Content

3 Specific Processes for Advanced Micro- and Nanoelectronics

Advanced Integrated Circuit Technology

3.1 Special CVD Processes

3.1.1 Metal CVD

(A) Tungsten (W) CVD

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

Status: 01.04.2014

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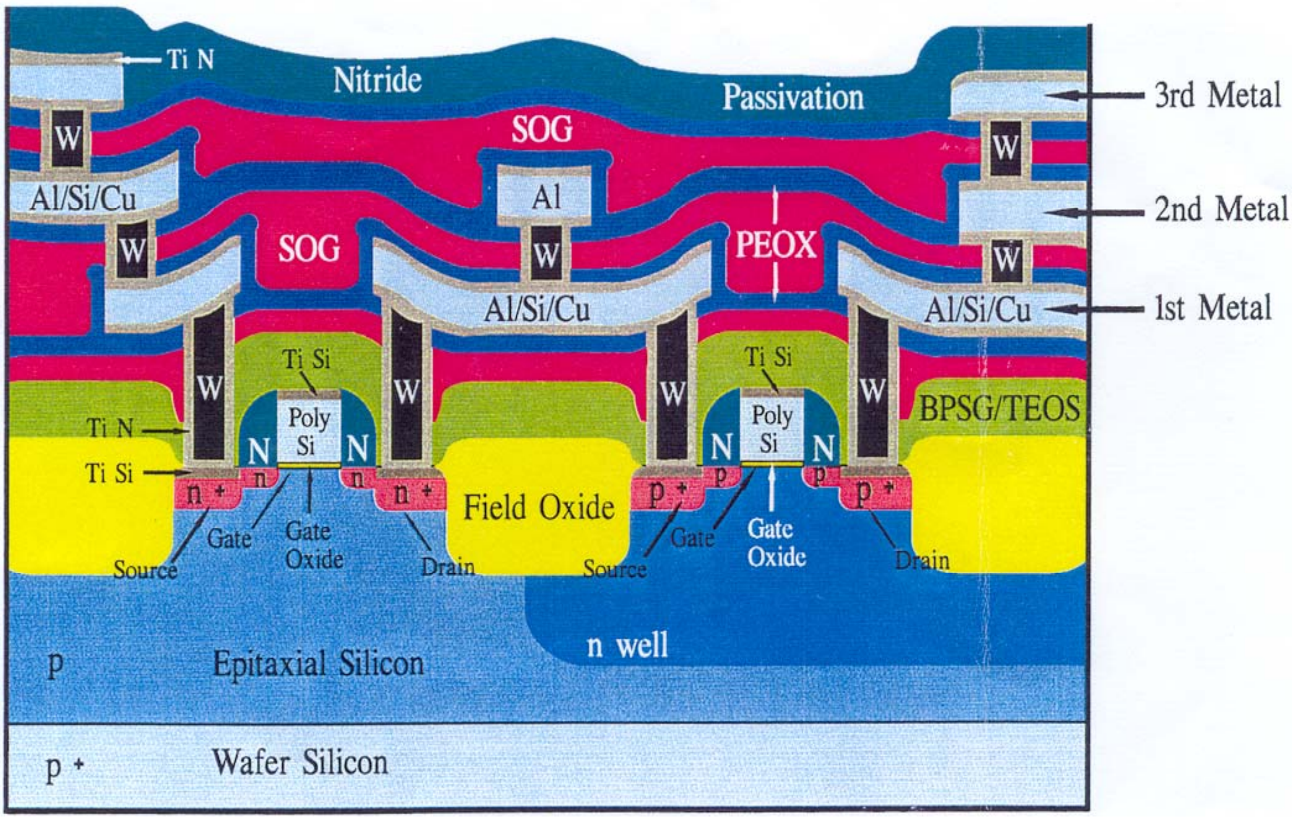
Application and integration aspects of CVD-W

