Cu-SiO_2 films for 3D filling in microelectronic applications by an organometallic chemical liquid deposition (OMCLD) route

Málaga
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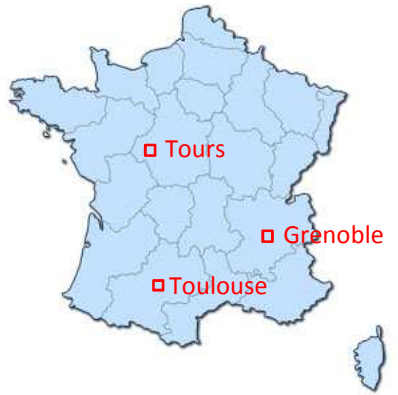
France

Mobile Multimedia Communication

Consumer
Multimedia
Wireless and wireline products

Computer Peripheral Group

Chips for computer peripherals (hard disk controllers, printers…)



STMicroelectronics

Micro, Power and Analog Group

Analog and power circuits for microcontrollers
Discrete semiconductor products

Memory Product Group

Stand-alone memory chips
Non-volatile memory chips

Automotive Product Group

Analog and digital chips
Broadcasting integrated circuits
Microcontrollers (automotive, power trains, safety)

Semiconductor sales leader in 2009

Rank	Company	Continent
1	Intel Corporation	USA
2	Samsung	South Korea
3	Toshiba	Japan
4	Texas Instruments	USA
5	STMicroelectronics	France/Italy
6	Qualcomm	USA
7	Hynix	South Korea
8	Renesas Technology	Japan
9	AMD	USA
10	Sony	Japan

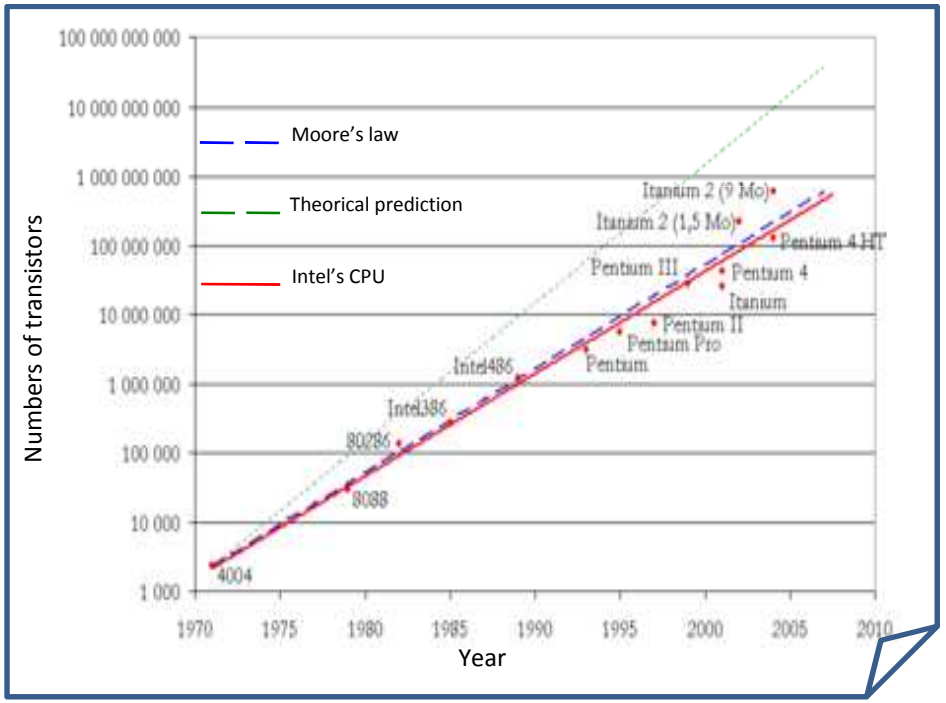
Introduction

- Copper is widely used in microelectronic.

- Techniques to deposit copper in microelectronics:
  - Chemical Vapor Deposition (CVD) (i.e Atomic Layer Deposition (ALD)*)
  - Physical Vapor Deposition (PVD)

- Integrated circuit's power
  - → downsizing device
    - → stacking of function 3D
- Common device
  - →up to 20 different layers of metal are present in small chips.

- Numerous deposition systems →high cost



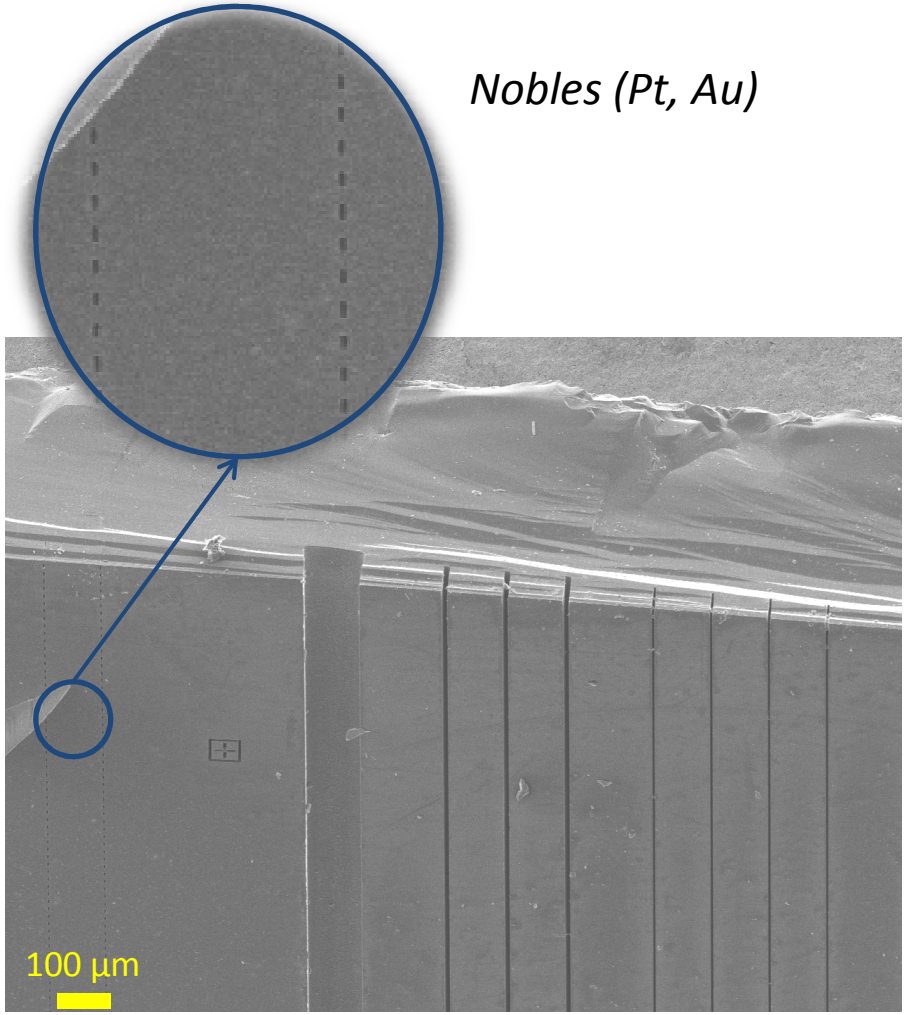
*Rosenberg, R.; Edelstein, D. C.; Hu, C.-K.; Rodbell, K. P. *Annu. Rev. Mater. Sci.* **2000**, *30*, 229-262.
Ritala, M.; Leskelä, M. In *Handbook of Thin films Materials*; Nalwa, H. S., Ed.; Academic Press: N-Y, 2001; Vol. 1, pp 103-159

Organometallic deposit of Cu and located metallisation in solution

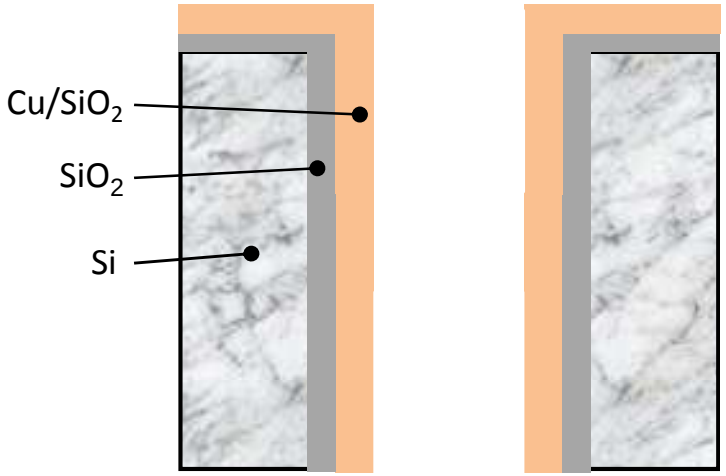
Aim: to develop a method of deposit in liquid phase from organometallic solutions in order to form either thin or thick conductive layers on planar and *3D*-structured (*vias* or trenches) substrates

Nobles (Pt, Au)

Oxidables (Cu, Ni, Ir…)



First step : deposition of a Cu-SiO_2 layer

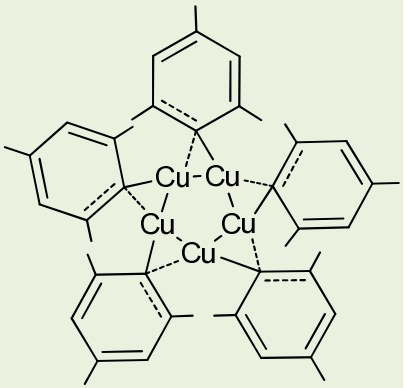


Scheme of a Cu-SiO_2 deposit in a crossing via

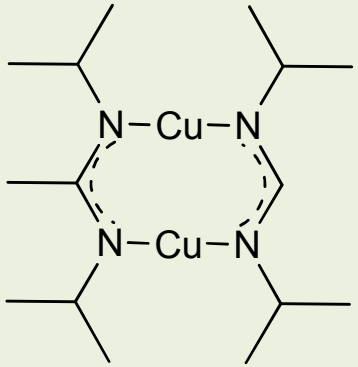
1. Copper Nanoparticles synthesis

Organometallic precursors:

Cu^{I}(Mesityl)



Cu^{I}(amidinate)

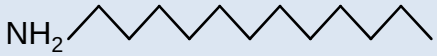


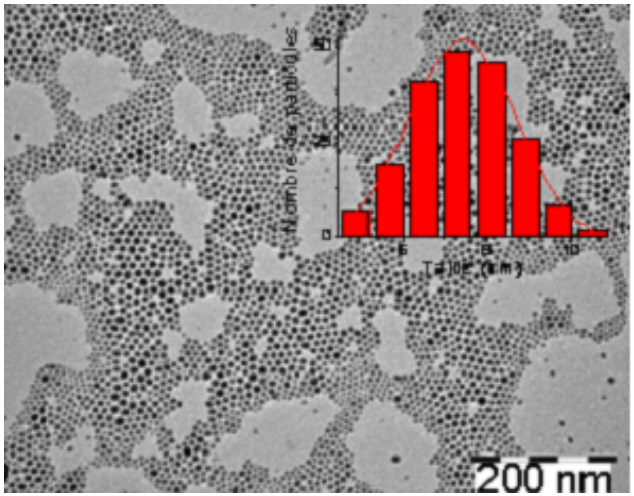
Solvent: Toluene

T=110°C

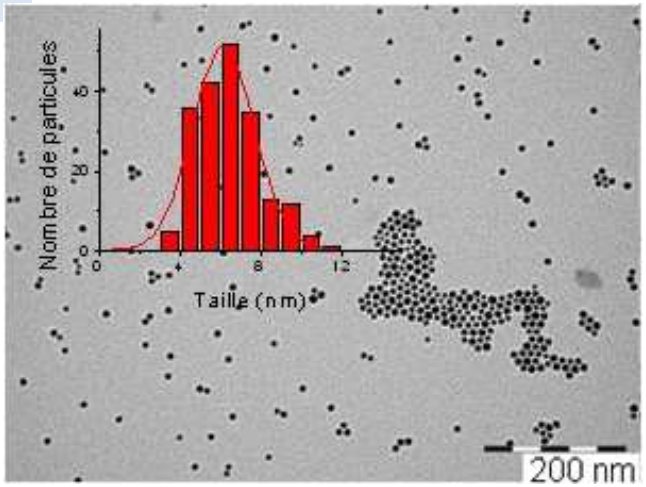
+ Reducing agent: H_2

Organic stabilizing agent: Dodecylamine C12 (DDA)

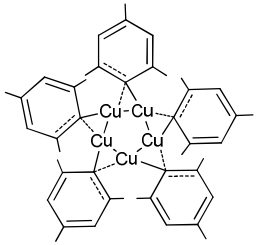




Transmission electron microscopy pictures



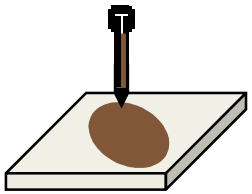
Meyer, E. M. *et al. Organometallics*, **1989**, *8*, 1067-1079
Gordon, R. *et al. Inorg. Chem.* **2005**, *44*, 1728-1735



Copper Nanoparticles deposition: Cu(mes)

Presence of ligand

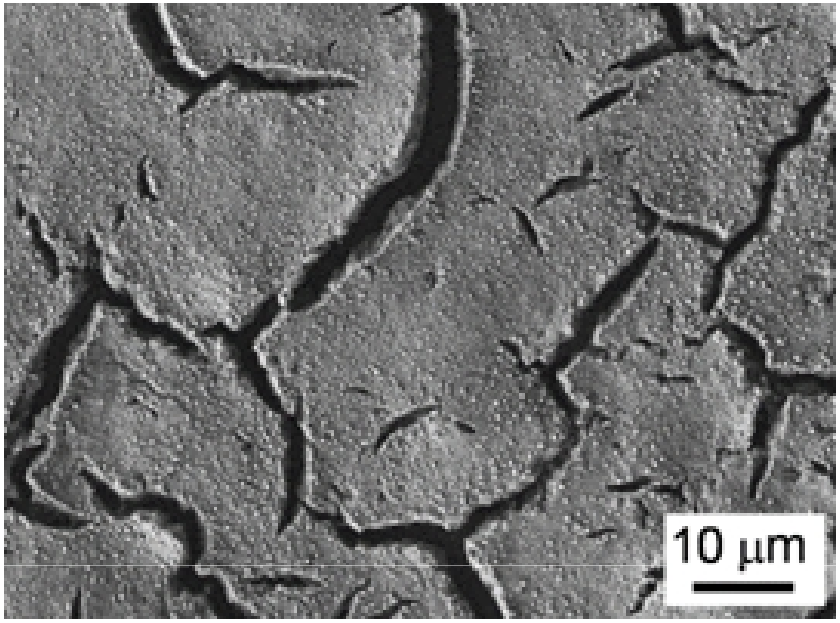
$$\text{Cu(mes)} + \text{DDA} \xrightarrow[\text{Toluene}]{\text{T°C, } P_{H_2}} \text{Cu NPs}$$



Drop deposition
+
annealing

Resistivity: 10.10^{-6} Ω.cm

silica substrate

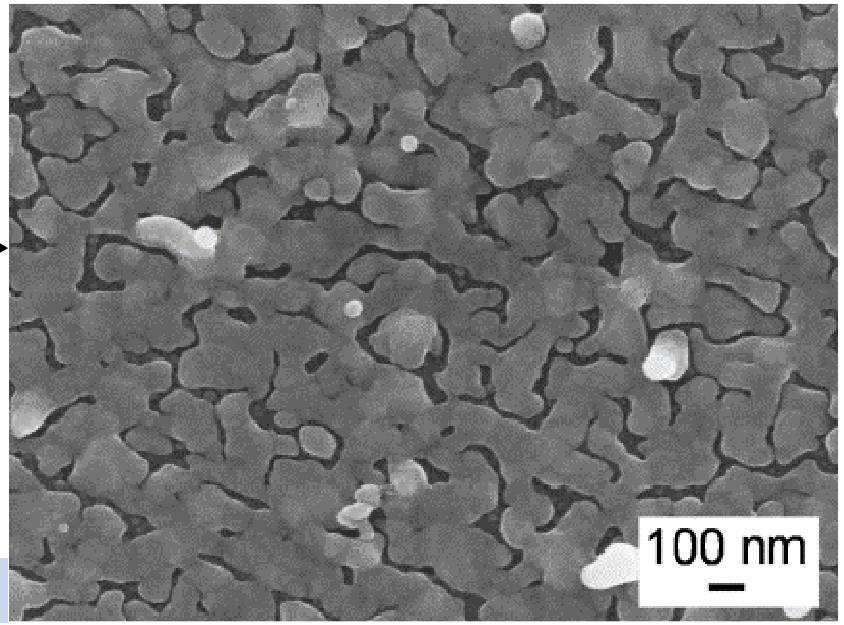


Scanning electron microscopy (SEM) pictures

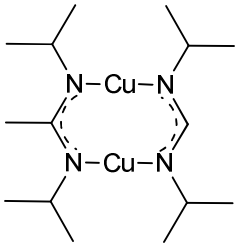
Absence of ligand

$$\text{Cu(mes)} \xrightarrow[\text{Toluene}]{\text{T°C, } P_{H_2}} \text{Direct deposition} + \text{annealing} \longrightarrow$$

Resistivity: 50.10^{-6} Ω.cm



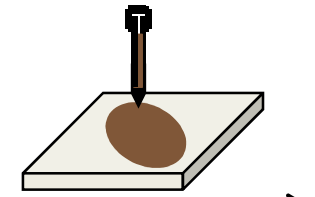
C. Barrière, P. Fau et al. J. Mater. Chem., **2008**, 18, 3084–3086



Copper Nanoparticles deposition: Cu(am)

