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 tools with CVD-chamber
- Direct liquid inject or vaporizer system for precursor delivery (variety of systems available by AMAT, Bronkhorst, MKS, Kemstream, ...)
- In situ chamber clean

Interaction with other processes / layers

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

Cost

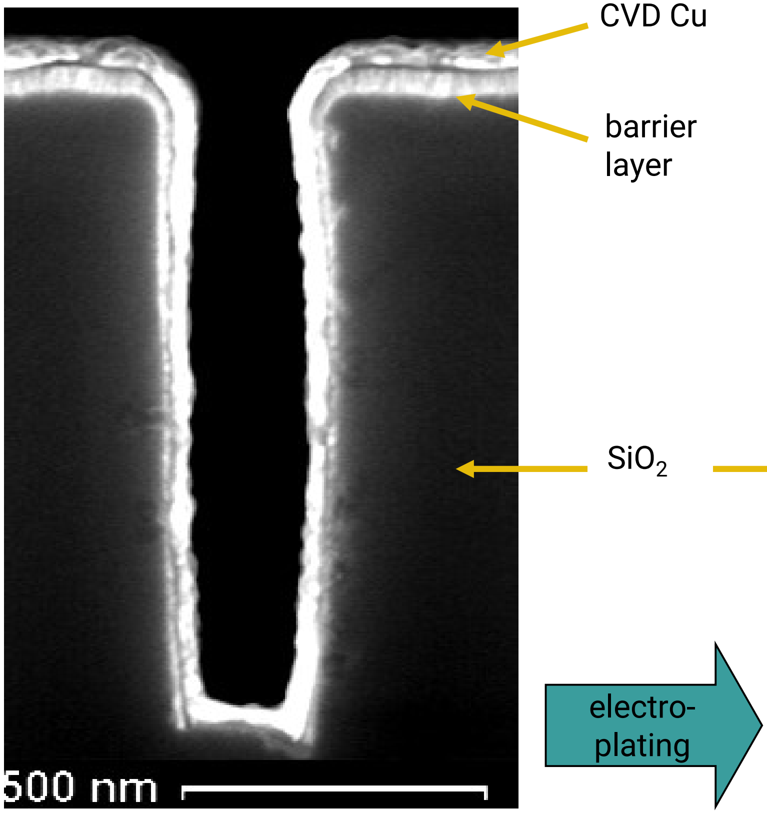
- Precursor cost (still) high – no high volume fabrication (yet)
- Partly limited throughput (depends on equipment, process, target thickness)

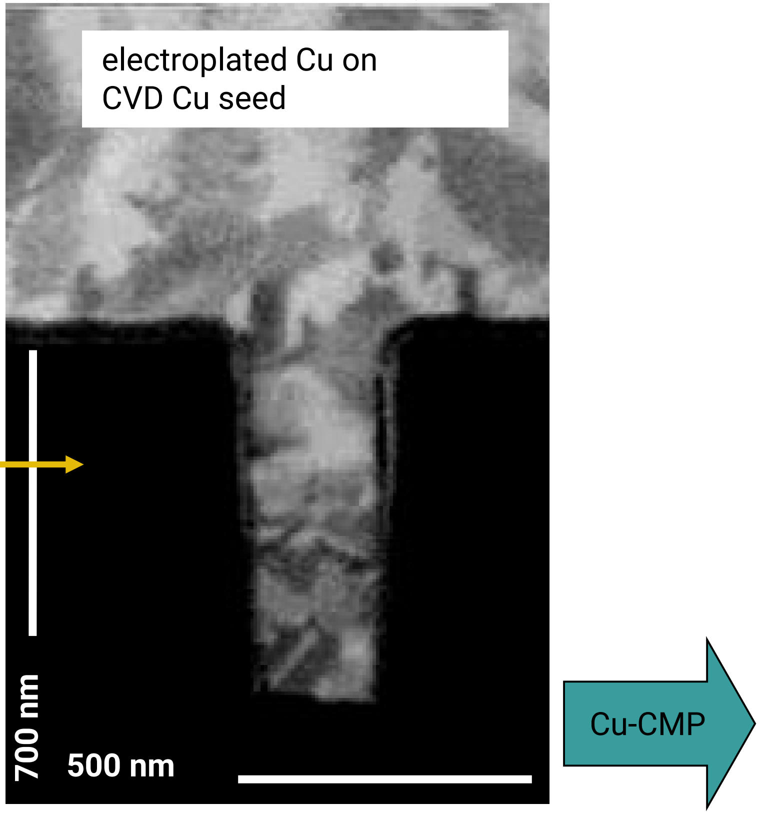
Copper CVD: Application and integration aspects