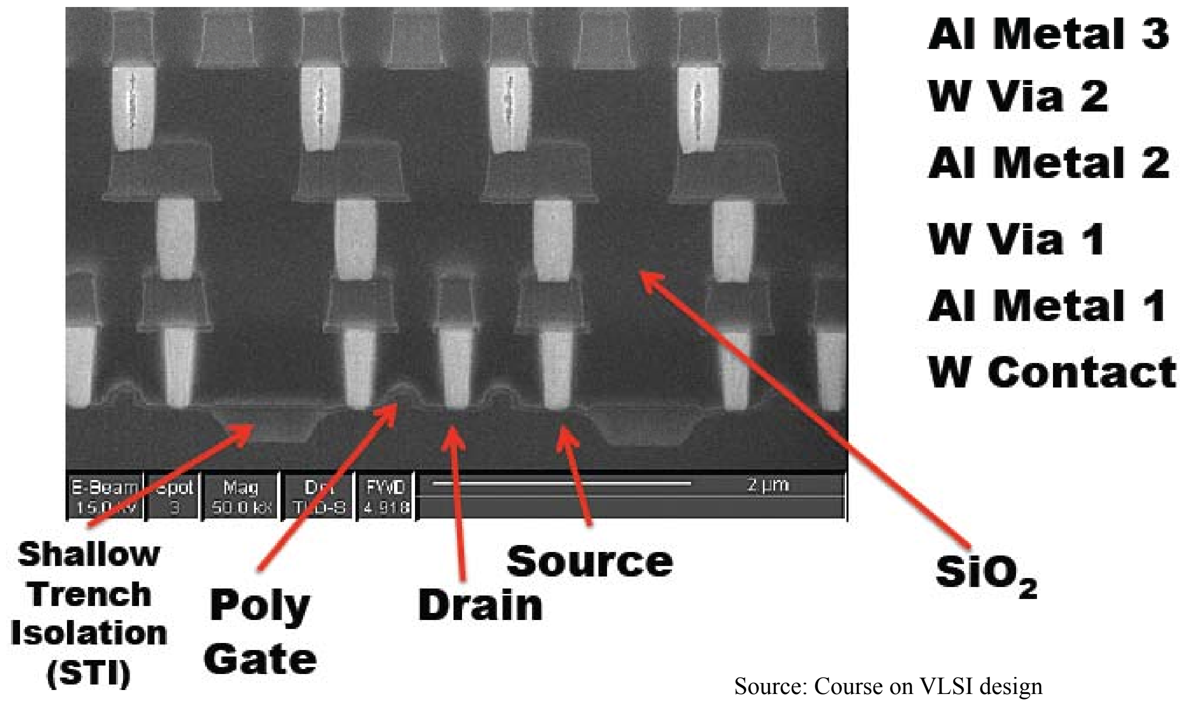
Three Metal Layer CMOS Device



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

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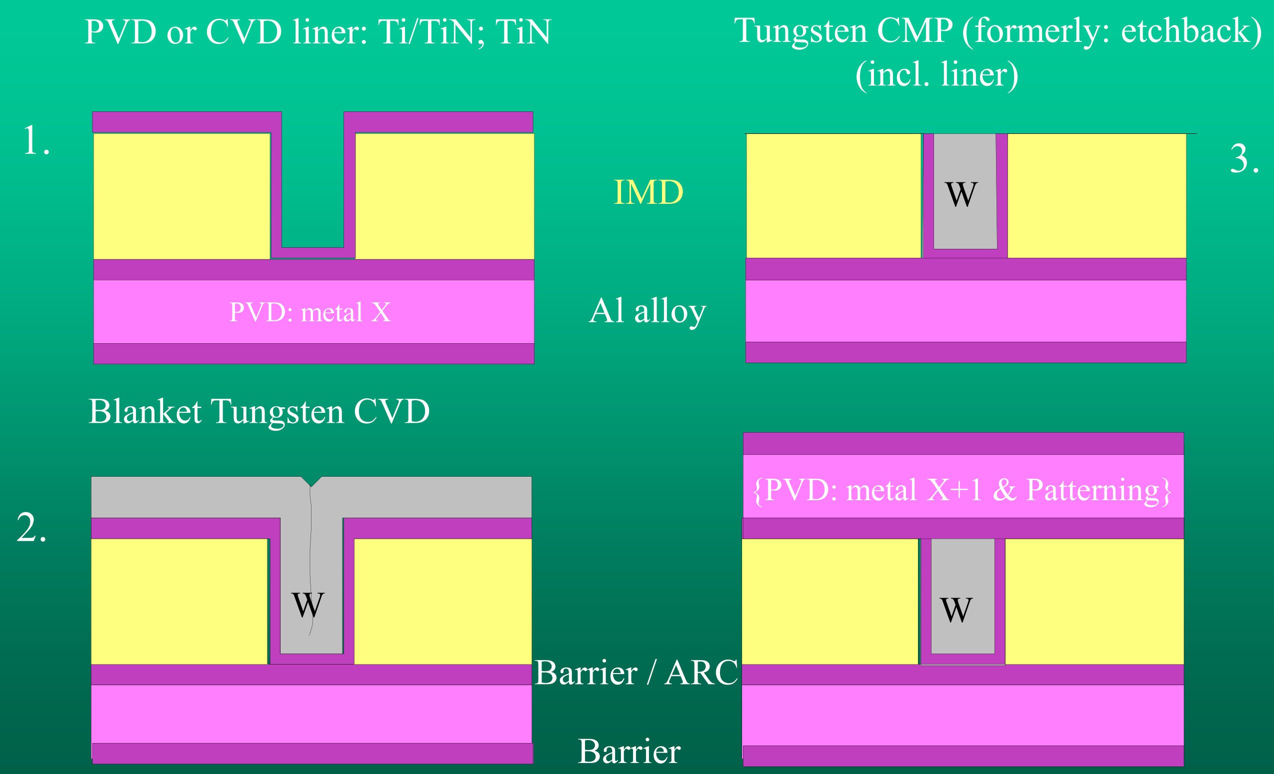
CVD Tungsten Via Fill: Process sequence („W plug")