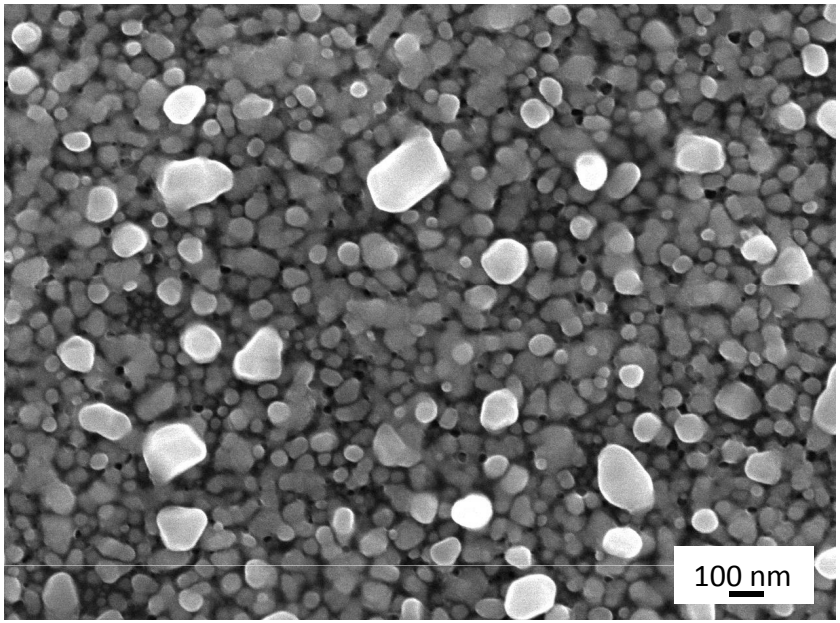
Presence of ligand

Cu(am) + DDA $\xrightarrow[\text{Toluene}]{\text{T°C, } P_{H_2}}$ Cu NPs



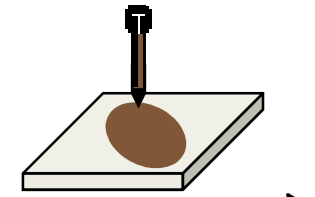
Drop deposition
+
annealing

silica substrate



Absence of ligand

Cu(am) $\xrightarrow[\text{Toluene}]{\text{T°C, } P_{H_2}}$ Cu NPs

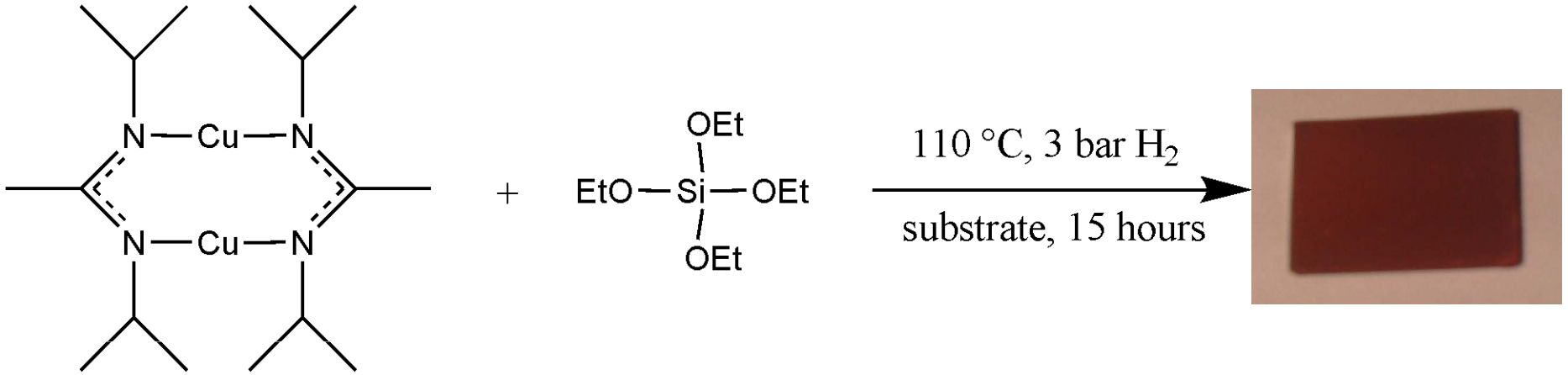


Drop deposition
+
annealing

- Film
- Nanoparticles
- Large aggregates precipitation

2. Cu-SiO_2 deposit

General reaction:



Cu(amidinate) *TEOS*

Annealing steps: 300°C (increments of 1°C/min) under air (1h)
300°C (increments of 1°C/min) under reducing gas H_2(10%)/Ar(90%) (1h).

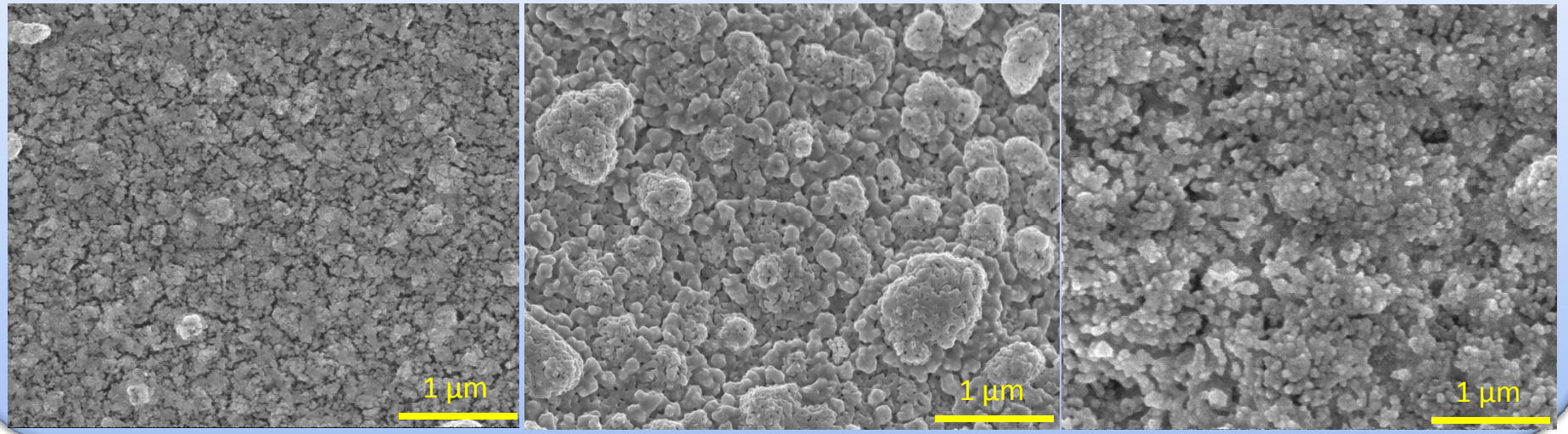
Deposits are made on Si/SiO_2 substrates that has first undergone plasma O_2.

Barriere, C. ; Fau, P. ; Chaudret, B. ; Margeat, O. ; Patent : WO 2009125143

Control of H_2O content

Variation of H_2O quantity (reaction time: 15 hours)

<10 ppm H_2O	200 ppm H_2O	500 ppm H_2O
60% Cu(am) consumed	65% Cu(am) consumed	95% Cu(am) consumed

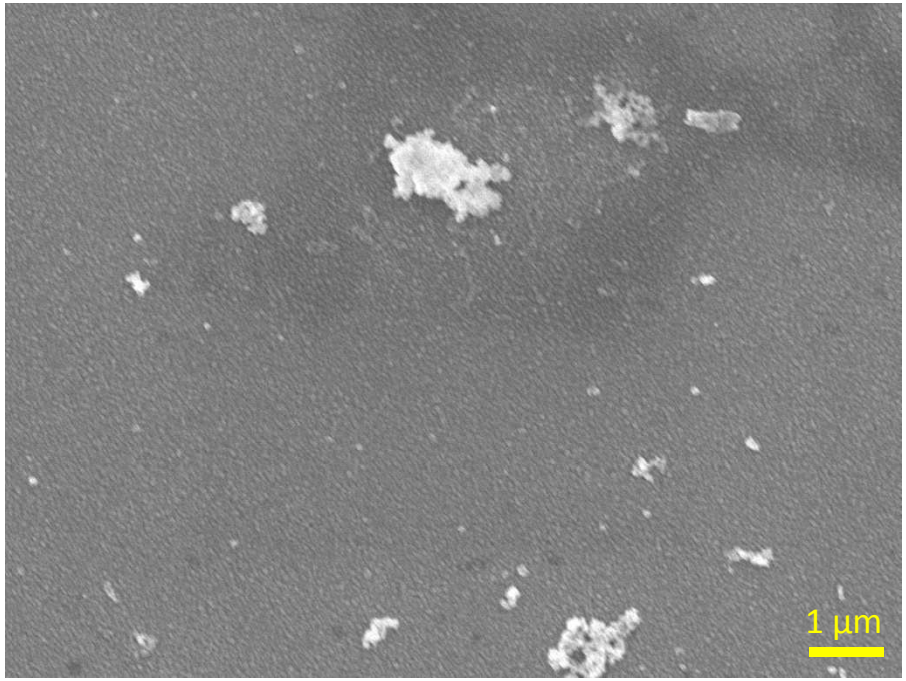


For a 15h reaction with control of the water at the beginning of the reaction:

