

Content

3 Specific Processes for Advanced Micro- and Nanoelectronics

- 3.1 Special CVD Processes
- 3.2 Epitaxy
- 3.3 Advanced PVD Processes
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- 3.5 Ion Implantation / Special Annealing Processes
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- 3.8 Chemical Mechanical Polishing/Planarization
- 3.9 Electrochemical Deposition and Electroless Deposition

**ZfM****Fraunhofer**
EMAS

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Chapter 3.1 - 1

3.1 Special CVD Processes

- 3.1.1 Metal CVD (W, Cu)
- 3.1.2 Metal Nitride CVD - Conductive Diffusion Barriers
- 3.1.3 Applications of CVD poly-Si, SiO₂, Si_xN_y ...
- 3.1.4 CVD of low-k dielectrics

3.1.1 Metal CVD

(A) Tungsten (W) CVD

- Application and integration aspects
- Precursors and reactions
- Process characteristics and film properties
- Selective process

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EMAS

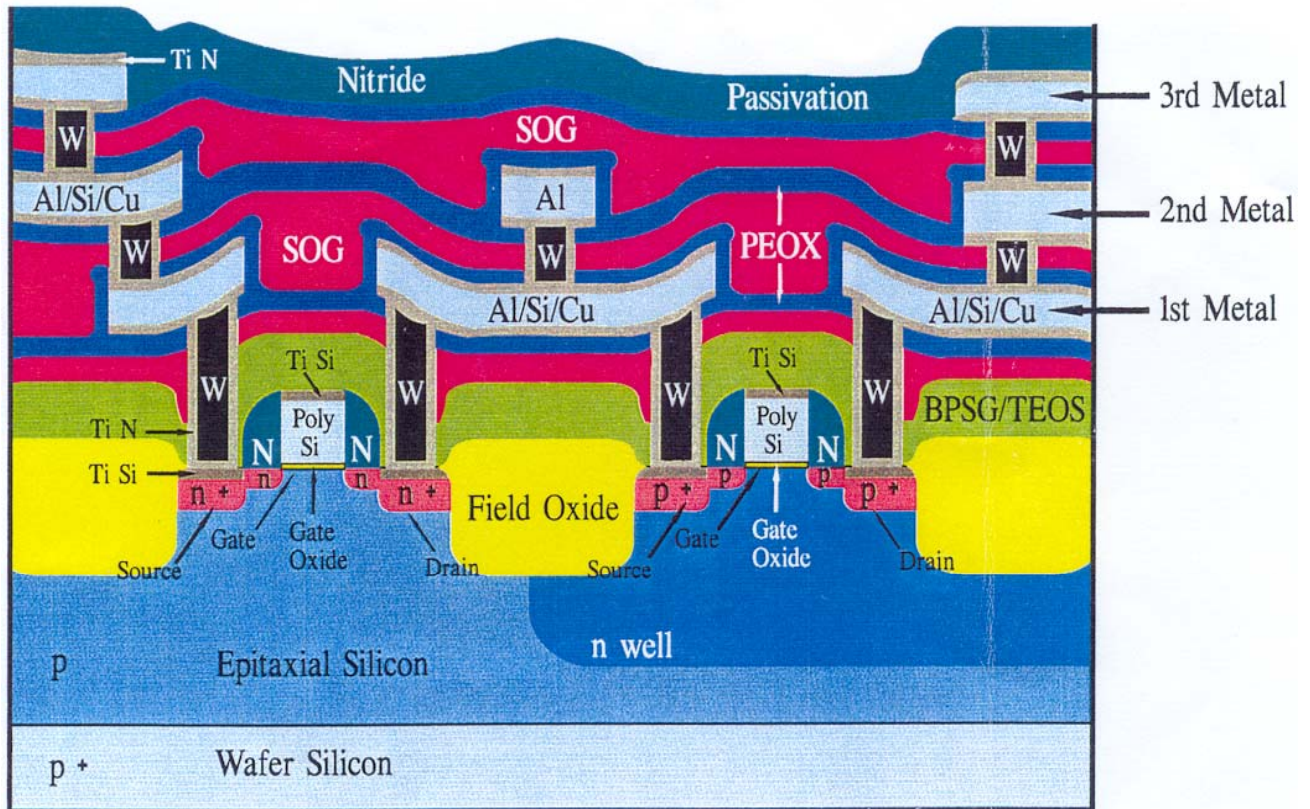
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Status: 01.04.2014