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



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Tungsten CVD: Precursors

Precusor	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*

$$WF_6 + 3\ H_2 \longrightarrow W\downarrow + 6\ HF\uparrow$$

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

$$2\ WF_6 + 3\ SiH_4 \longrightarrow 2\ W\downarrow + 3\ SiF_4\uparrow + 6\ H_2\uparrow$$

$$WF_6 + 2\ SiH_4 \longrightarrow W\downarrow + 3\ SiHF_3\uparrow + 3\ H_2\uparrow$$

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

$$2\ WF_6 + 3\ Si \longrightarrow 2\ W\downarrow + 3\ SiF_4\uparrow \quad < 400°C$$

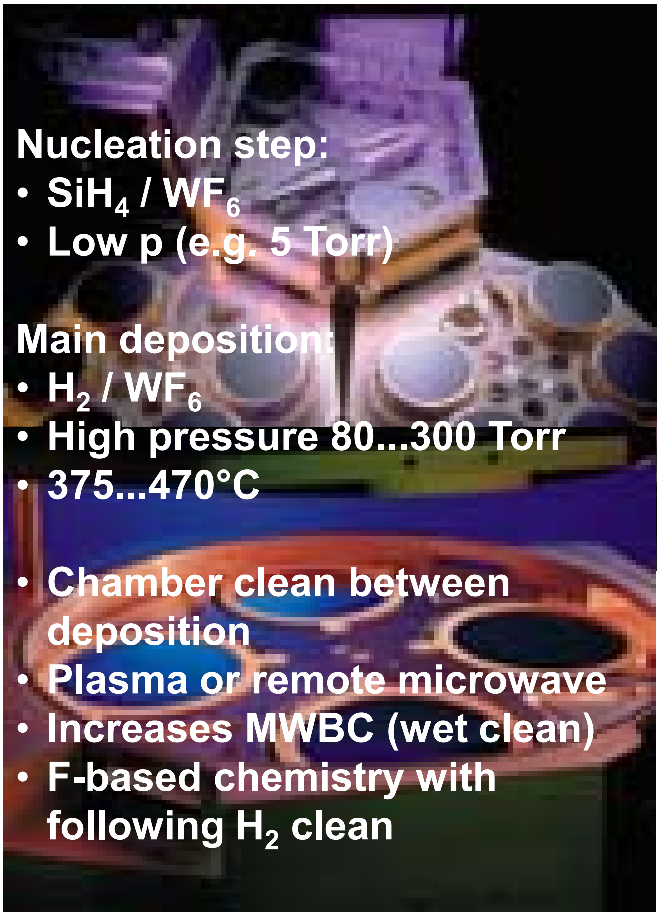
$$WF_6 + 3\ Si \longrightarrow W\downarrow + 3\ SiF_2\uparrow \quad > 500°C$$

Aluminium reduction of WF_6: *parasitic reaction during via fill*

$$WF_6 + 2\ Al \longrightarrow W\downarrow + 2\ AlF_3\downarrow$$

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

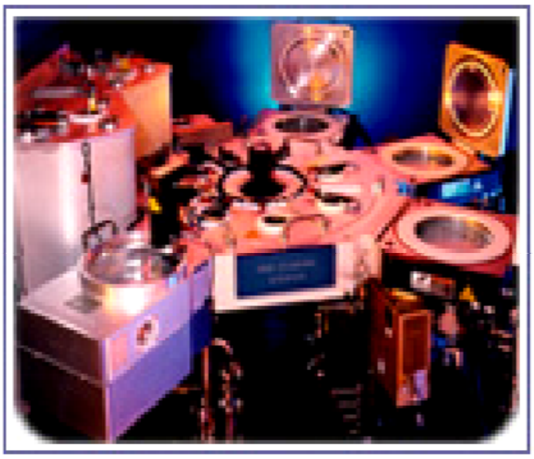
Tungsten CVD: Process characteristics



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 ↓ :)