total consumption of the copper precursor

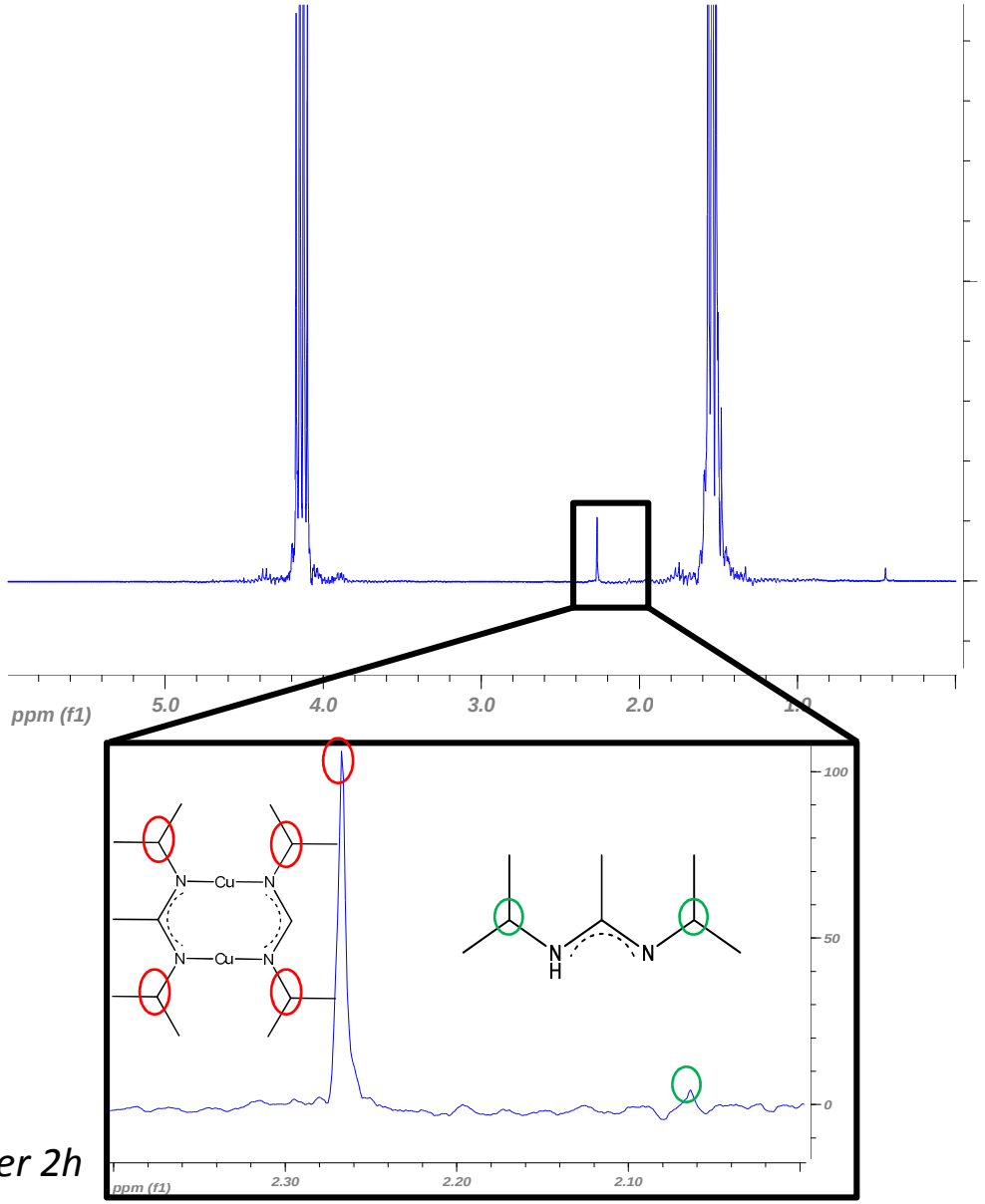
poor adherence on SiO_2 substrate

Data after 2 hours of reaction
500 ppm H_2O



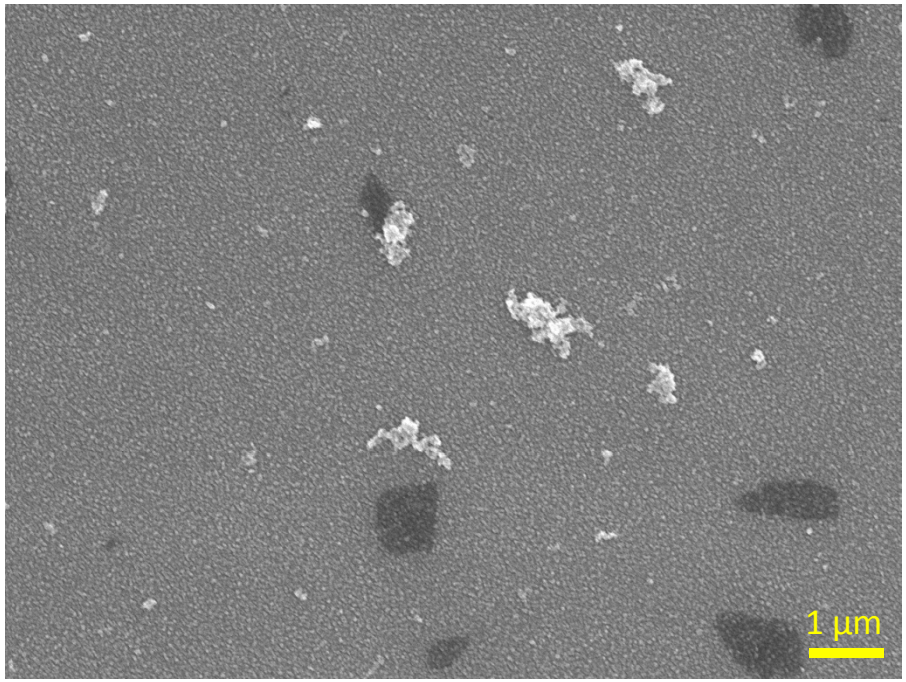
SEM picture of the deposit

Approximately 5% of the copper precursor is consumed

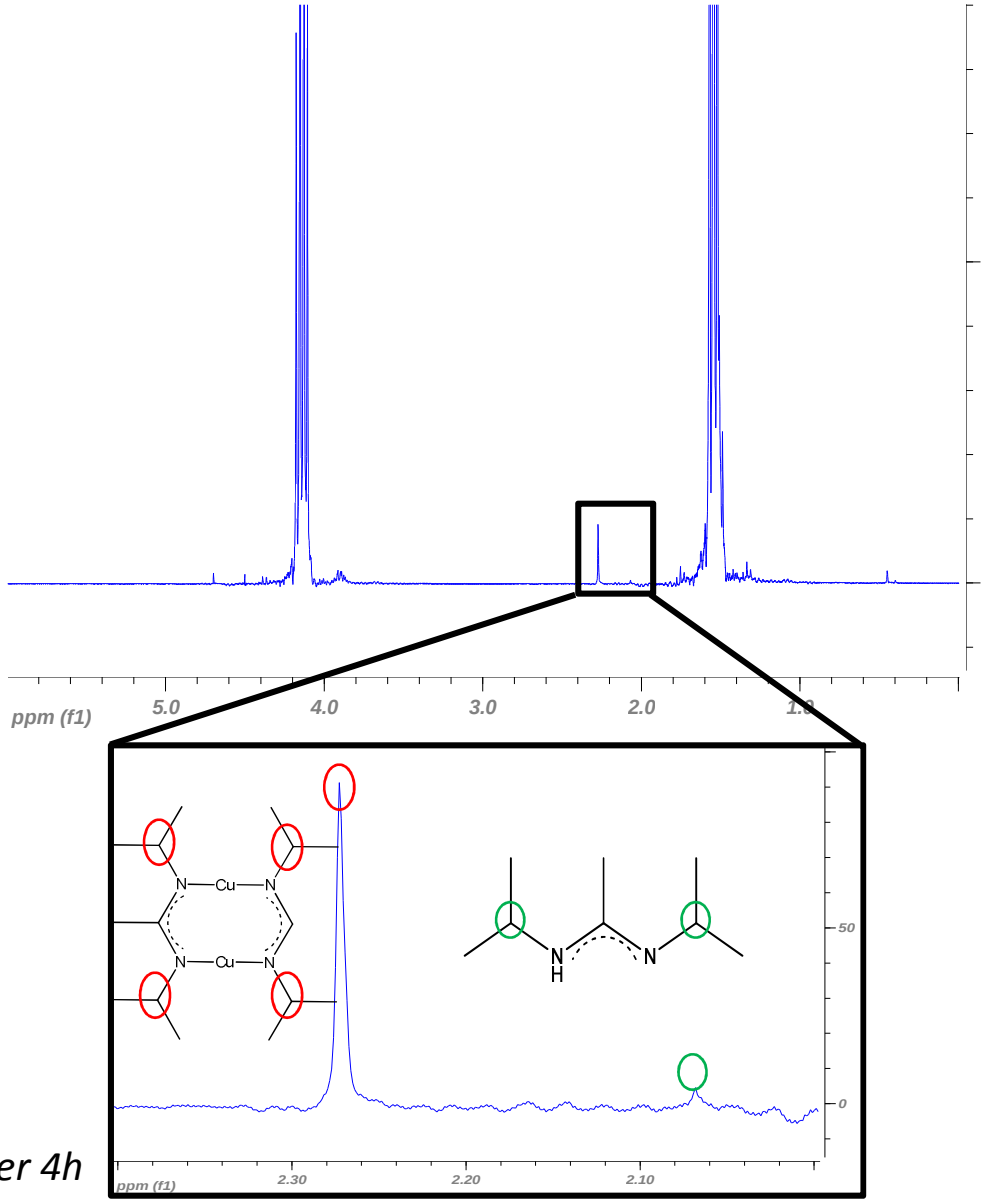


^1H NMR after 2h

Data after 4 hours of reaction
500 ppm H_2O



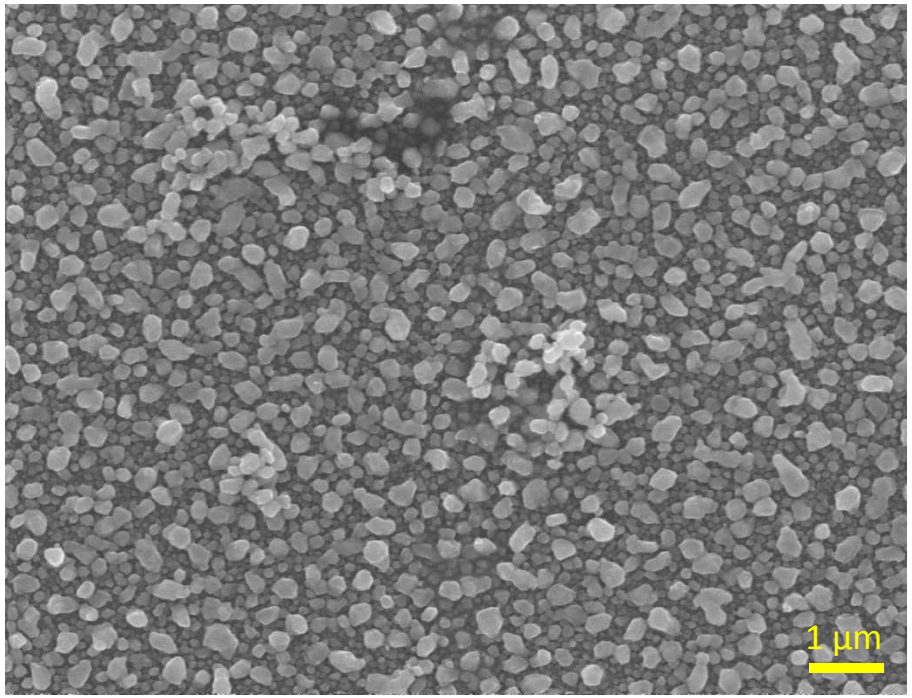
SEM picture of the deposit



