Role of surface chemistry and metal oxides in conditioning of materials for particle accelerators

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Context

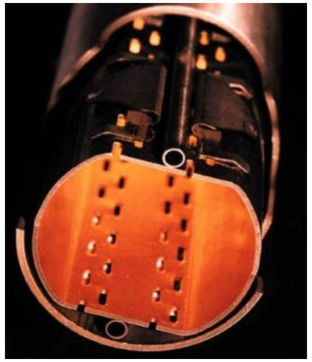
Surface conditioning of vacuum chamber walls is paramount in high energy accelerators (e.g. scrubbing run for the LHC):

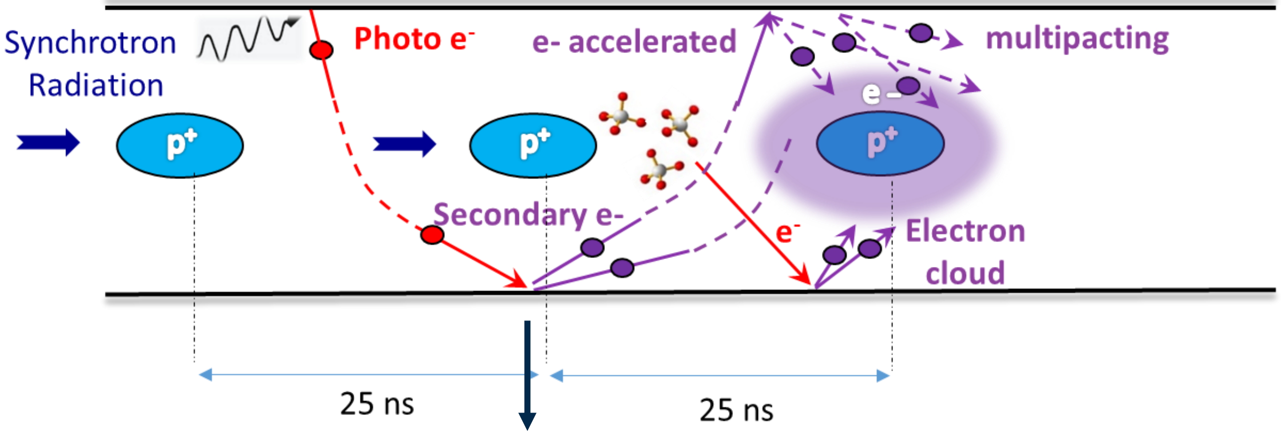
- To limit increases of pressure during beam operation

- To mitigate the e-cloud build up (source of heat load onto the cryogenics system= critical issue)

→Secondary electron yield = a key parameter for the e-cloud formation

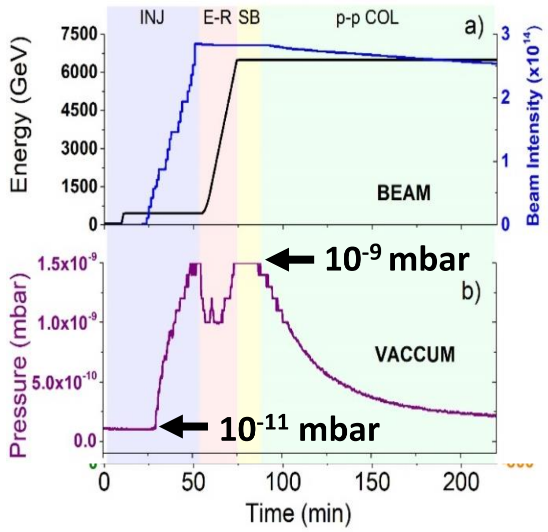
LHC beam screen





$$SEY = \frac{I_{secondary\ e-}}{I_{incident\ e-}}$$

Dynamic pressure in the LHC (Vacuum Pilot Sector Station 4)

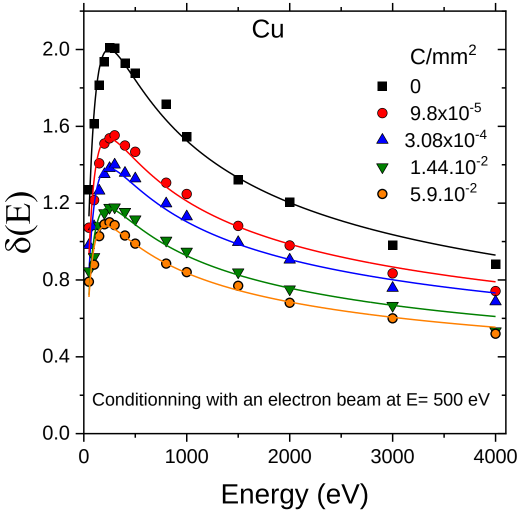


S. Bilgen, PhD thesis, 2020

Conditioning of copper and SEY : reminder

Modification of the "C-chemistry" under electron-bombardment

No conditioned surface : SEY ≈ 2.1
Fully conditioned by e- irradiation : SEY ≈ 1.1