Chapter 3.1 - 2

Application and integration aspects of CVD-W

Three Metal Layer CMOS Device



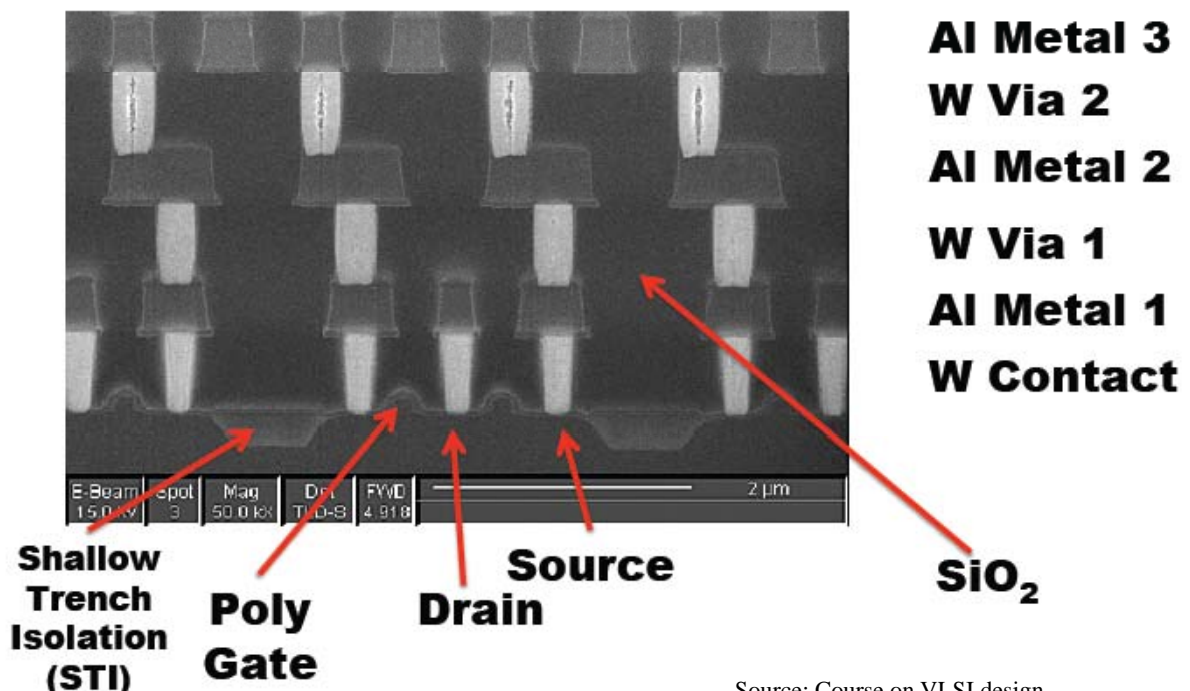
Source: PTI Seminars, Inc, 1749 Gilsinn Ln, St. Louis, MO 63026

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Chapter 3.1 - 3

Application and integration aspects of CVD-W

TSMC 0.18 CMOS Cross Section



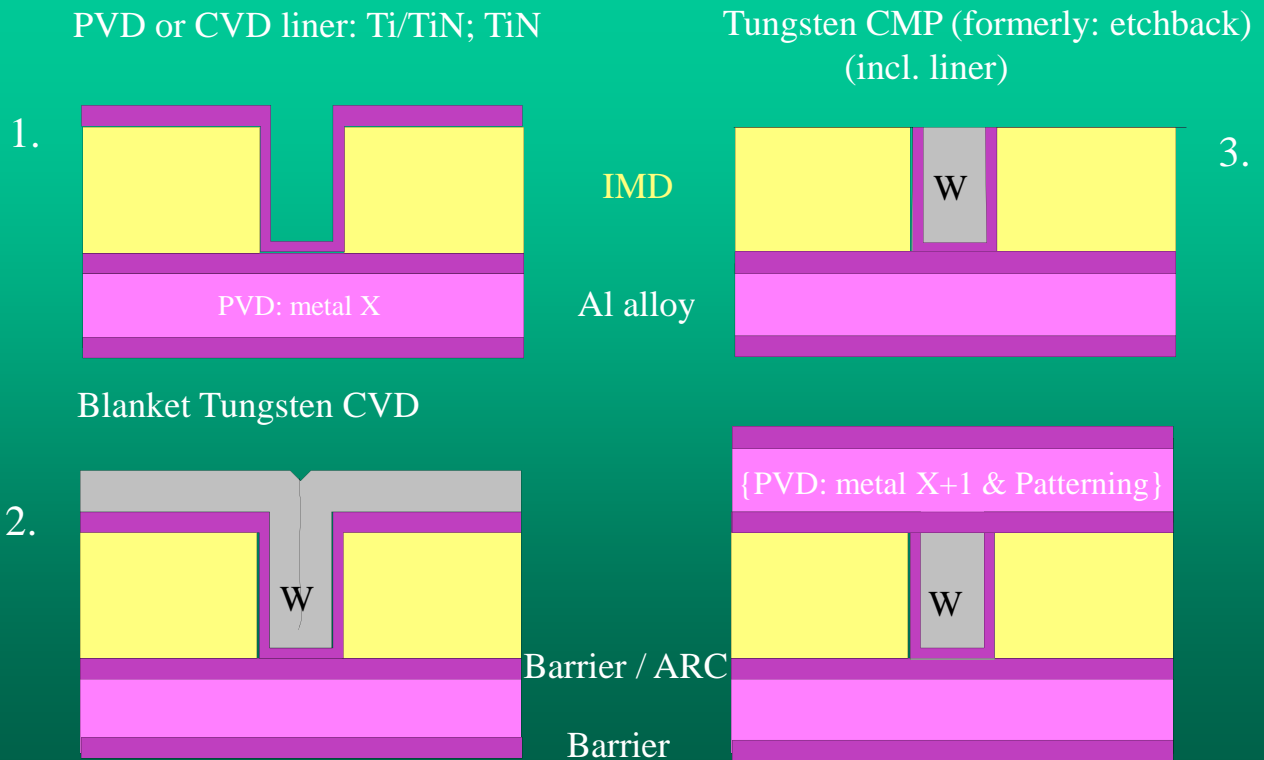
Source: Course on VLSI design
Peter Kogge, Joseph Nahas (University of Notre Dam)