- resistivity ↑
- step coverage ↓
- deposition rate ↓

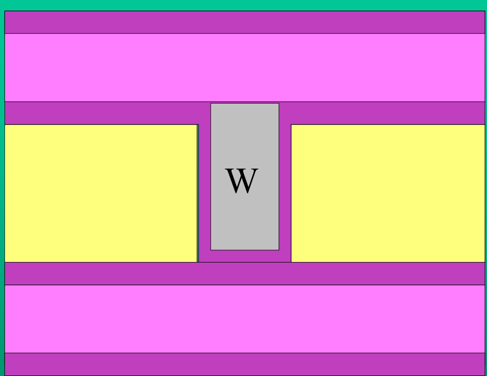
Tungsten CVD: Film properties

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

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

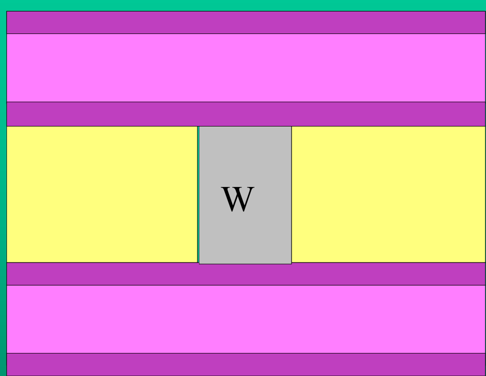
Tungsten CVD: Selective deposition

Blanket Tungsten CVD



Via clean
Liner deposition
W CVD
W CMP

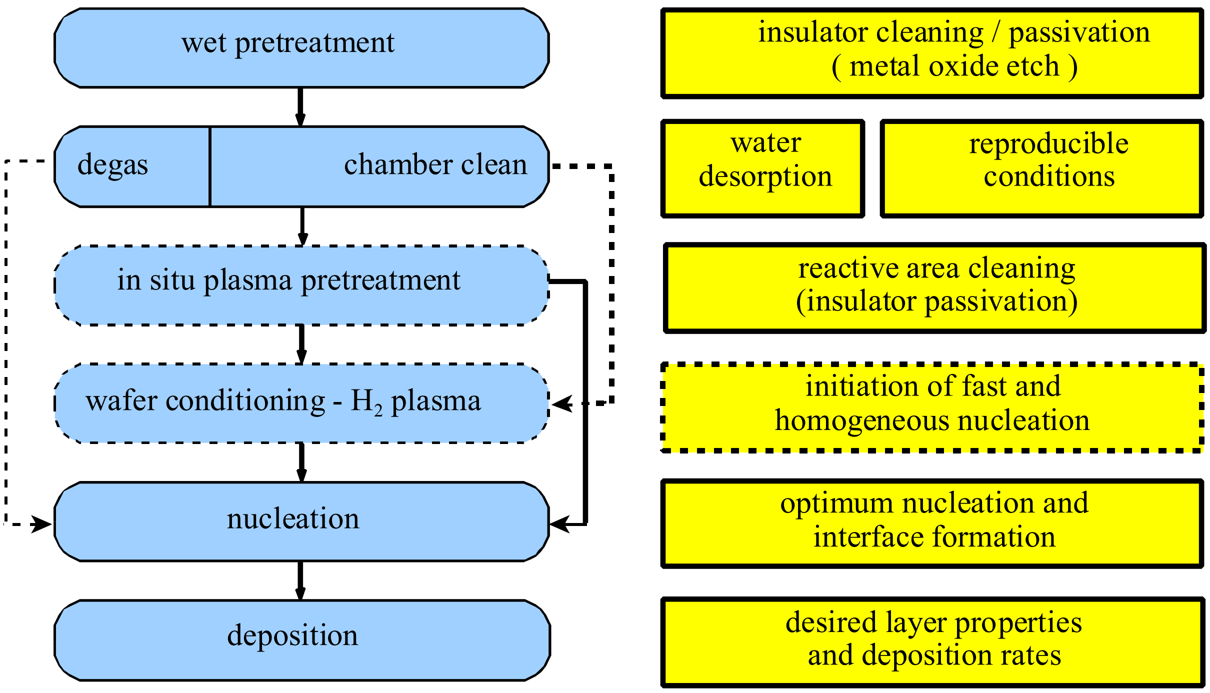
Selective Tungsten CVD



Via clean

W CVD

Tungsten CVD: Selective deposition

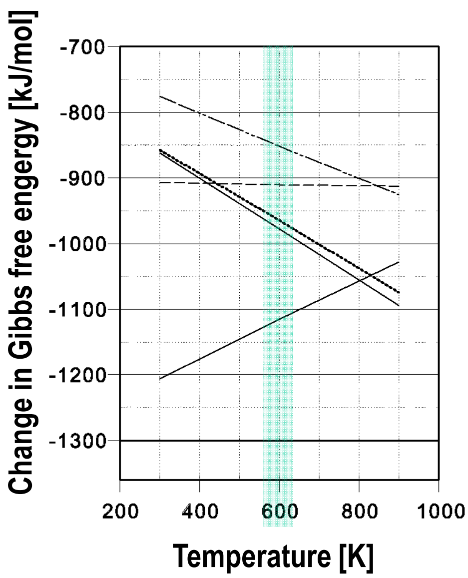


required process steps depend on reactive area material (e.g. Al, TiN)