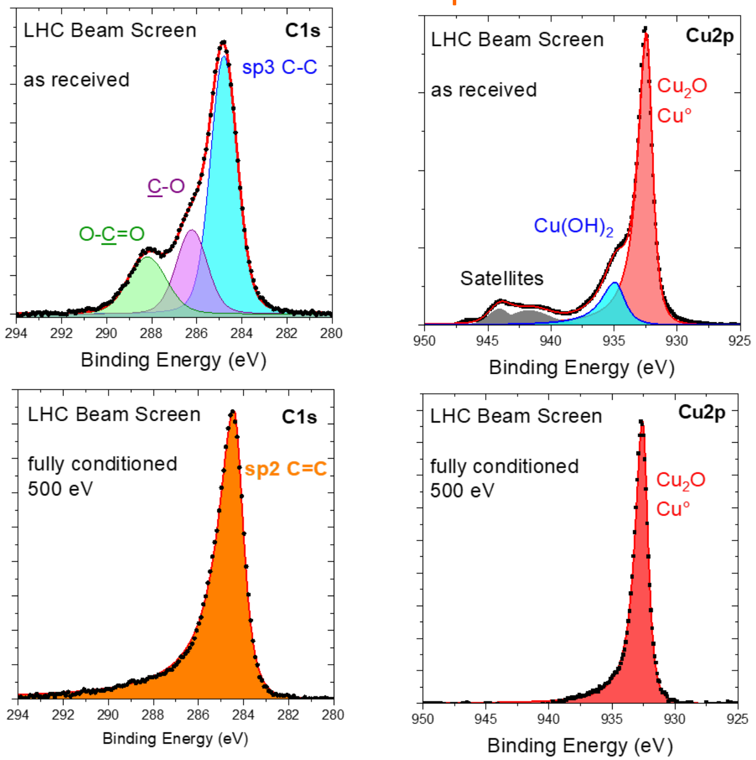


*Phenomenological model used for the **fit***

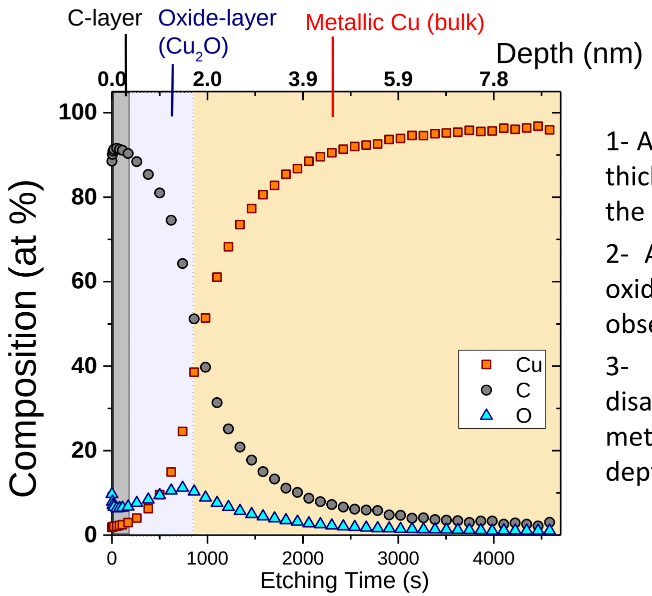
$$\delta(E) = \delta_{max} \frac{s * \left(\frac{E}{E_{max}}\right)}{s - 1 + \left(\frac{E}{E_{max}}\right)^{s}}$$

XPS

C1s peak



Depth profiles of elements in a fully conditioned Cu



1- A carbon layer (≈ 0.5 nm thick) is first detected at the extreme surface.

2- At a larger depth, the oxide layer (Cu_2O) is observed of ≈1.4 nm thick.

3- Copper oxide disappeared and finally metallic Cu is detected at a depth larger than 2 nm.