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CVD Tungsten Via Fill: Process sequence („W plug“)

Tungsten via fill (W plug) using blanket W-CVD (contact fill accordingly)



Tungsten CVD: Precursors

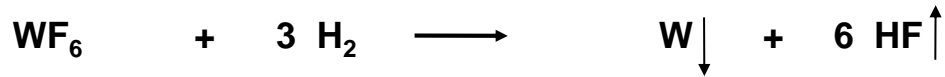
Precursor	Phase (@RT, air pressure)	vapour pressure
WF_6	gaseous	880 Torr (21 °C)
WCl_6	solid	0.7 ... 7 Torr (150...200 °C)
$W(CO)_6$	solid	10 ... 50 mTorr (30 °C)
metalorganic		

Tungsten deposition using WF_6 is very sensitive to the wafer surface materials:

- faster nucleation on metallic and conducting surfaces
- bad nucleation and adhesion on insulators
- liner for blanket deposition required
- selective deposition mode possible

Tungsten CVD: Reactions

Hydrogen reduction of WF_6 : blanket W deposition for contact and via fill



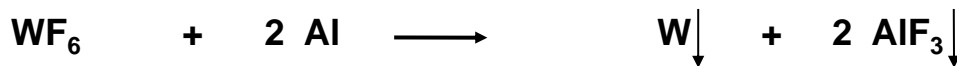
*Silane reduction of WF_6 : nucleation step for blanket W CVD
selective deposition for contact or via fill*



Silicon reduction of WF_6 : parasitic reaction during contact fill on Si



Aluminium reduction of WF_6 : parasitic reaction during via fill



AlF_3 increases via resistance: liner as barrier against WF_6 diffusion required

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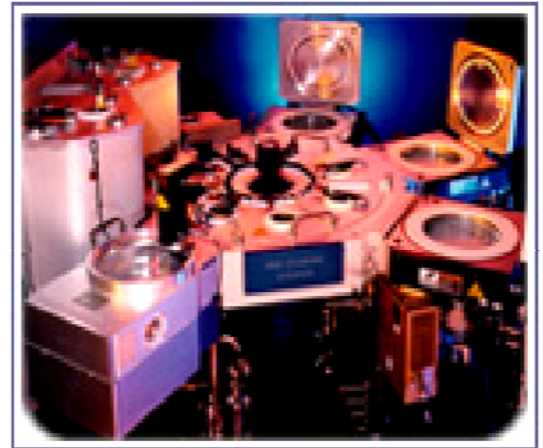
Tungsten CVD: Process characteristics

Nucleation step:

- SiH_4 / WF_6
- Low p (e.g. 5 Torr)

Main deposition:

- H_2 / WF_6
- High pressure 80...300 Torr
- 375...470°C
- Chamber clean between deposition
- Plasma or remote microwave
- Increases MWBC (wet clean)
- F-based chemistry with following H_2 clean



Temperature effect ($T \downarrow$:)

- resistivity \uparrow
- step coverage \downarrow
- deposition rate \downarrow

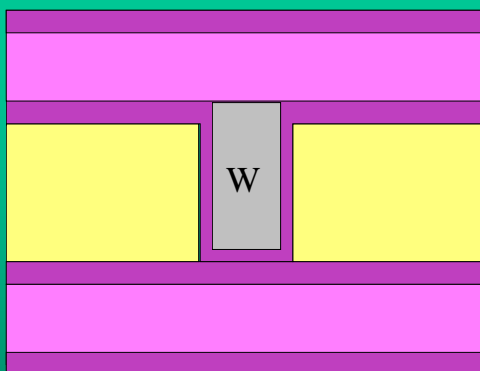
Tungsten CVD:**Film properties**

Parameter	Via Fill	Interconnect
W Thickness	500 nm	350 nm
Bulk resistivity	< 11.5 $\mu\Omega\text{cm}$	< 10.5 $\mu\Omega\text{cm}$
film reflectance (bei 480 nm)	60%	70%
Stress $T_{\text{dep}} = 440^\circ\text{C}$	1.5 GPa	1.5 GPa
$T_{\text{dep}} = 375^\circ\text{C}$	1.9 GPa	1.9 GPa
Step coverage		
0.25 μm , 8:1 AR $T_{\text{dep}} = 375^\circ\text{C}$	90%	NA
0.30 μm , 5:1 AR $T_{\text{dep}} = 440^\circ\text{C}$	90%	NA
Sheet resistance uniformity		
WIW (1σ)	< 2%	< 2%
WTW (1σ)	< 2%	< 2%

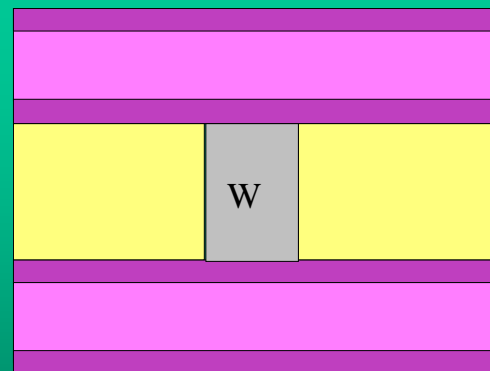
Source: Applied Materials (<http://appliedmaterials.com/products>)