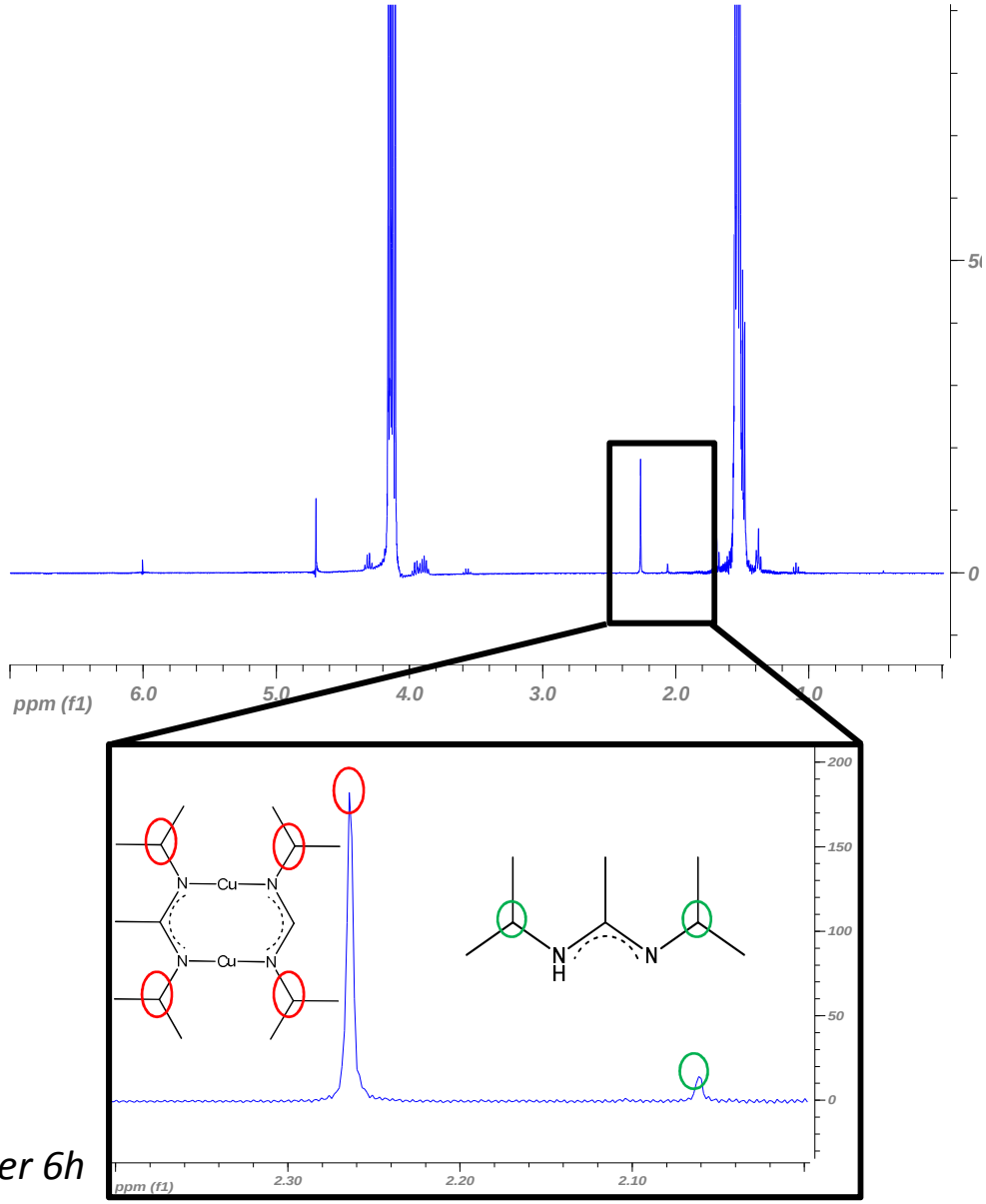
^1H NMR after 4h

Approximately 6% of the copper precursor is consumed

Data after 6 hours of reaction
500 ppm H_2O



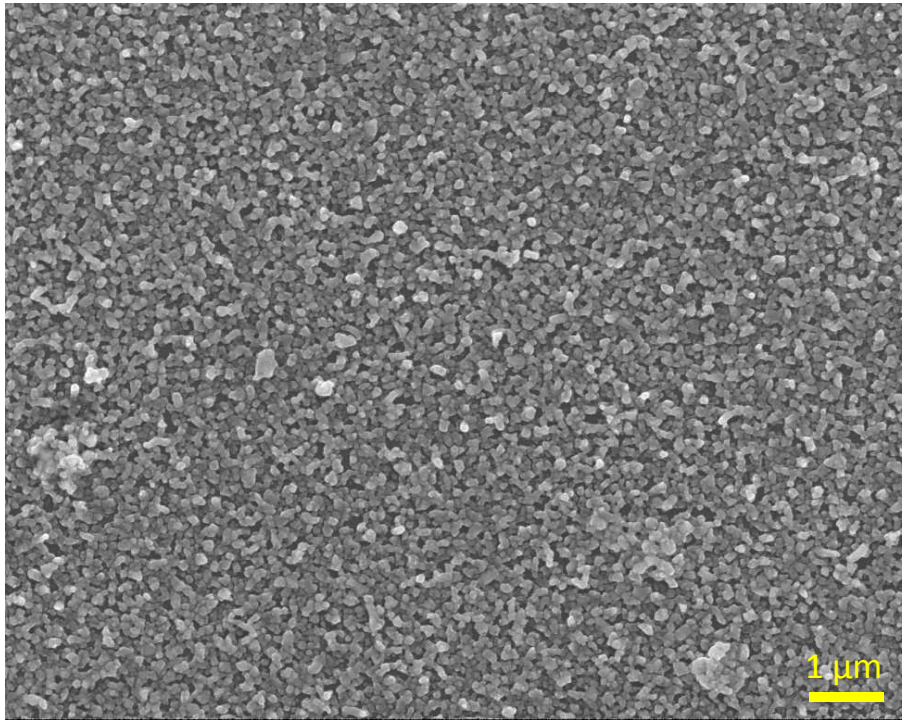
SEM picture of the deposit



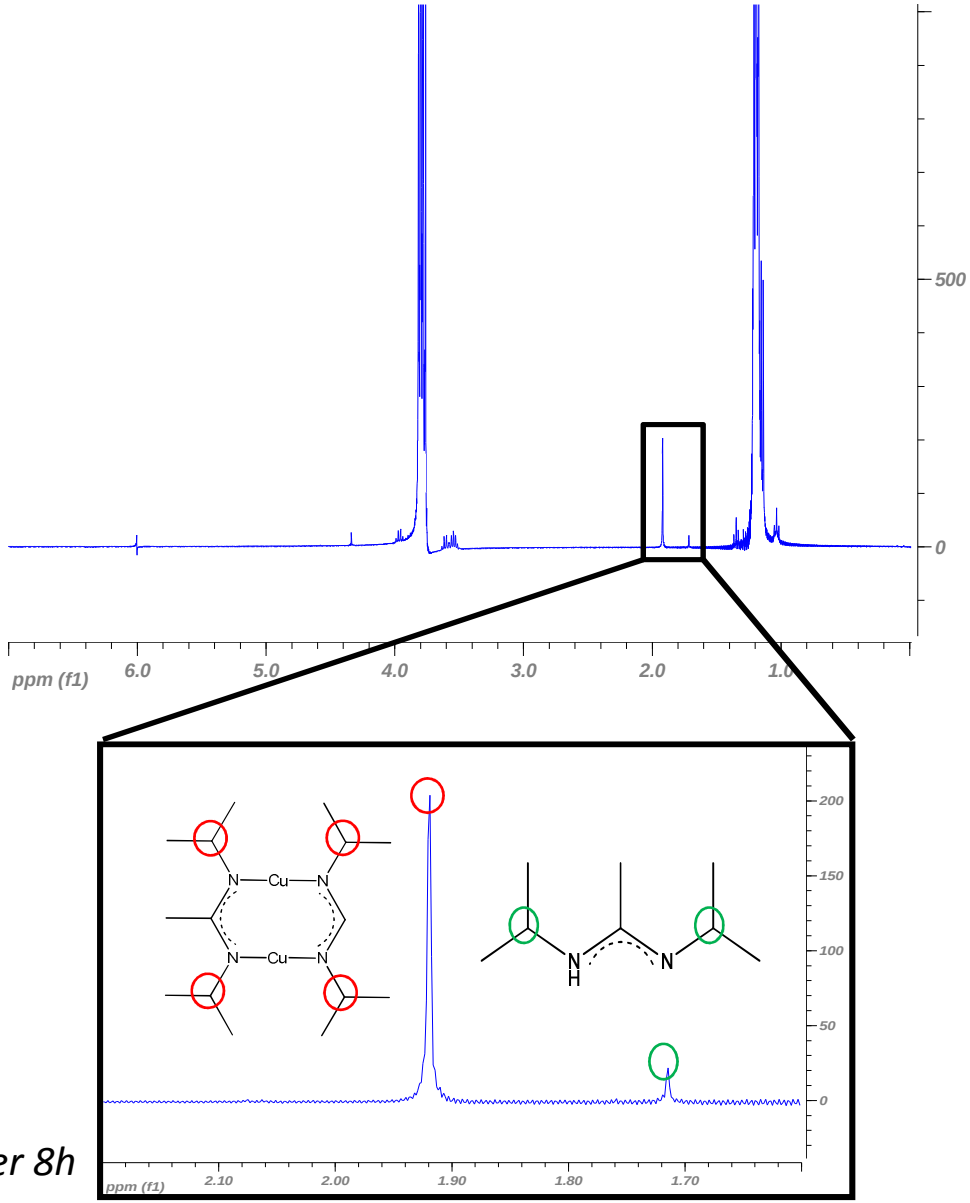
^1H NMR after 6h

Approximately 7,5% of the copper precursor is consumed

Data after 8 hours of reaction
500 ppm H_2O

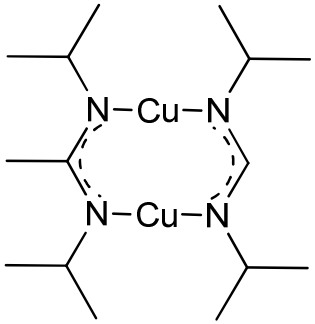