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

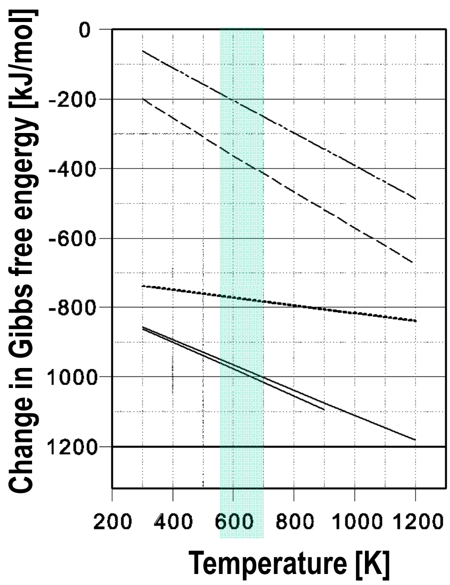
Tungsten CVD:

Reactions - Thermodynamic considerations



Reduction reactions on Al

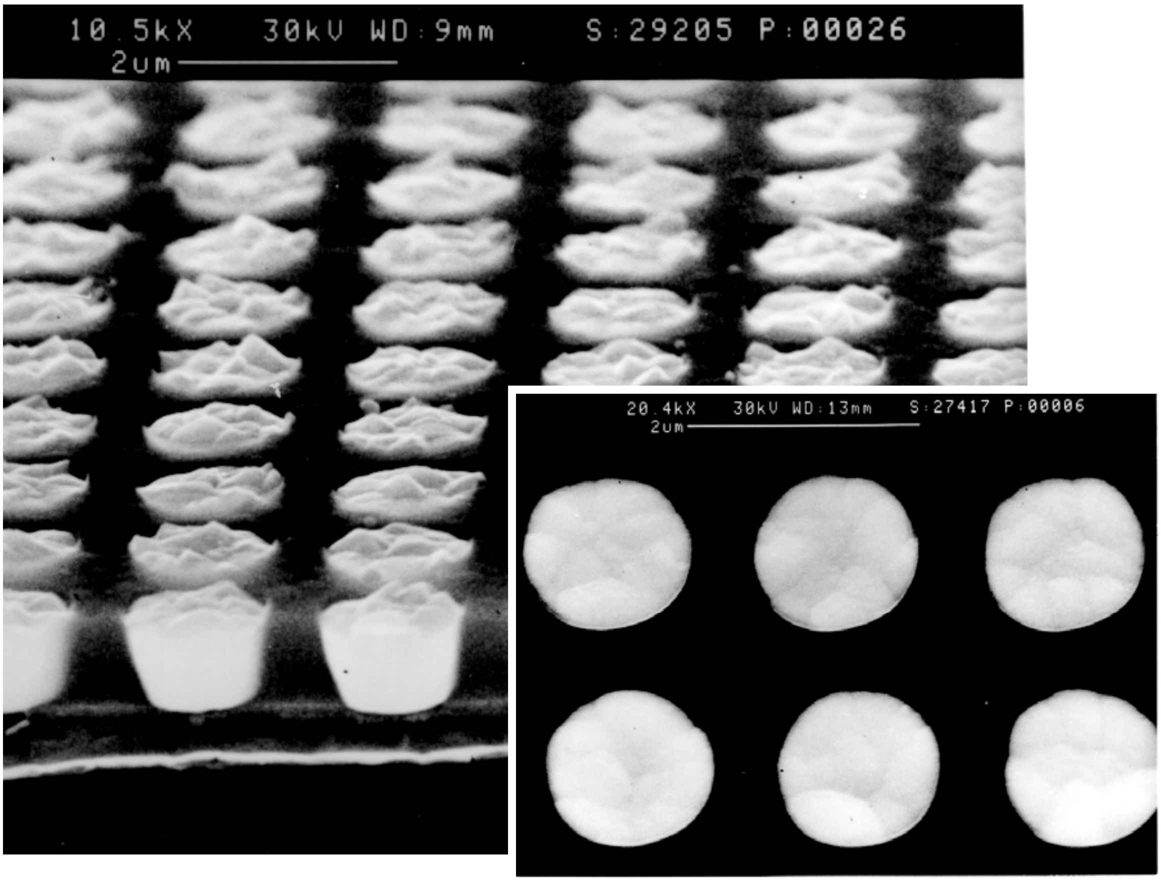
— - - -	Al	[AlF3 (g)]
— — —	Al	[(AlF3)2 (g)]
········	SiH4	[SiF4/H2]
———	SiH4	[SiHF3/H2]
———	Al	[AlF3 (s)]