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Tungsten CVD:**Selective deposition****Blanket Tungsten CVD**

Via clean
Liner deposition
W CVD
W CMP

Selective Tungsten CVD

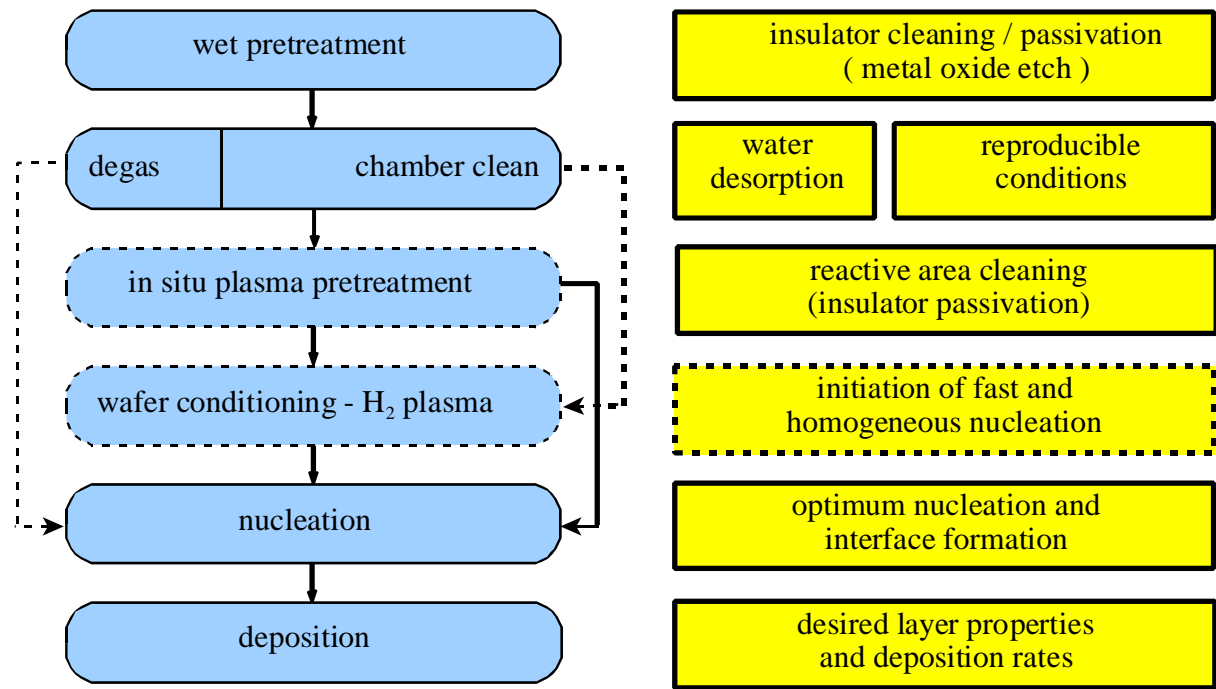
Via clean
W CVD

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Tungsten CVD:

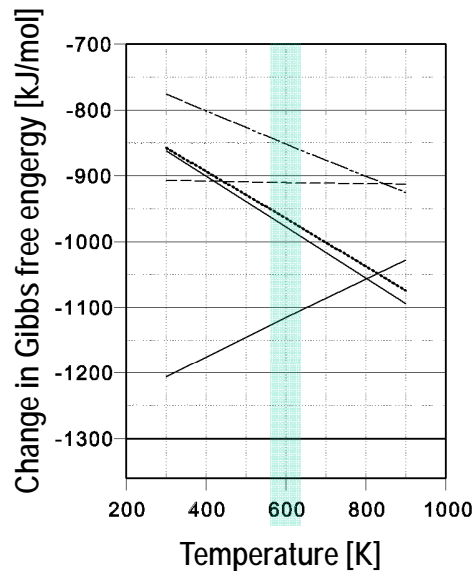
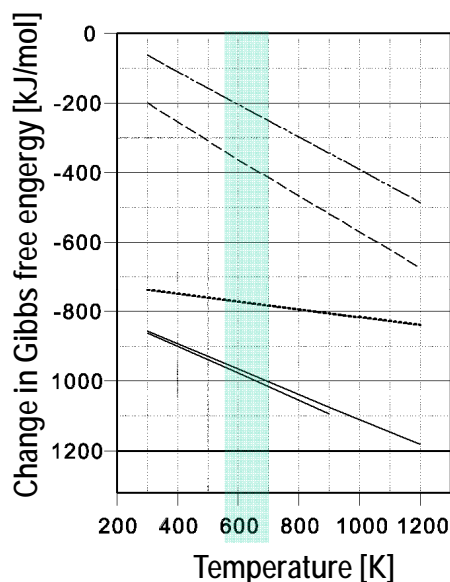
Selective deposition



required process steps depend on
reactive area material (e.g. Al, TiN)