SEM picture of the deposit

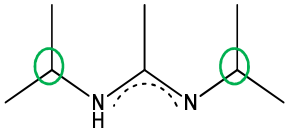


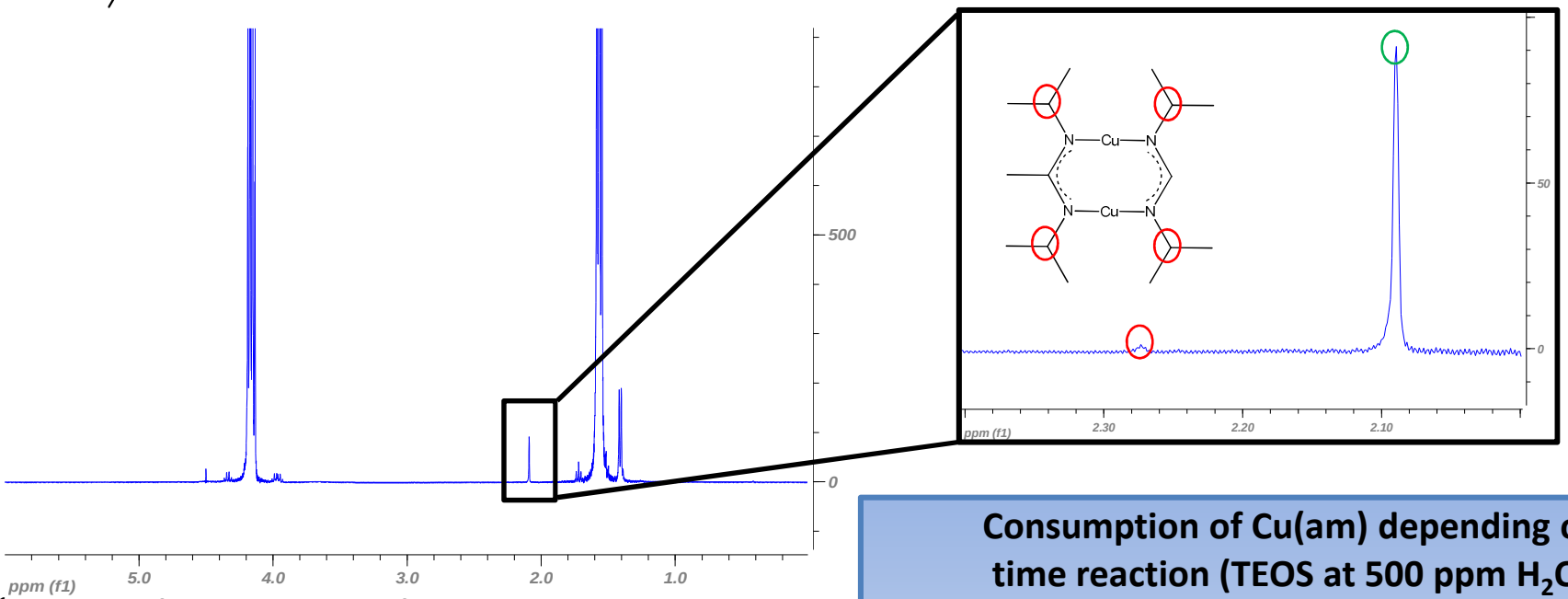
Approximately 11% of the copper precursor is consumed

^1H NMR after 8h



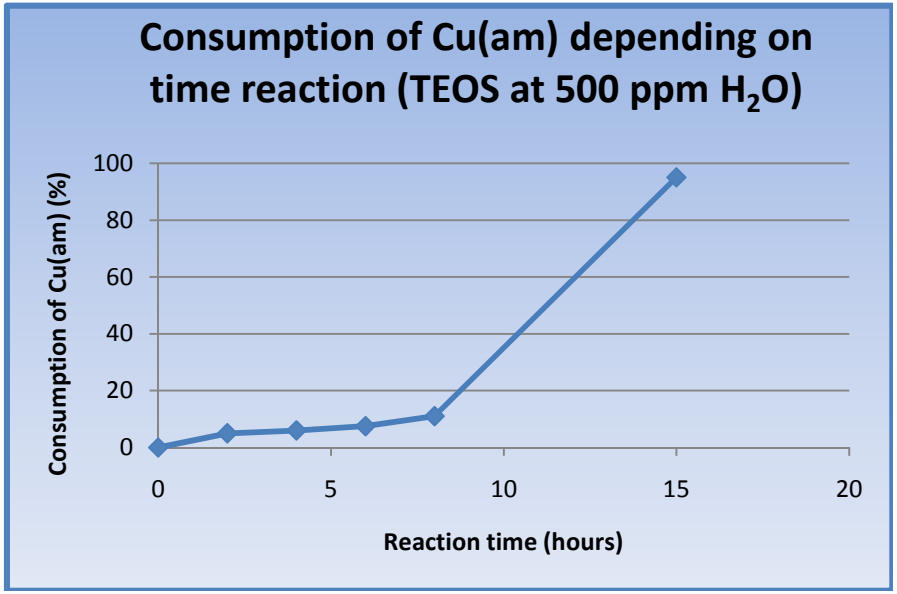
^{1}H NMR of the reaction
H_2O content in TEOS: 500 ppm





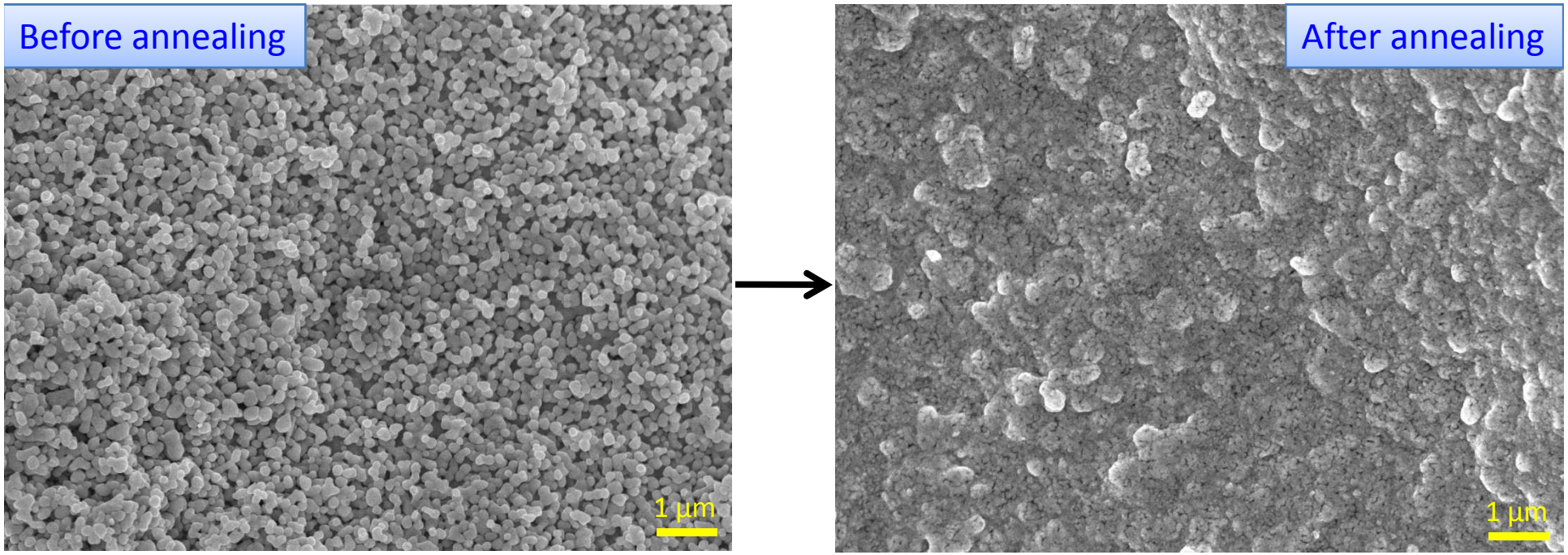
^{1}H NMR after 15h: 95% of the precursor is consumed

Between 8 and 15h, significant increase of the consumption of the copper precursor



