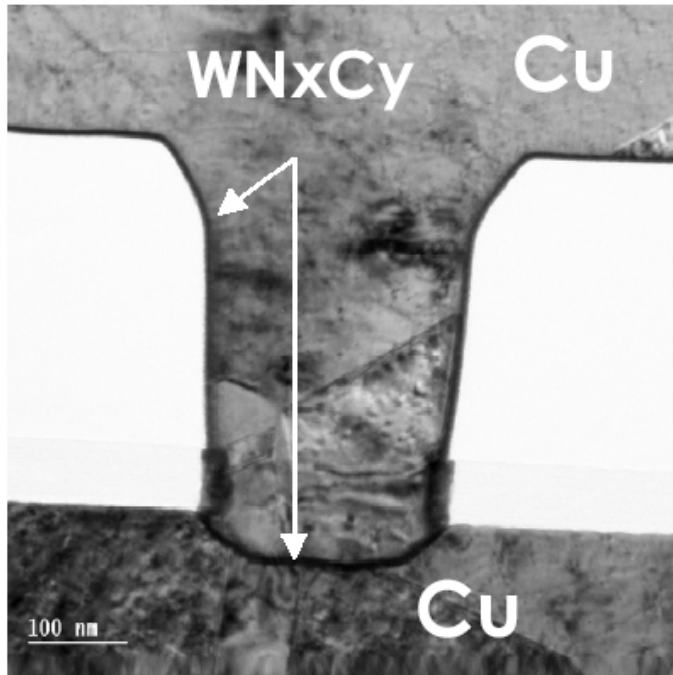
KM © imec 2001

Interconnect Technologies and Silicides (ITS)

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 16

Atomic Layer Deposition of WCN barrier films



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

Application of ALD to barrier films

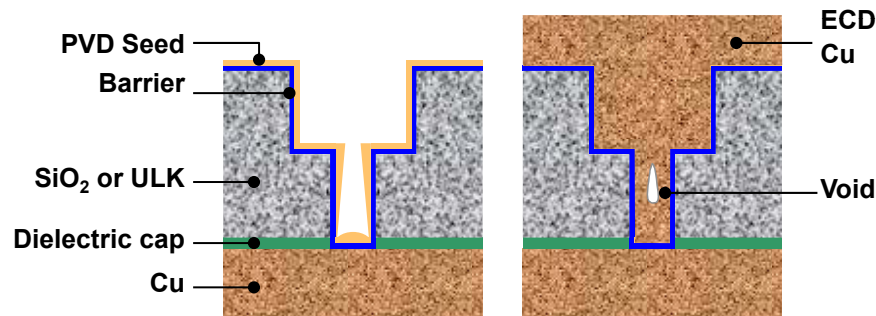
Advantages:

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

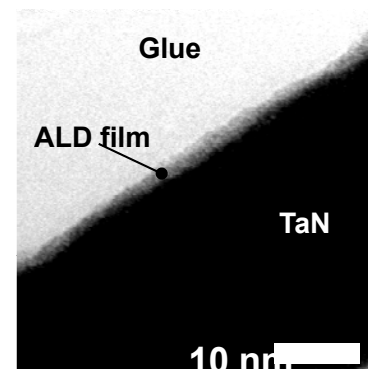
Disadvantages/Challenges:

- 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

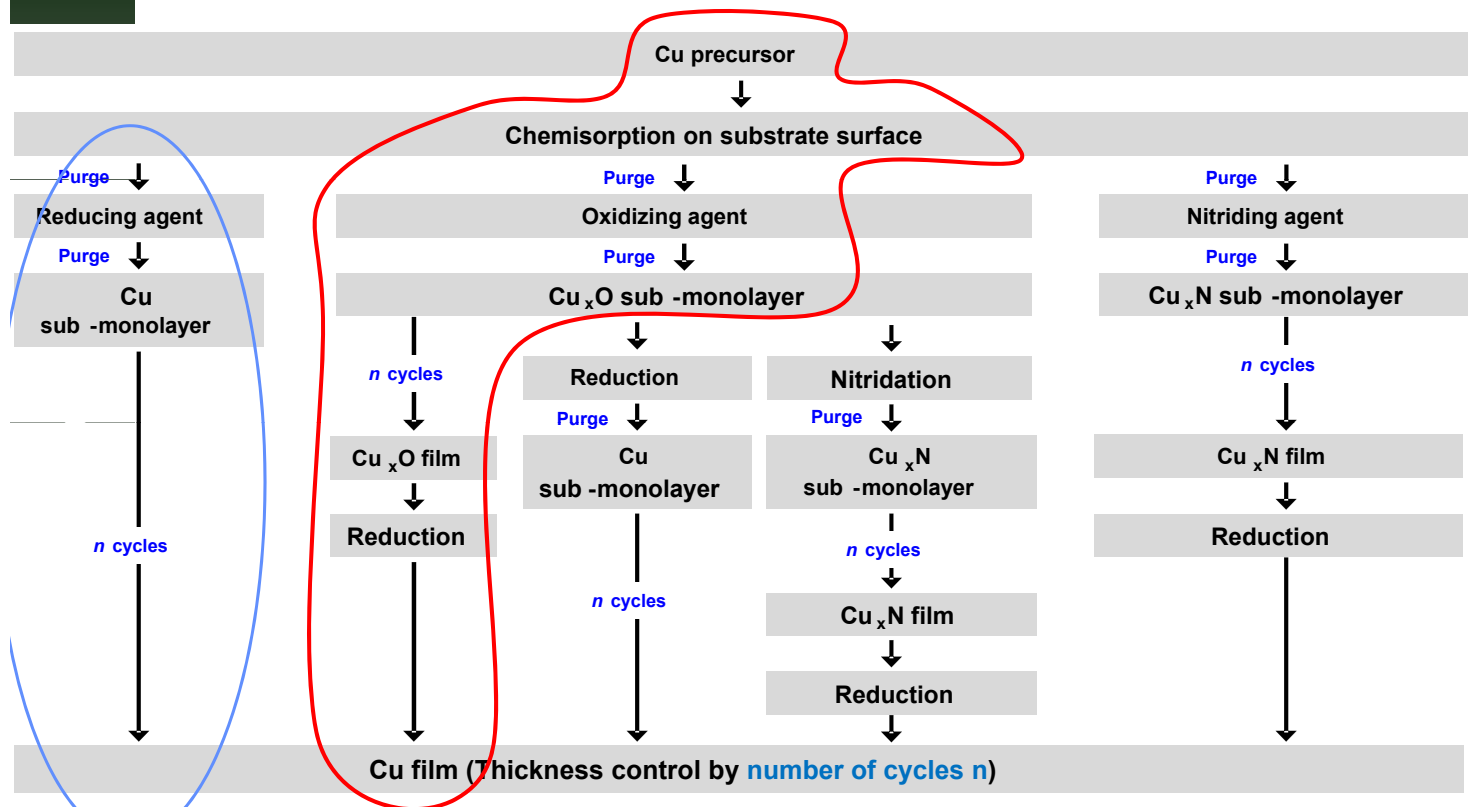
**Why copper ALD?**

- Seed layer for Cu damascene process
- Metallization of narrow holes and trenches, e.g. through-silicon vias (TSV)
- Conformally coating 3D nanostructures (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.)



ZfM

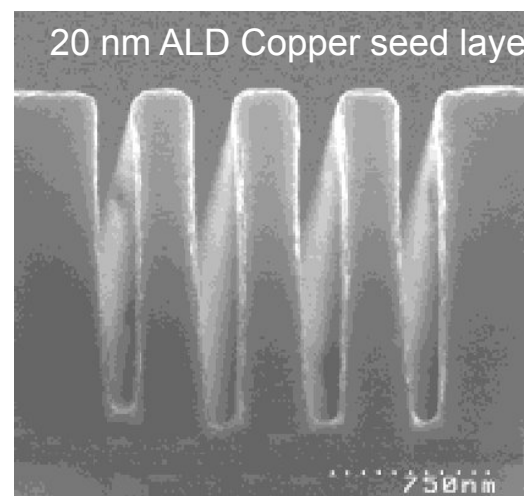
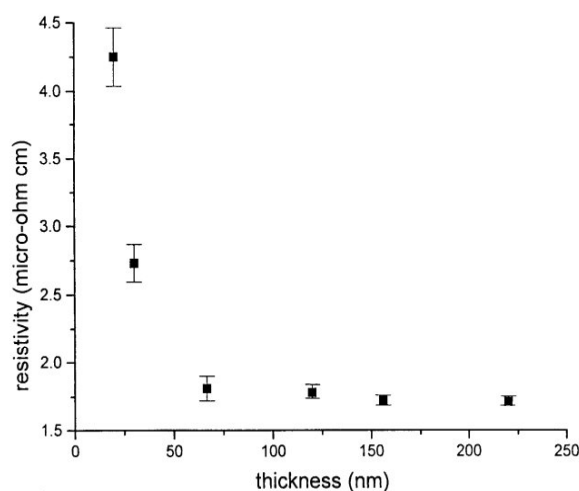
Fraunhofer
EMAS

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 19

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

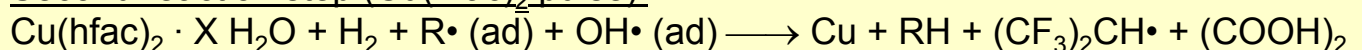
- Cu source: Cu(II) hexafluoroacetylacetonate (Cu(hfac)₂)
- Reducing agents: Methanol, Ethanol, Isopropyl alcohol (IPA), Formalin
- Typical deposition temperature: 300°C



Possible ALD reaction mechanism

First reaction step (alcohol pulse): $\text{ROH} \longrightarrow \text{R}^\bullet (\text{ad}) + \text{OH}^\bullet (\text{ad})$ R.. Alkyl group