Source: S.E. Schulz, PhD thesis, TU Chemnitz, 1996

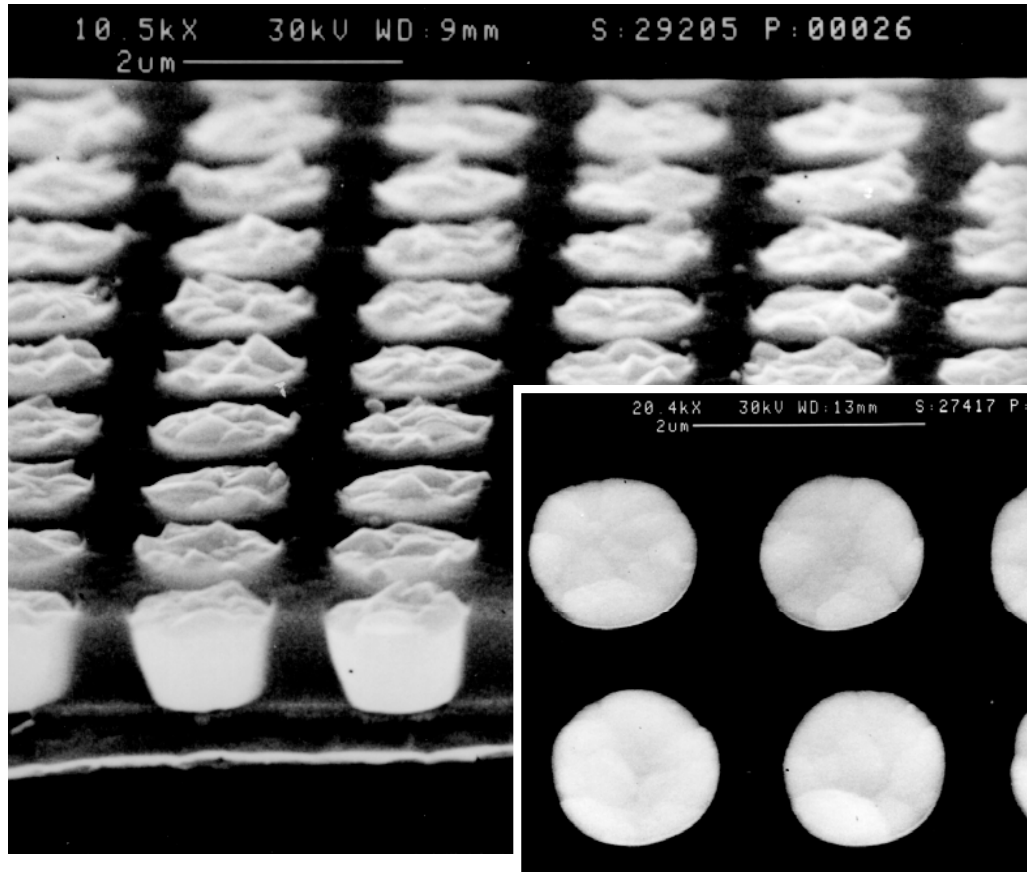
Tungsten CVD:

Reactions -
Thermodynamic
considerationsReduction reactions
on Al

- Al [AlF₃ (g)]
- Al [(AlF₃)₂ (g)]
- SiH₄ [SiF₄/H₂]
- SiH₄ [SiHF₃/H₂]
- Al [AlF₃ (s)]

Reduction reactions on Si

- H₂-Red.
- Si-Red. (SiF₂)
- Si-Red. (SiF₄)
- SiH₄-Red. (SiF₄)
- SiH₄-Red. (SiHF₃)

Tungsten CVD:**Selective deposition**

Source: S.E. Schulz, PhD thesis, TU Chemnitz, 1996

3.1.1 Metal CVD

(B) Copper (Cu) CVD

- Application and integration aspects
- Precursors and reactions
- Process characteristics and film properties
- Adhesion of copper

Copper CVD: Application and integration aspects

Potential fields of application (not yet in production!):

- Patterns with high aspect ratios can be covered conformal
- Metallization of on-chip Cu damascene interconnects or through silicon vias (TSVs) for 3D integration (see chapter 6):
 - Complete fill of via/trench or TSV patterns
 - Seed layer for subsequent fill using copper electroplating

Technical requirements for use

- State of the art single wafer cluster tool with CVD-chamber
- Direct liquid inject or vaporizer system for precursor delivery (variety of systems available by AMAT, Bronkhorst, MKS, Kemstream, ...)
- Efficient in situ chamber clean (not available yet)

Interaction with other processes / layers

- Adhesion is an critical issue
- Process has low thermal budget, applicable for temperature sensitive materials