<u>Adventitious carbon (C-O, O-C=O) is removed by electron irradiation</u>:

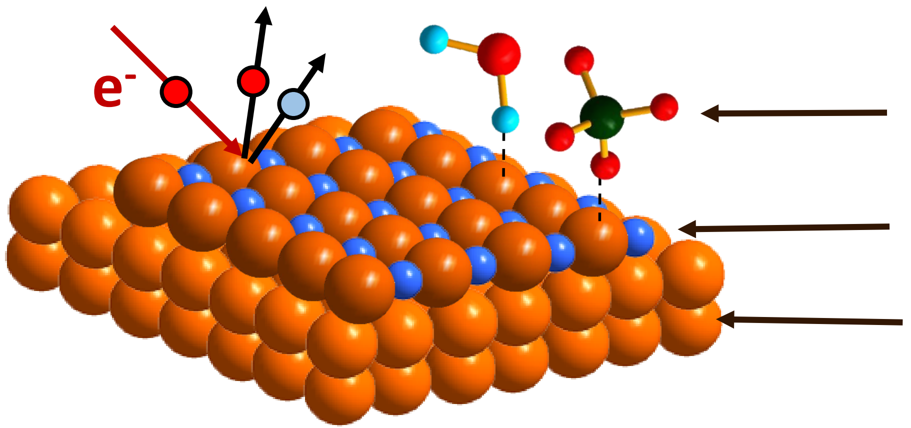
Specific peaks associated with organic molecules on the surface, disappear after the surface cleaning by the e- bombardment.

<u>Modification of the C hybridization induced by electron irradiation:</u>

Shift of the max of the peak towards low energies (XPS analysis): signature of a modification of C chemical bonds: from C-C bonds (sp3) to C=C bonds (sp2)

→ in agreement with the literature [R. Cimino et al, 2020] [V. Petit , 2019]

Materials for accelerators → technical surfaces



- surfaces in accelerators are **technical surfaces** (and not pure Cu surfaces in the case of Cu LHC Beam Screen)
- there are **always contaminants** deposited on the surface + native oxide layers (Cu_2O et $Cu(OH)_2$)

- Solution to reduce SEY : thin film deposition (a-C coating, NEG coating) or laser treated surfaces
- But only the extreme surface is involved in the secondary electron emission process (escape depth of electrons ≈ 10 nm)

OUTLINE

- **What is the minimum C-layer thickness to decrease SEY?**
- **What is the role played by the native oxides of the metal (e.g. Cu)?**
- **Comparison of SEY for several conditioned materials**

C-coating on copper

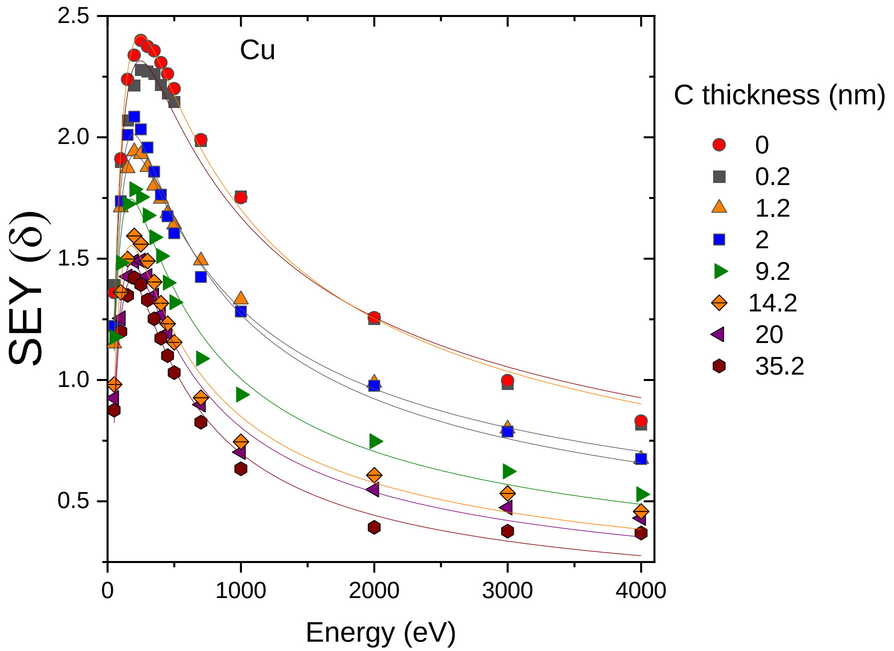
- Aim : investigate the minimum thickness of carbon coating to reduce the SEY of copper
- a-C coatings with different thicknesses were deposited on copper
- SEY was measured + XPS analysis
- Inspire from work performed by M. Angelucci et al (Phys. Rev. Res. 2020)