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

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

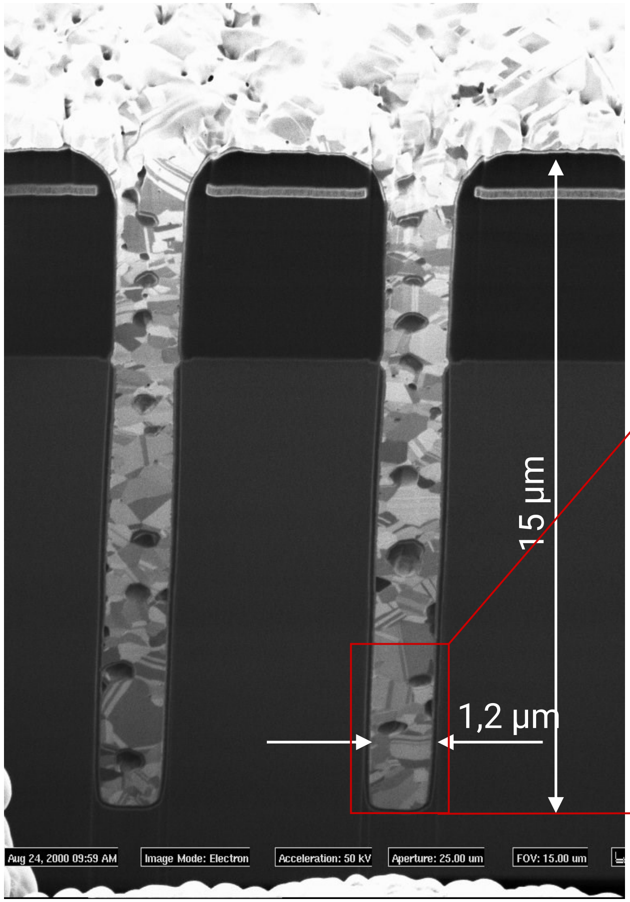
Oxide trench filled with Cu after electroplating *(note: tilted FIB picture)*

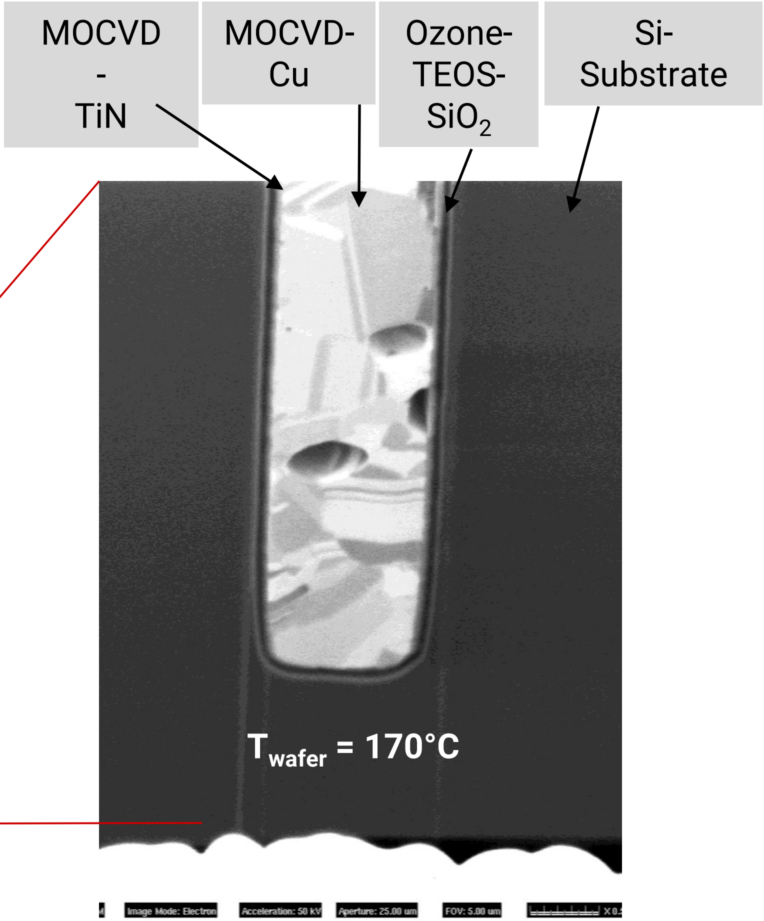




Copper CVD: Application and integration aspects

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

Copper CVD: Precursors and Reactions

inorganic

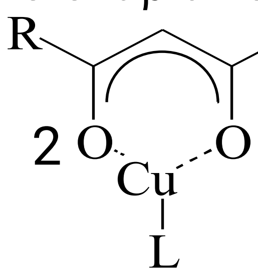
$$CuCl_2 + H_2 \xrightarrow[\textit{at high temperature (up to 1000°C)}]{\textit{reduction of metal halide}} Cu + 2HCl$$

organic

classification after oxidation state of the copper atom:

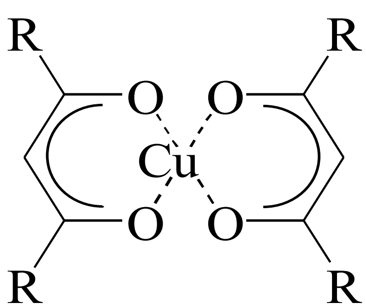
copper (**I**) compounds:

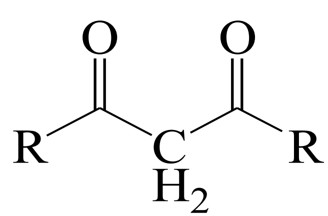
different β-diketonates, stabilized by ligands (various Lewis bases possible)

2 

$\xrightarrow[\textit{reaction}]{\textit{disproportion}}$ Cu + 2L + Cu(II) -compound

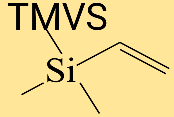
copper (**II**) compounds:



$+ \; H_2 \xrightarrow{\textit{reduction}} Cu + 2$ 

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 (nowadays) is:

Cu(I) hexafluoro acetylacetonato trimethylvinylsilan

Abbreviation: Cu(hfac)TMVS (Trade name: CupraSelect®, supplier: Versum Materials)

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
– Only the half of the copper atoms are available for film growth
– Reaction byproducts with low volatility (long pump down between processes)

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

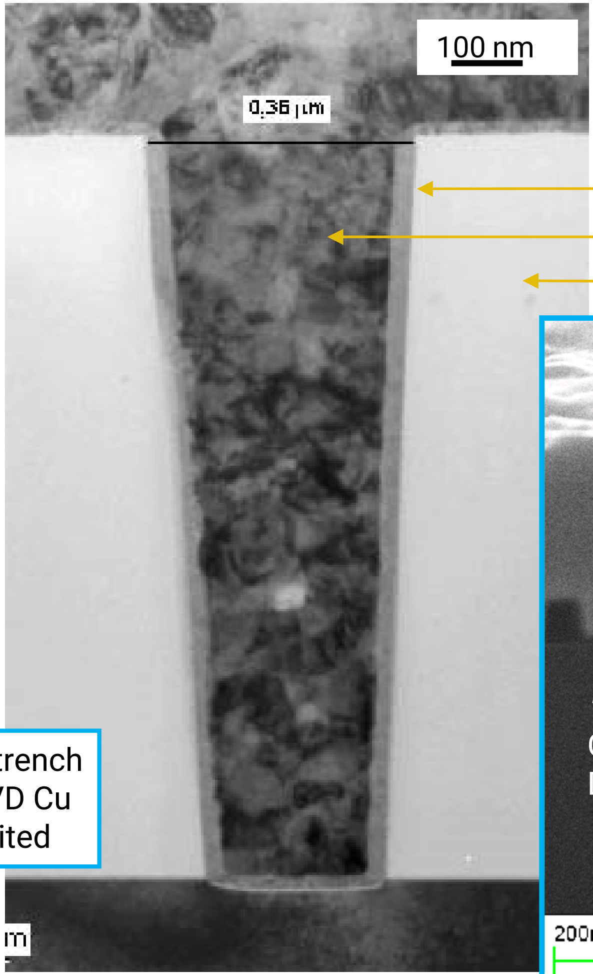
  ⇒ liquid delivery system is a must, care must be taken for complete vaporising of the precursor