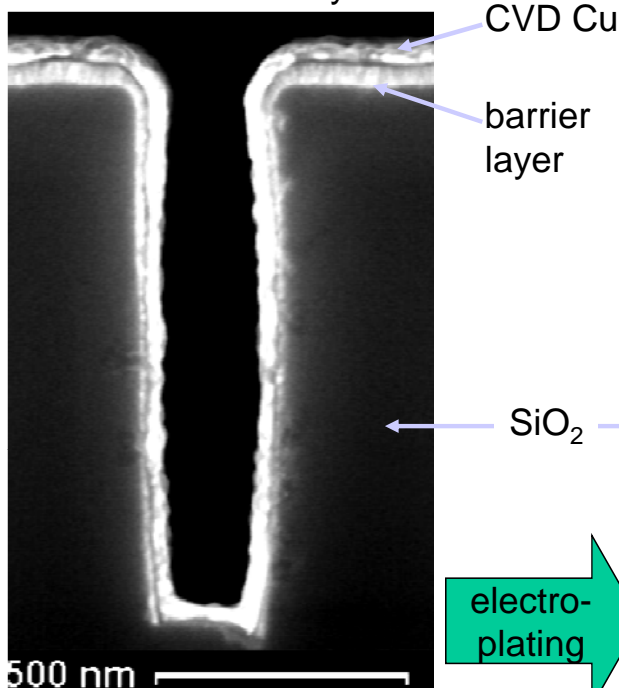
Cost

- Precursor cost (still) high – no high volume fabrication
- Limited throughput

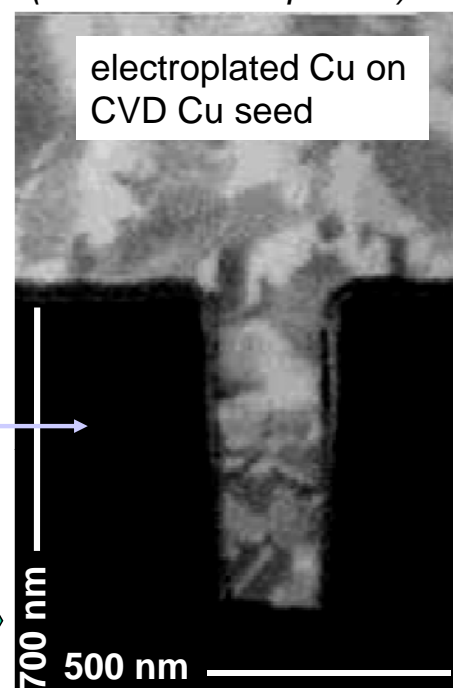
Copper CVD: Application and integration aspects

Example of use: CVD-Cu as seed layer for electroplating of Cu

Oxide trench covered with barrier layer and CVD Cu as seed layer



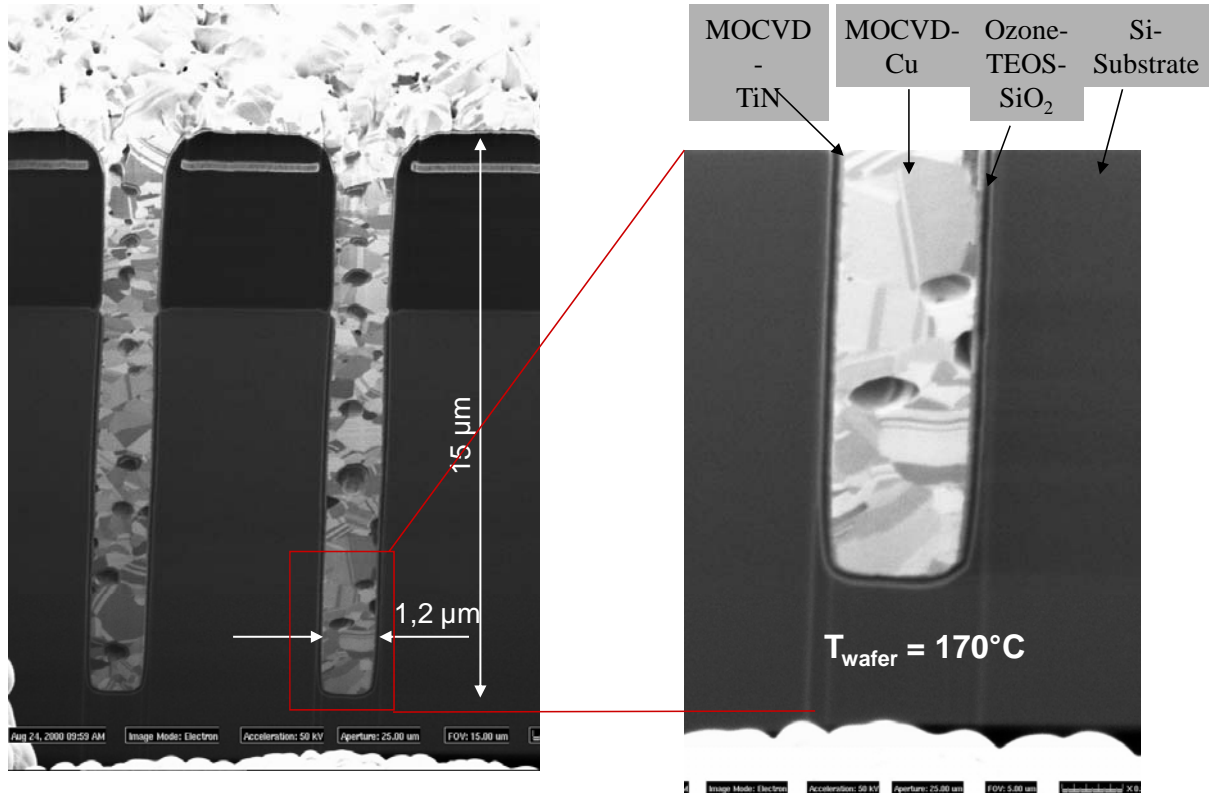
Oxide trench filled with Cu after electroplating (note: tilted FIB picture)



electro-plating

Cu-CMP

Example: CVD-Cu for interchip via fill in Vertical System Integration



FIB cut of a via hole with AR of 12.5 after CVD-Cu fill and anneal

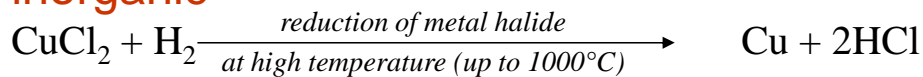
Source: S.Riedel et al., MAM 2001

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Copper CVD: Precursors and Reactions