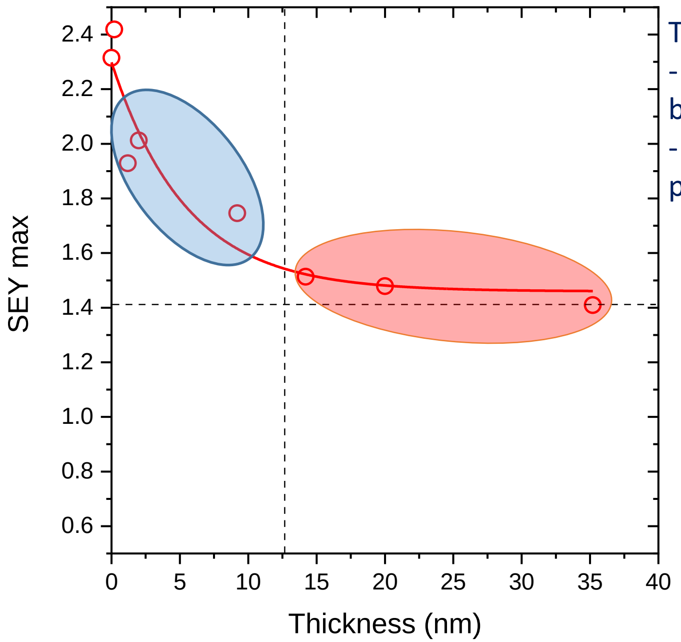
C-coating on Cu : SEY of as-received sample

- Cu Flag + polishing with SiC grinding paper (grit 1000) + ethanol cleaning + glow discharge plasma cleaning

- C-layer on Cu by evaporation coating with several thicknesses (0.2 to 35.2 nm measured by a quartz crystal microbalance)

Before conditioning





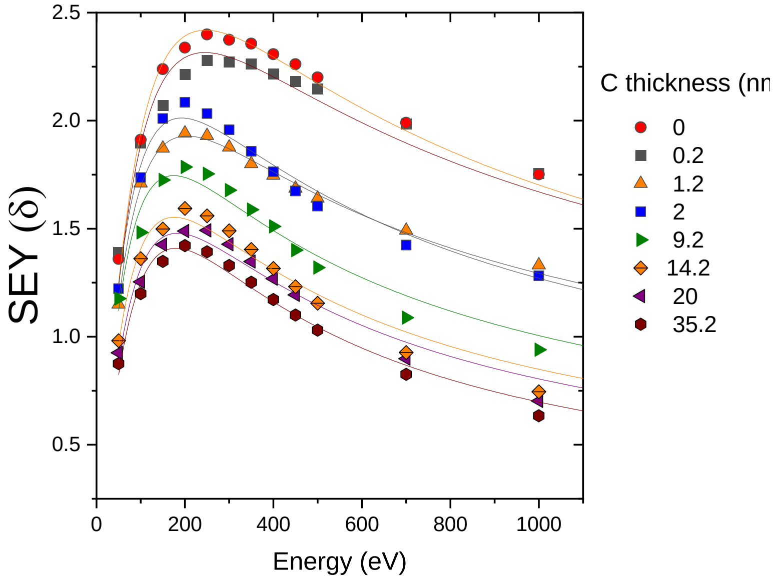
Thickness < 12 nm
- Electrons emitted by the surface both by C-coating and Cu-substrate
- SEY driven by both materials properties

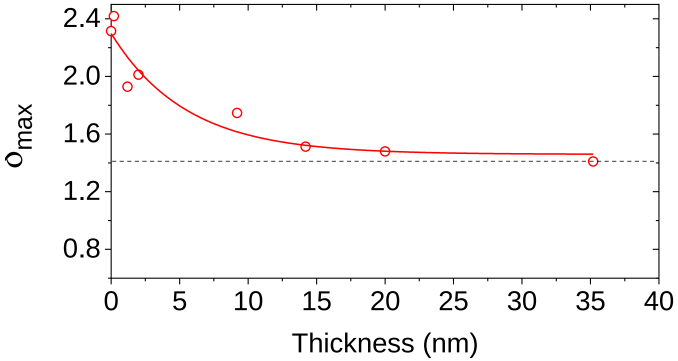
Thickness > 12 nm
SEY dominated by the C-layer properties

δ_{max} decreases (from ≈ 2.3 down to ≈ 1.4) when the thickness of the C-coating increases
It reaches a threshold ≈ 1.4
A thickness of ≈ 12 nm is sufficient to reach the minimum SEY value before conditioning