Equipment: Commercial and R&D tools available

SPTS, KOBUS, Applied Materials, Novellus Systems

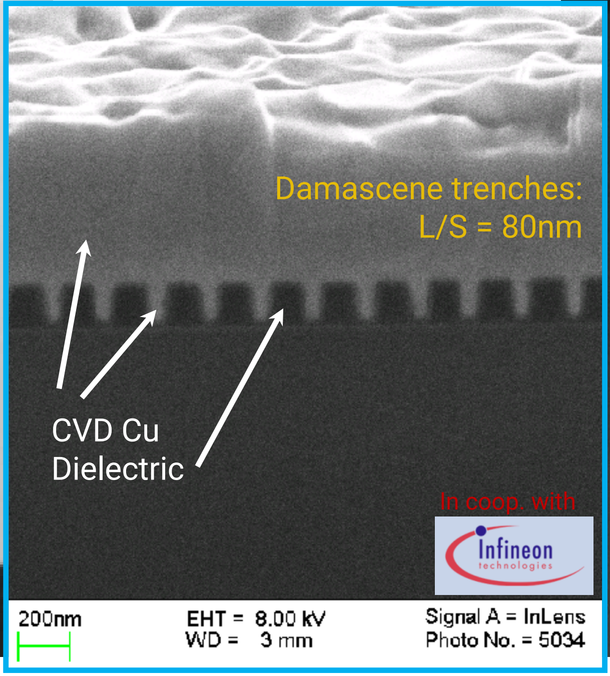
Copper CVD: Process characteristics

Fill capability for damascene structures

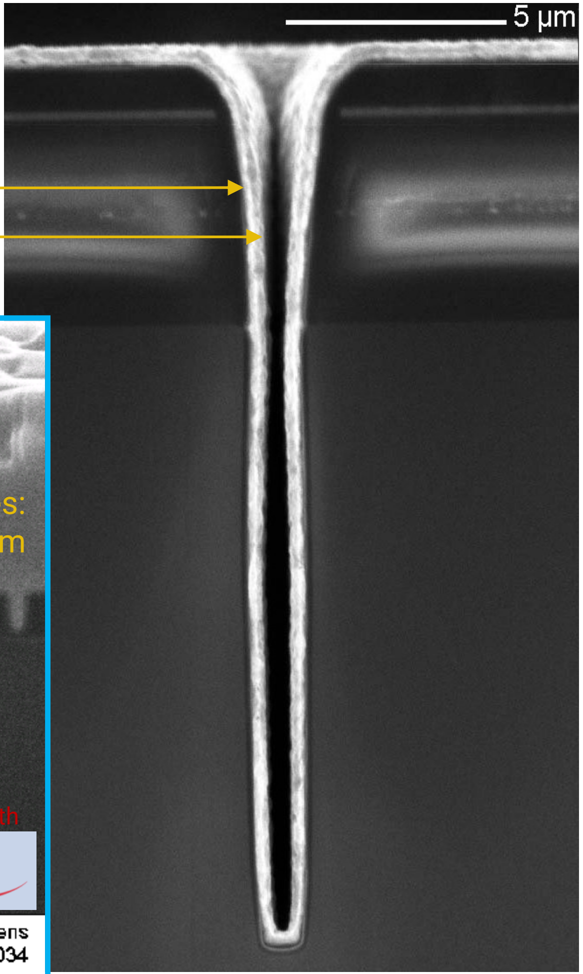


0.35 µm trench
AR~3, CVD Cu
as deposited

CVD-TiN
CVD-Cu
SiO_2



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



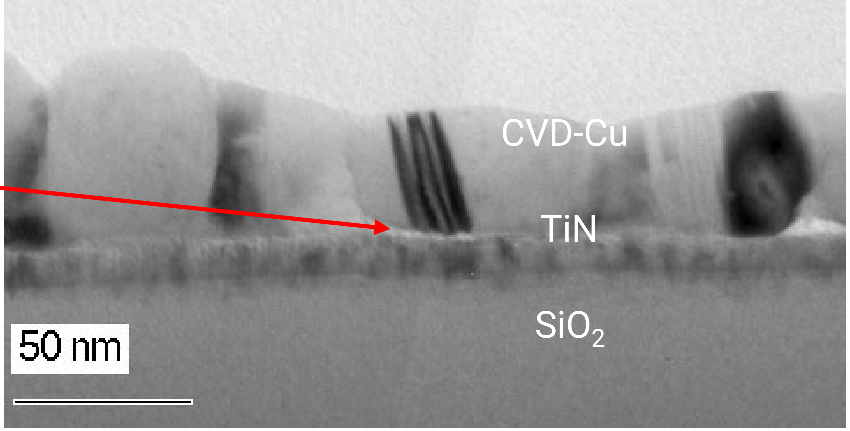
Copper CVD: Film characteristics

- 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

Copper CVD: Adhesion

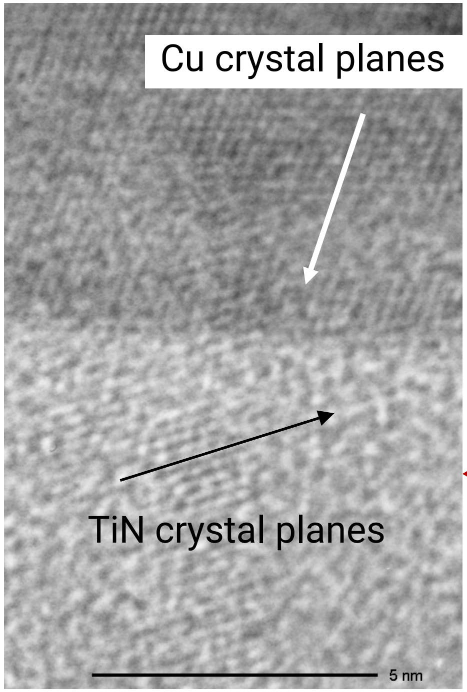
General issues

- 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)