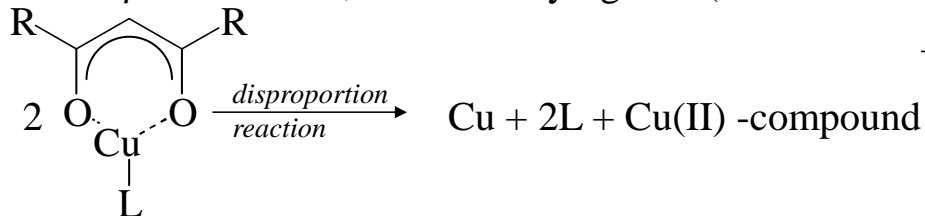
inorganic



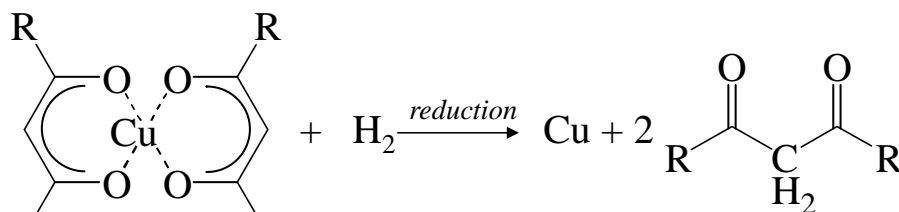
organic

classification after oxidation state of the copper atom:

copper (I) compounds:

different β -diketonates, stabilized by ligands (various Lewis bases possible)

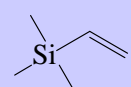
copper (II) compounds:



$\text{R} = \text{CH}_3, \text{CF}_3$ or t-butyl
R, L determine vapour pressure and stability

CupraSelect® :

$\text{R} = \text{CF}_3$
 $\text{L} = \text{TMVS}$



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Copper CVD: Application and integration aspects

Precursor related information

The only production worthy precursor (now a days) is:

Cu(I) hexafluoro acetylacetonato trimethylvinylsilan

Abbreviation: Cu(hfac)TMVS (Trade name: CupraSelect®, supplier: Air Products/Schumacher)

because it is the most **stable** precursor with the highest **vapour pressure**.

Potentials:

- + Clean films at low temperatures enabled by disproportion reaction
- + No corrosive byproducts
- + Precursor is stable at normal storage conditions
- + Precursor is a liquid with a sufficient vapour pressure, 2 Torr at 65°C
- + Commercially available in microelectronics quality
- + Process can be installed at standard CVD single wafer clustertools

Drawbacks:

- Precursor decomposes at storage/ vaporising temperatures above 65°C
- Expensive
- Only the half of the copper atoms are available for film growth
- Reaction byproducts with low volatility (long pump down between processes)



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Copper CVD: Process characteristics

Important parameters:

Temperature range: 150°C ... 210°C

- below 150°C deposition rate < 40 nm/min
 - 150°C ... 180°C very high conformality,
 low deposition rate ~ 80 nm/min
 - 180°C ... 210°C reduced conformality,
 high deposition rate ~ 200 nm/min
 - above 210°C very rough films consisting of loosely
 connected grains
- Chamber pressure: 0.5 Torr ... 20 Torr, is not a critical parameter;
wide range can be used for optimisation
 - Precursor feed rate: 1 ... 1.5 g/min for 200 mm Wafers
-  liquid delivery system is a must, care must be taken for complete vaporising of the precursor

Equipment: not yet commercialized; tools used in R&D:

P5000 or Endura (Applied Materials), ALTUS (Novellus Systems), SPTS, ALTATECH



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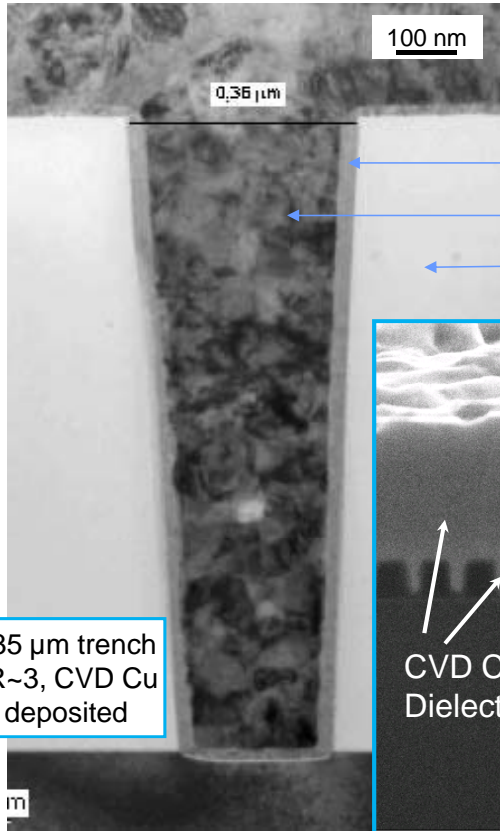


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Copper CVD: Process characteristics