Second reaction step (Cu(hfac)₂ pulse):



Ref.: R. Solanki, ALD Conference 2001



ZfM

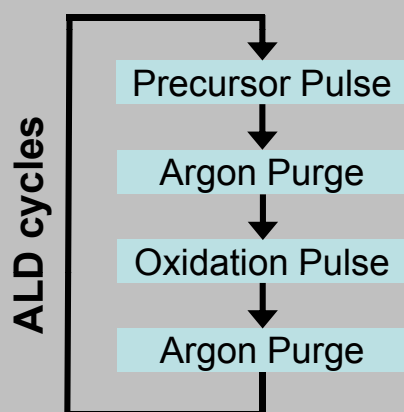
Fraunhofer
EMAS

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

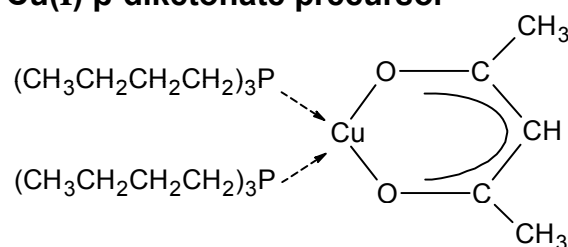
Chapter 3.4 - 20

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

1st step: Copper oxide ALD



• Cu(I) β -diketonate precursor



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

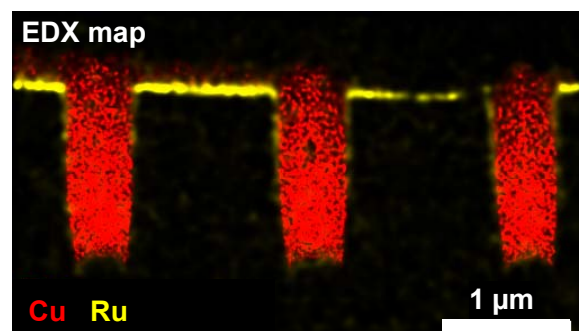
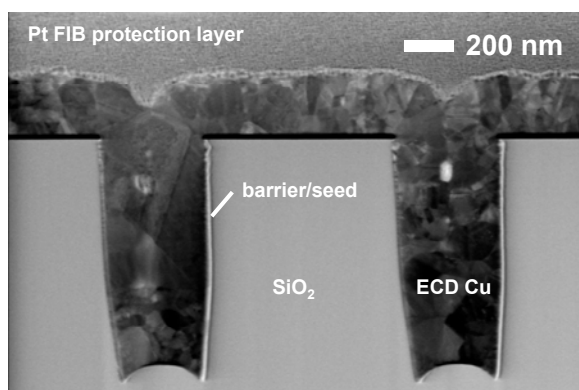
• Oxidation by a mixture of water vapor and O₂ (“wet O₂“)

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 bottom up fill !)
- PVD TaN/Ru stack showing strong thickness inhomogeneity within features
- Good conformality and step coverage of ALD copper seed

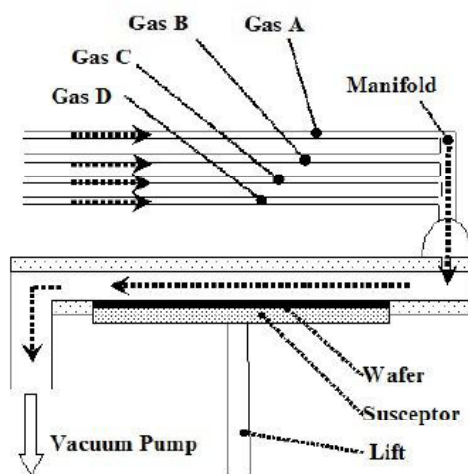
Combination Ru/ALD Cu could enable nanoscale interconnect metallization

Equipment: Reactor Types

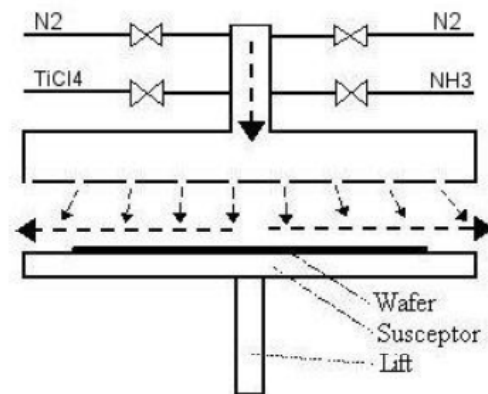
Source:



Reactor Flow-type



Cross-flow Reactor



Perpendicular flow Reactor
"showerhead"



ZfM

Fraunhofer
EMAS

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 23

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)



ZfM

Fraunhofer
EMAS

Only for internal use at TU Chemnitz for study purposes.
Unauthorized copying and distribution is prohibited.

Chapter 3.4 - 24