SEM pictures

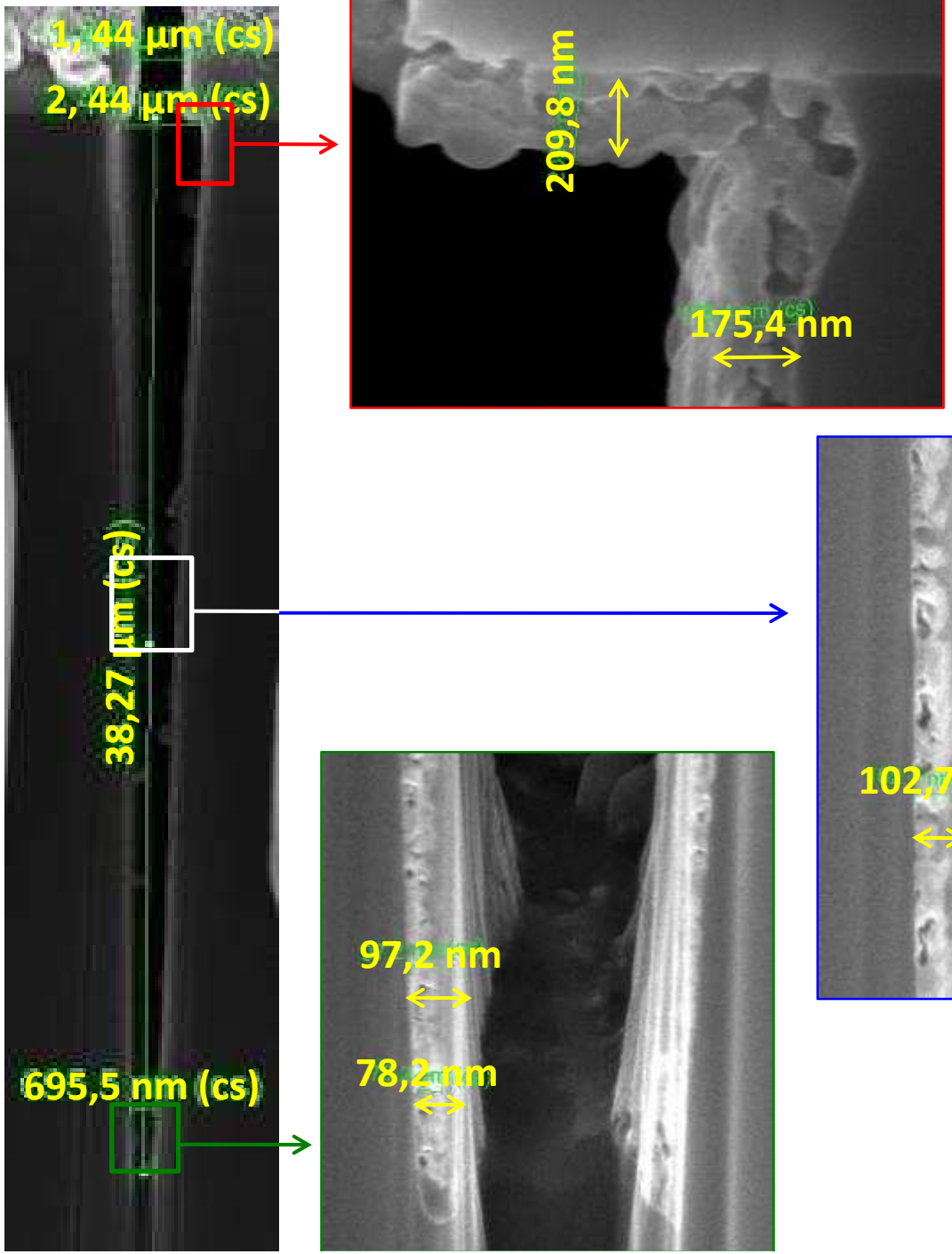
After 15 hours of reaction



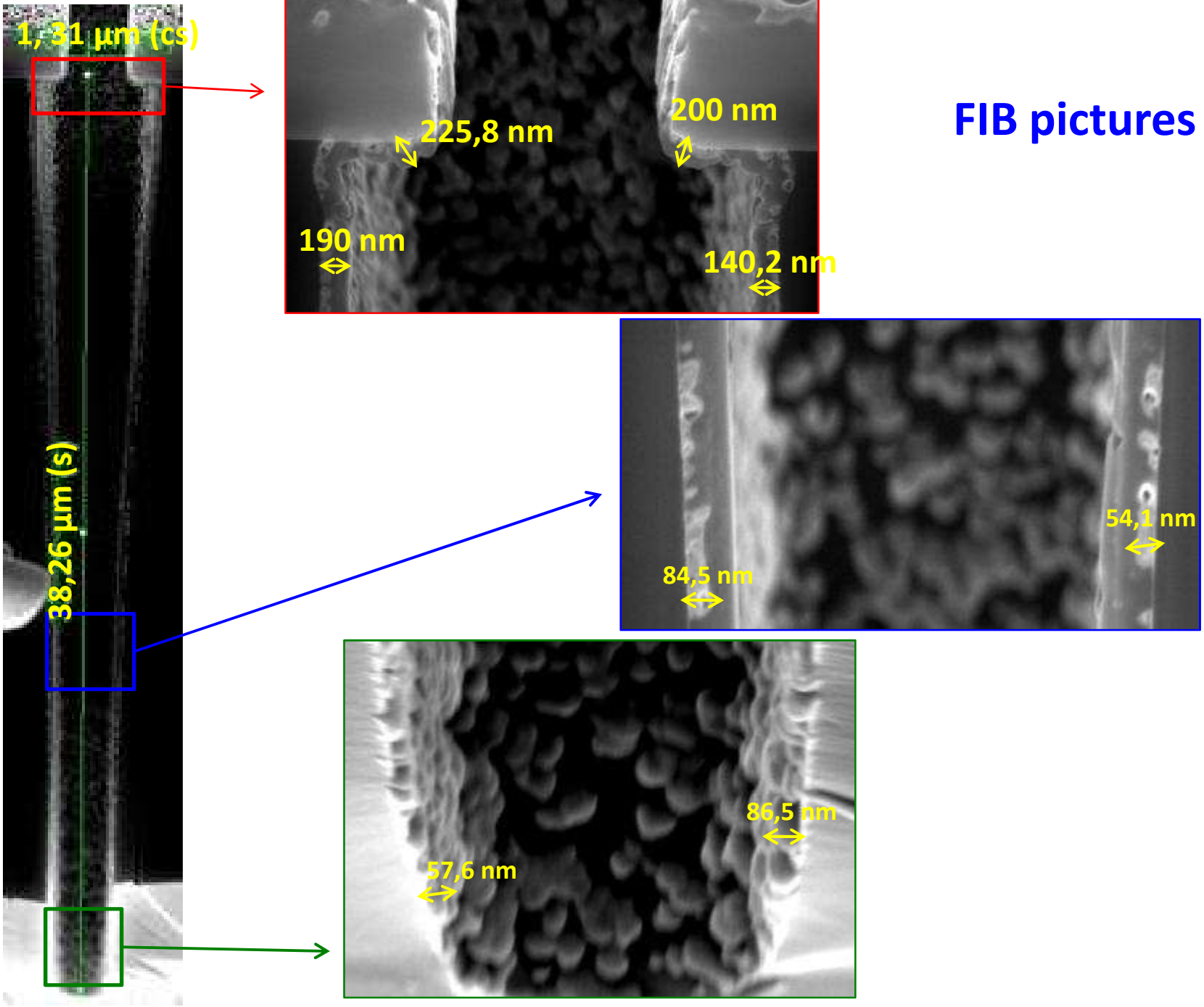
Effect of the annealing on the morphology of the deposit.

Annealing steps: 300°C (increments of 1°C/min) under air (1h)
300°C (increments of 1°C/min) under reducing gas H_2(10%)/Ar(90%) (1h).

Focused Ion Beam (FIB) pictures



FIB pictures



Electroless copper bath

Principle:

- Reduction of a Cu^{2+} salt by reducing agent
- Autocatalytic reaction:
  deposit of copper *only* on metallic parts

Redox reaction (example):

$$Cu(EDTA)^{2-} + 2\ HCHO + 4\ OH^- \longrightarrow Cu + 2\ HCOO^- + H_2 + 2\ H_2O + EDTA^{4-}$$

Characteristics:

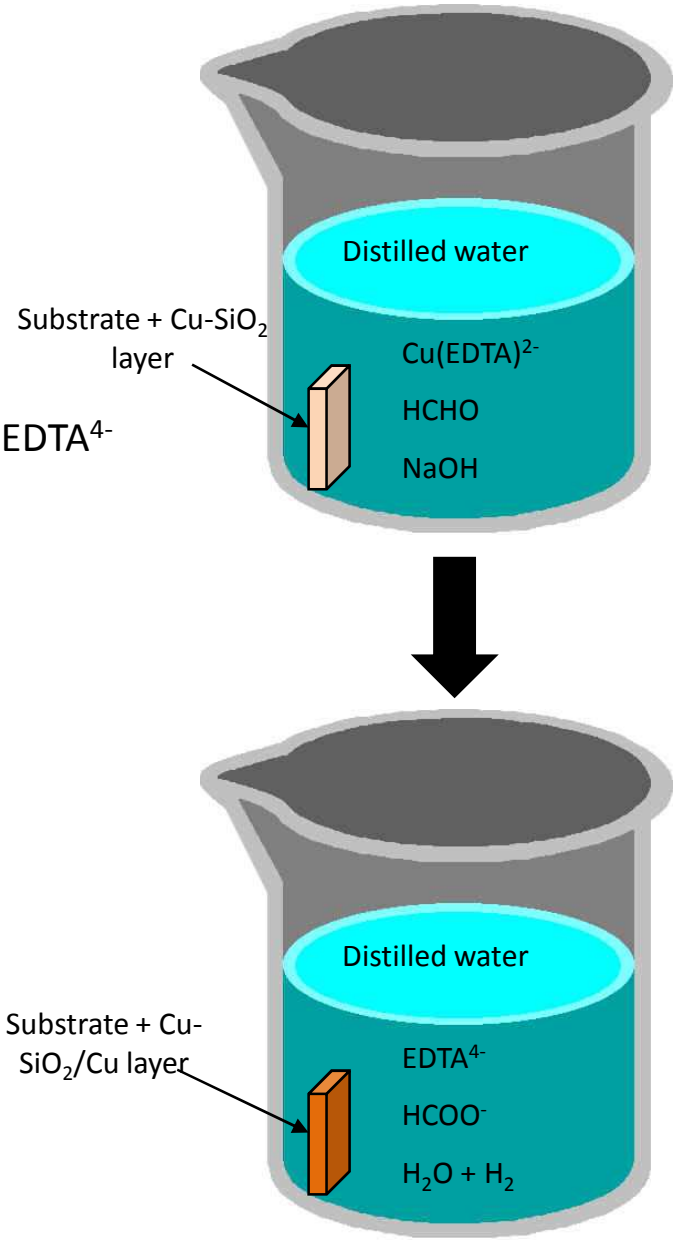
- Catalytic surface increases reaction rate: deposit on the catalyst
- Electron provided by the catalytic oxidation of a reducing agent

Advantages:

- Very good distribution in thickness (homogeneous layer)
- No need of a conductive substrate (≠ electrodeposition)