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

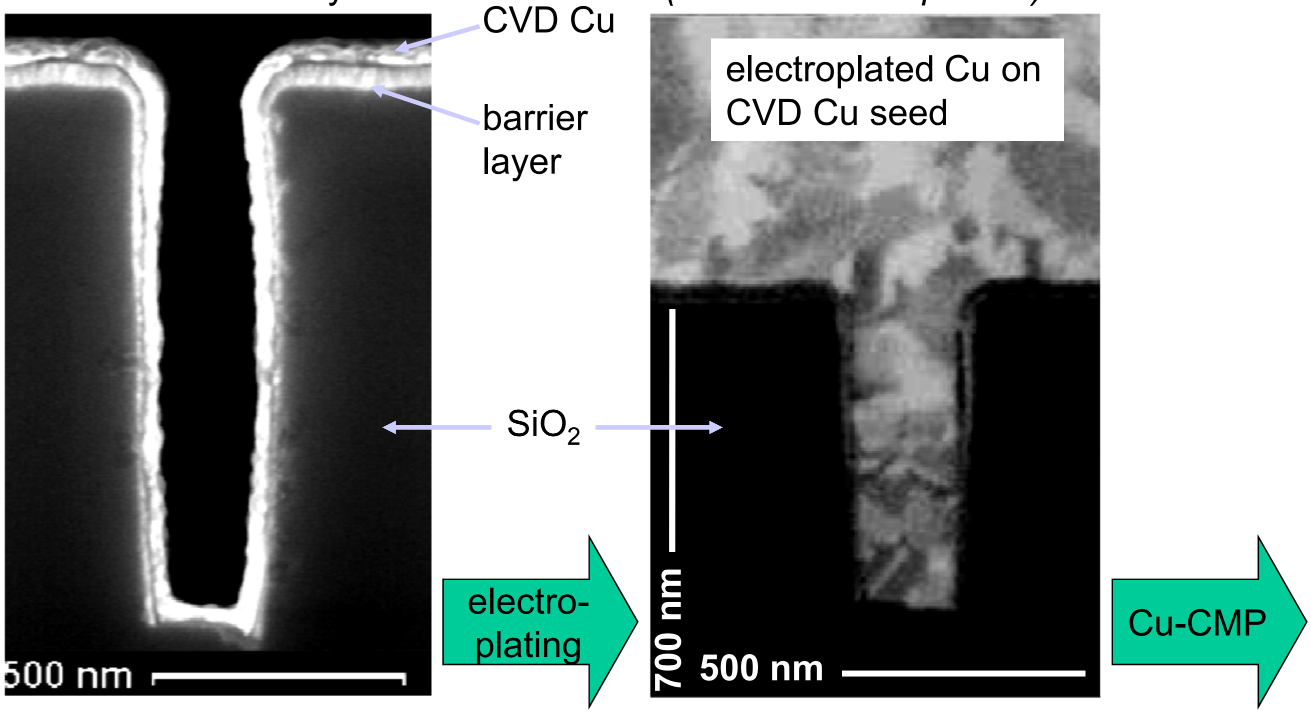
- Precursor cost (still) high – no high volume fabrication
- Limited throughput