Fill capability for damascene structures

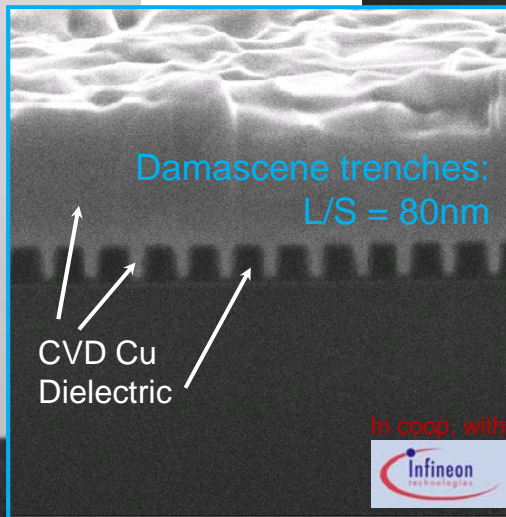


0.35 μm trench
AR~3, CVD Cu
as deposited

CVD-TiN

CVD-Cu

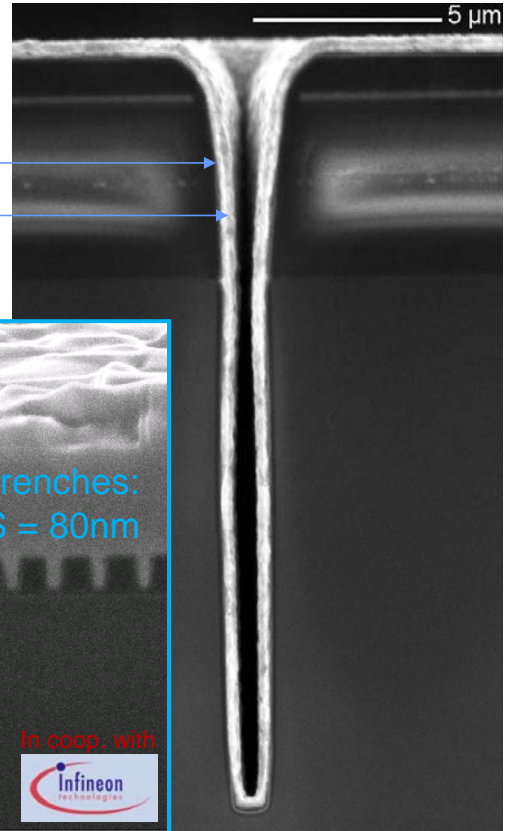
SiO₂



Damascene trenches:
L/S = 80 nm

CVD Cu
Dielectric

Step coverage at very high aspect ratios (AR = 12)



Copper CVD: Film characteristics

- Specific electrical resistivity: 2.0 ... 2.5 $\mu\Omega\text{cm}$ (dependent on film thickness and grain size)
- Film stress: $\leq 280 \text{ MPa}$ (2.8 Gdyn/cm²)
- Roughness: $R_a = 17 \text{ nm}$ (film thickness of 350 nm, deposition temperature of 200°C)
- Grain size: 110 nm (evaluated from TEM for a film thickness of 350 nm perpendicular to the surface), columnar structure
- Density: 8 ... 8.5 g/cm³ (90% ... 96% of bulk value)
- Impurities: Si/Cu < 1 at%, F/Cu < 0.3 at%,
C/Cu < 1 at%, O/Cu < 1 at% (all below detection limit AES)
- Adhesion: depends on base layer and process flow special issue

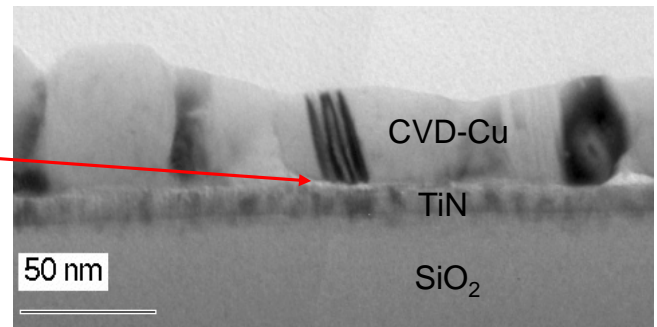
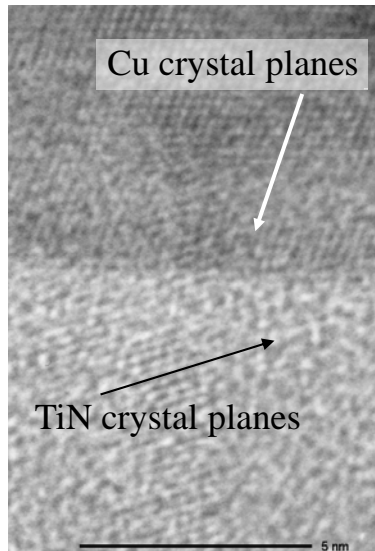
Copper CVD: Adhesion

- **General issues**

- CVD is a low energy process related to the incident precursor molecules
- Diffusion barrier and copper must not interact / chemical reaction between the both are not allowed

- **Special problem:**

Formation of an amorphous intermediate layer (fluorocarbon)



- **Solutions**

- Sputtered copper seed layers (Cu flash layer)
- Application of reactive adhesion layers (for instance modified MOCVD-TiN), with post deposition anneal
- Fluorine-free precursor (not mature yet)