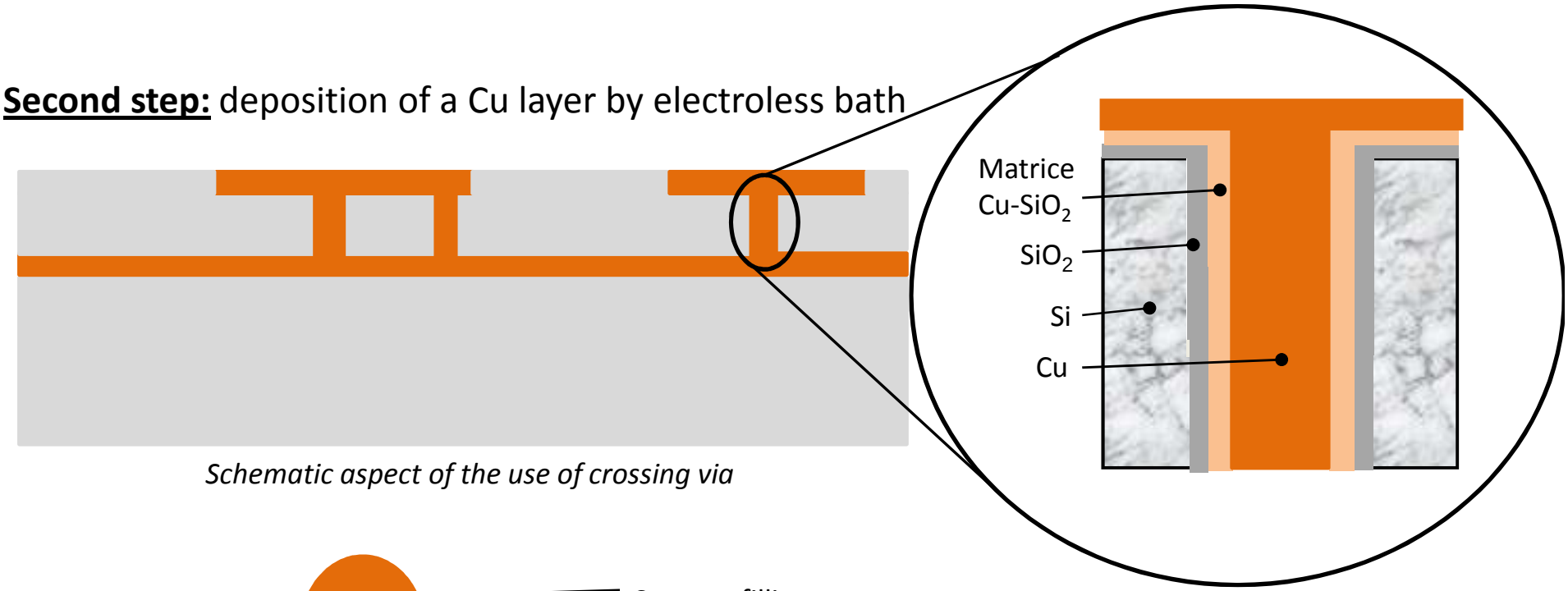
Limitations:

- Low deposit rate
- Instability of the bath
- Needs a metallic seed layer adherent to the substrate
- Seed layer has to be conductive to catalyse the reaction

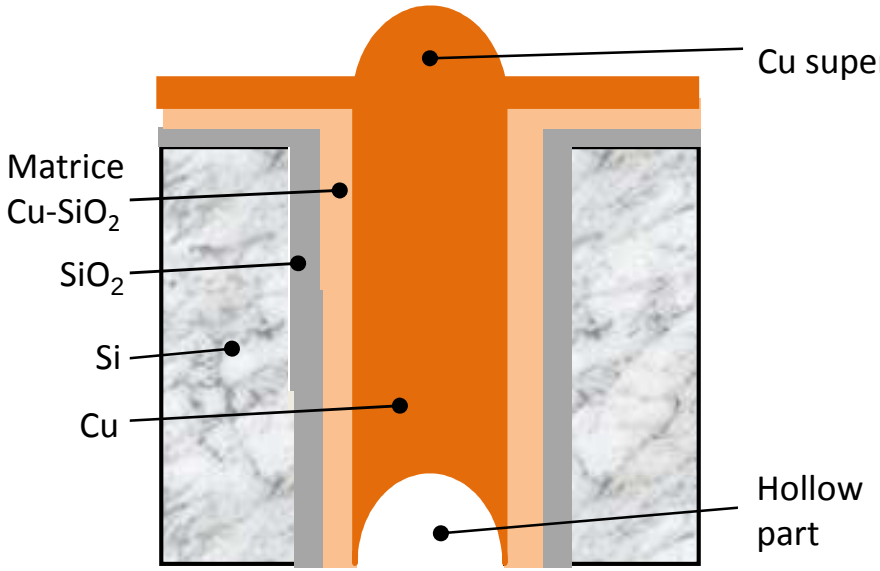


Electroless deposition

Second step: deposition of a Cu layer by electroless bath



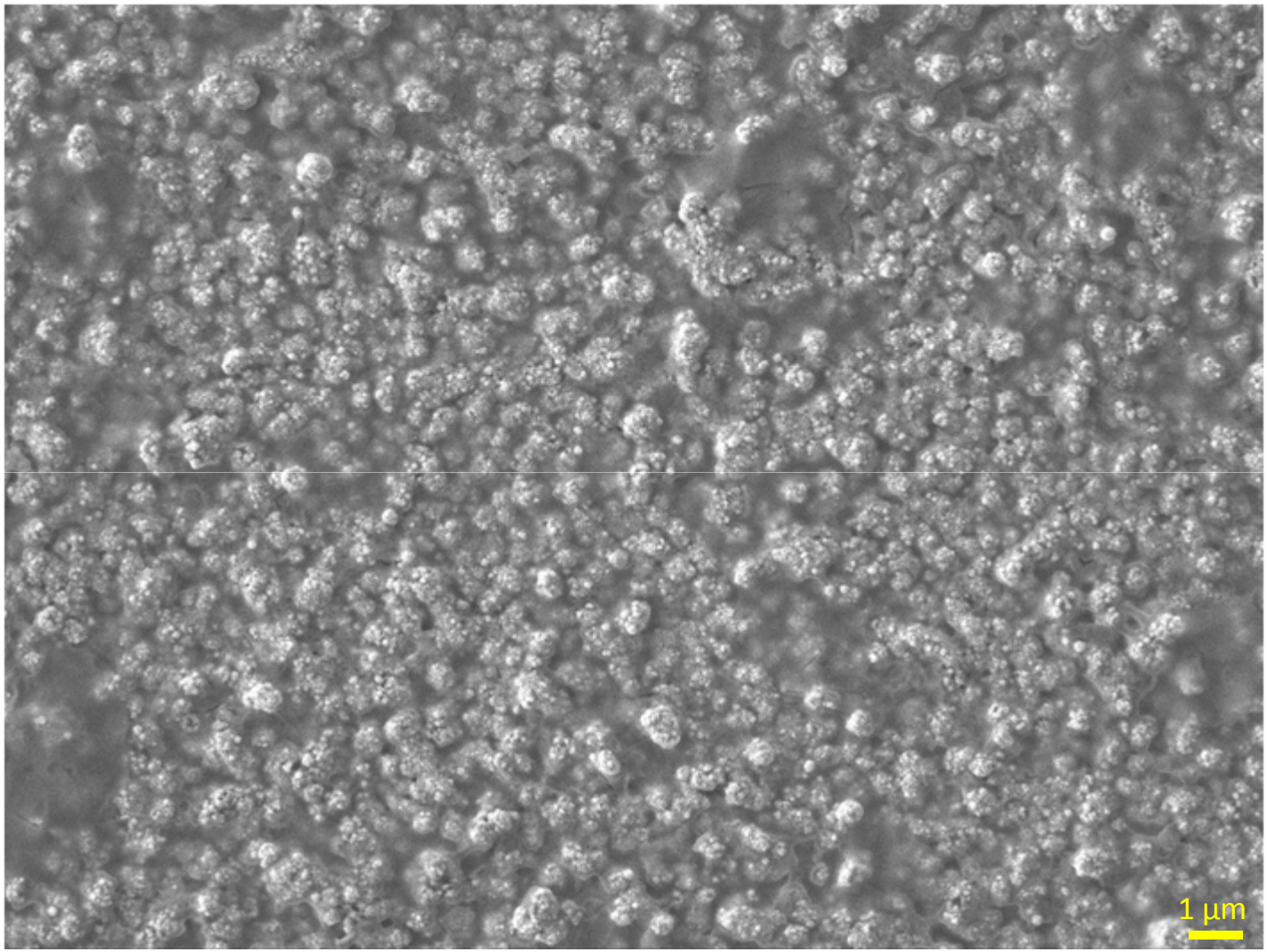
Schematic aspect of the use of crossing via



Main problems encountered is the superfilling of the via, or the presence of a hollow part in the end of the via.

Schematic aspect of the superfilling and hole in a crossing via

Electroless bath copper deposition



Copper electroless deposition on a glass substrate

Conclusion

- Deposition in *3D*-structures can be achieved with a good « *step coverage* »
- Comprehension of the mechanism for the Cu-SiO_2 deposit will lead to the control of all parameters that are operating during the reaction.
- Electroless bath is under investigation. Copper deposit has been observed but the technique has to be mastered.

Aknowledgments

Yannick COPPEL (NMR), Vincent COLLIERE (SEM), Dominique GENARD (FIB)

Pôle de compétitivité CAPI, CIFRE, STMicroelectronics

L team →

Thank you for your attention!


Toulouse

Merci de votre attention!

¡Gracias por su atención!

Cu-SiO_2 films for 3D filling in microelectronic applications by an organometallic chemical liquid deposition (OMCLD) route

Málaga
March, 24th 2010

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