Copper CVD: Application and integration aspects

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

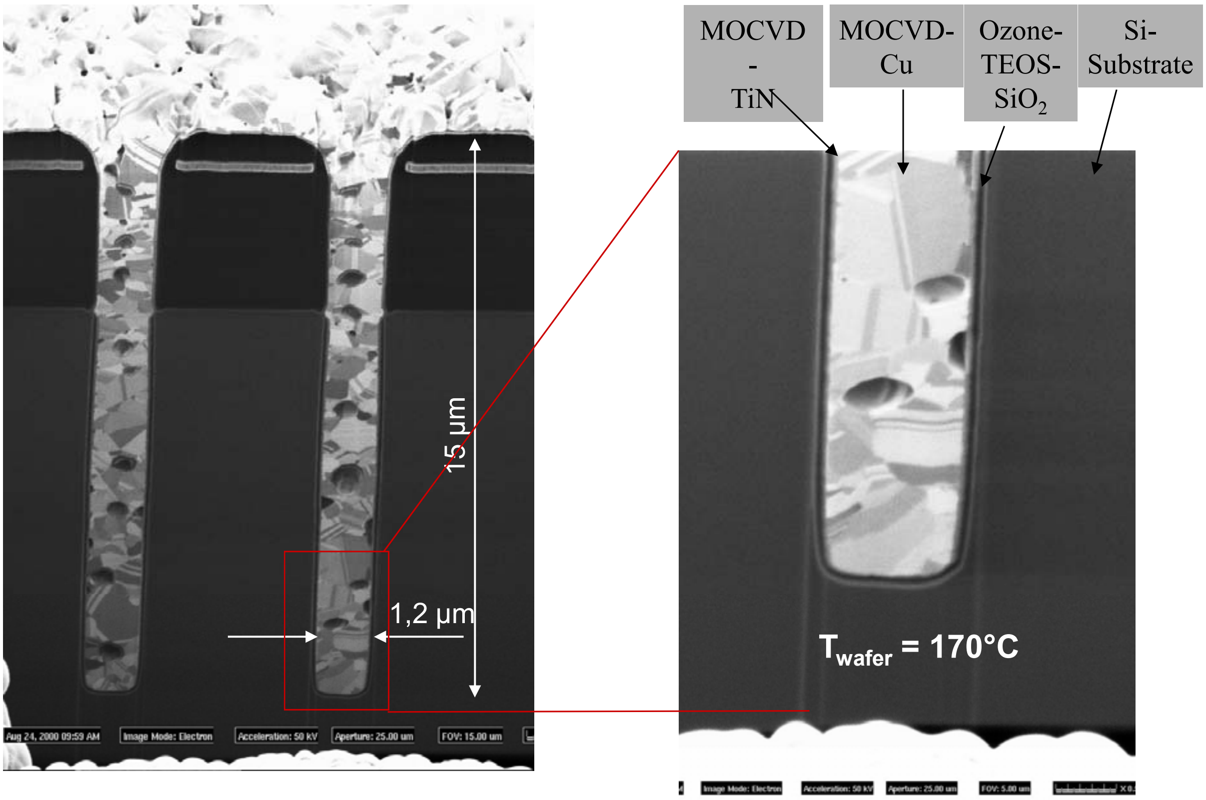
Oxide trench covered with barrier layer and CVD Cu as seed layer

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



Copper CVD: Application and integration

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

Copper CVD: Precursors and Reactions

inorganic

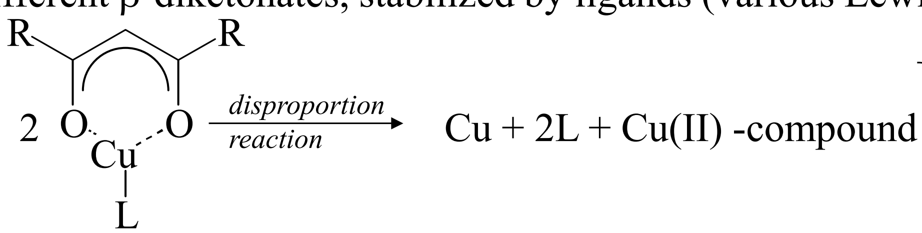
$$CuCl_2 + H_2 \xrightarrow[\text{at high temperature (up to 1000°C)}]{\text{reduction of metal halide}} Cu + 2HCl$$

organic

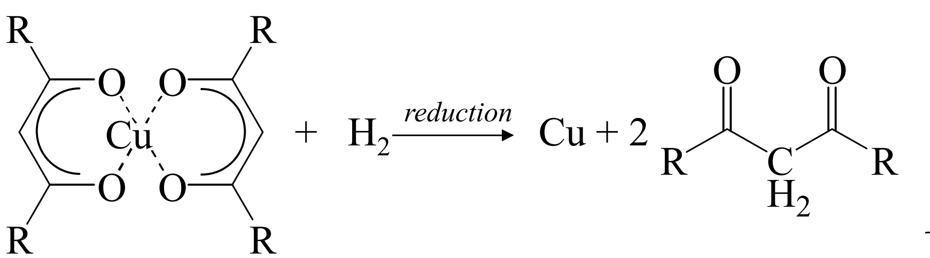
classification after oxidation state of the copper atom:

copper (I) compounds:

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

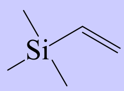


copper (II) compounds:



R = CH_3, CF_3 or t-butyl
R, L determine vapour pressure and stability

CupraSelect ® :
R = CF_3
L = TMVS



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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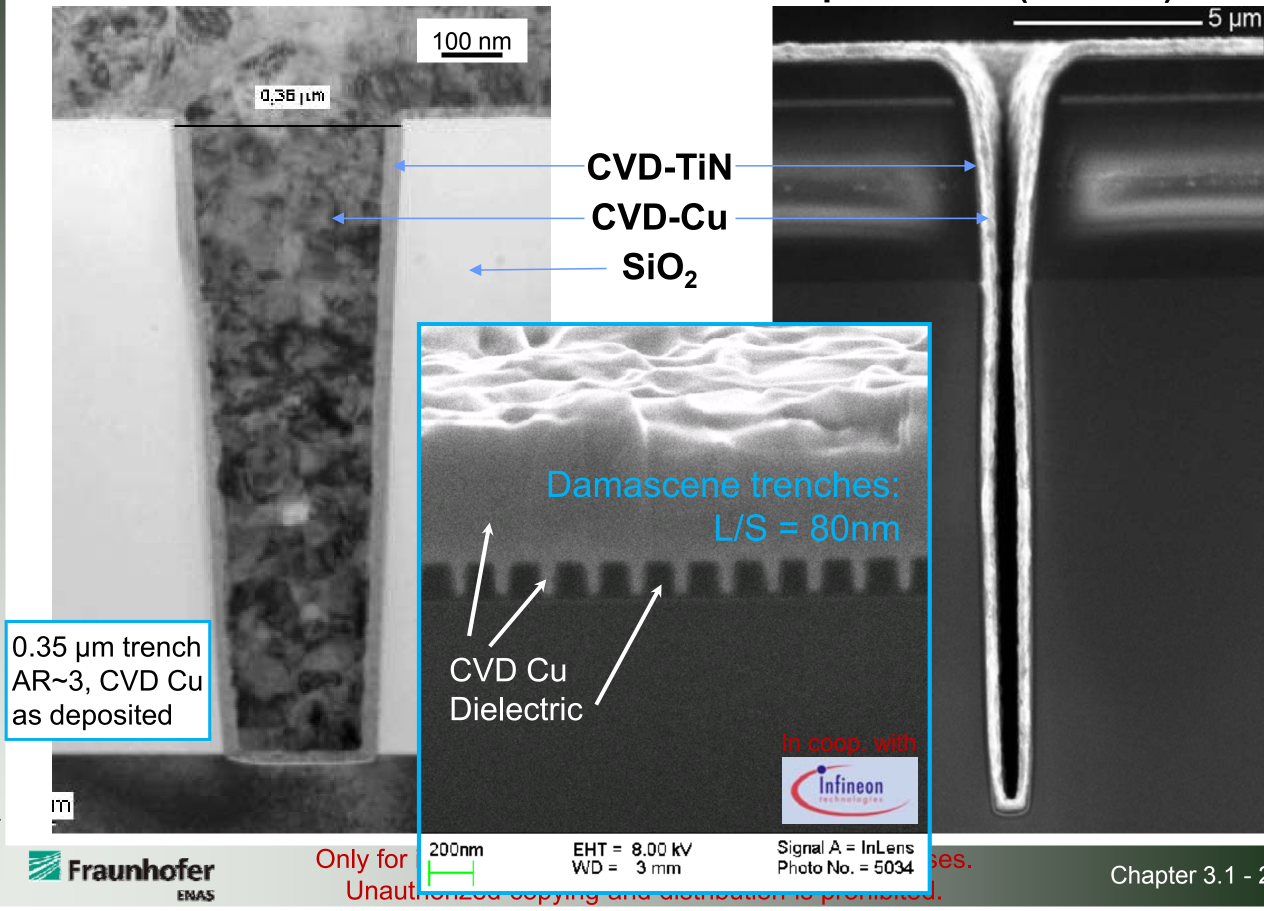
Copper CVD: Process characteristics

Fill capability for damascene structures

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

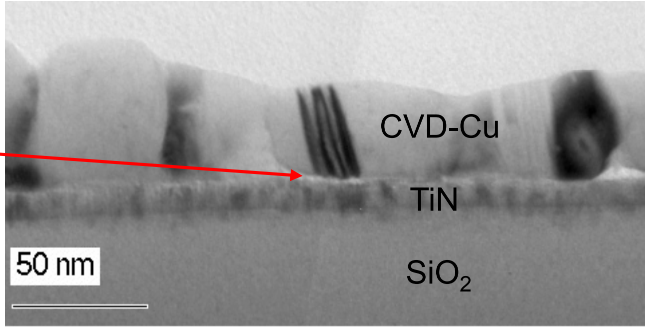


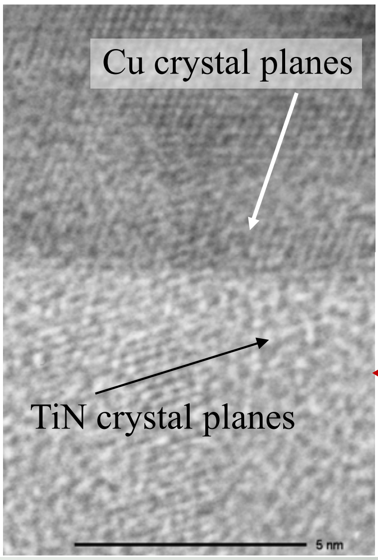
Copper CVD: Film characteristics

- Specific electrical resistivity: 2.0 ... 2.5 µΩcm (dependent on film thickness and grain size)
- Film stress: ≤ 280 MPa (2.8 Gdyn/cm²)
- Roughness: R_a = 17 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)*