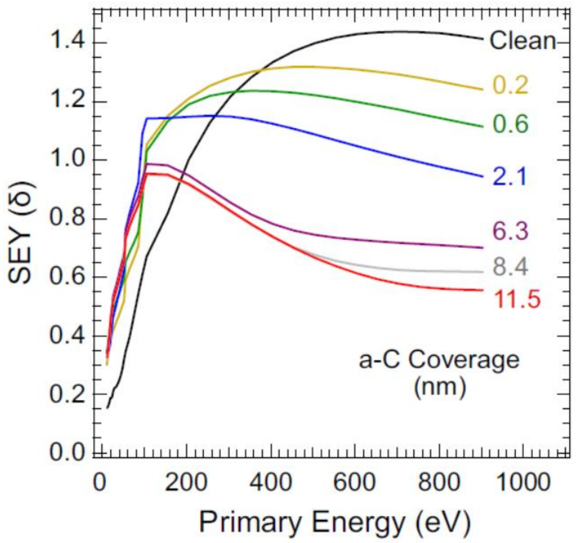
Effect of C-coatings on SEY : a benchmark study

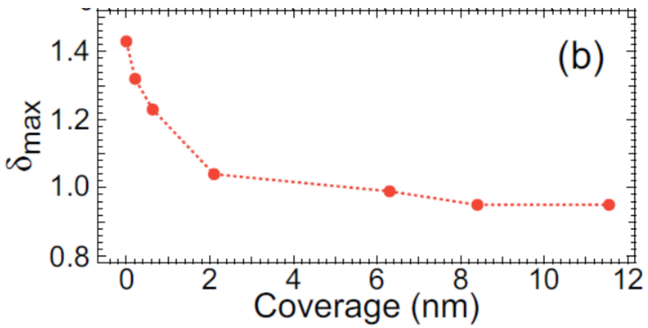
Our results





M. Ancelutti et al (Phys. Rev. Let. 2020)





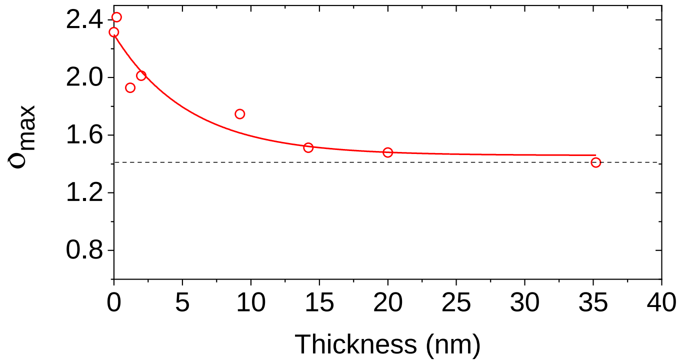
- Cu cleaned by Ar sputtering
+heat treatment
- C deposition with a very low pressure (UHV)

Main differences :

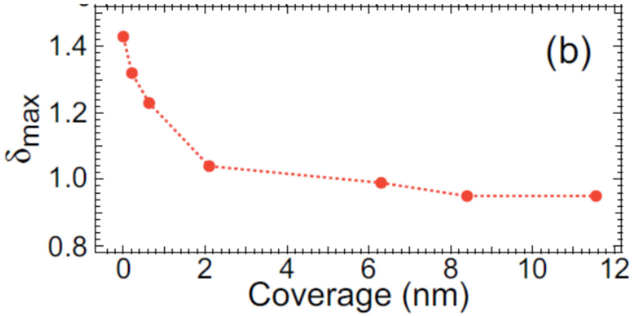
- Initial δ_{max} is lower
- It decreases from 1.4 (cleaned Cu) to less than 1 (6 nm C-coating)

Effect of C-coatings on SEY : a benchmark study

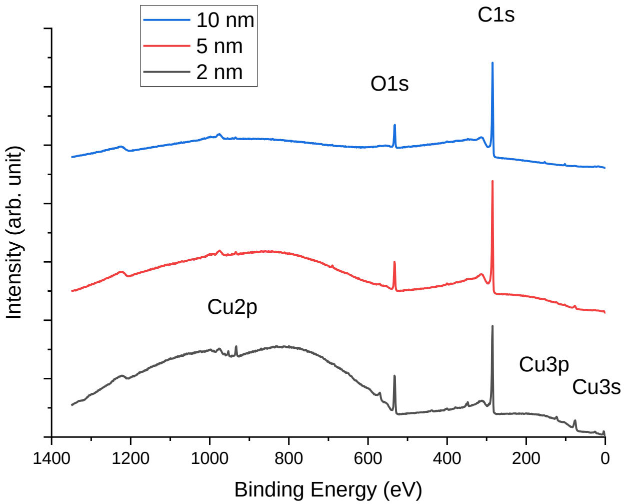
Our results

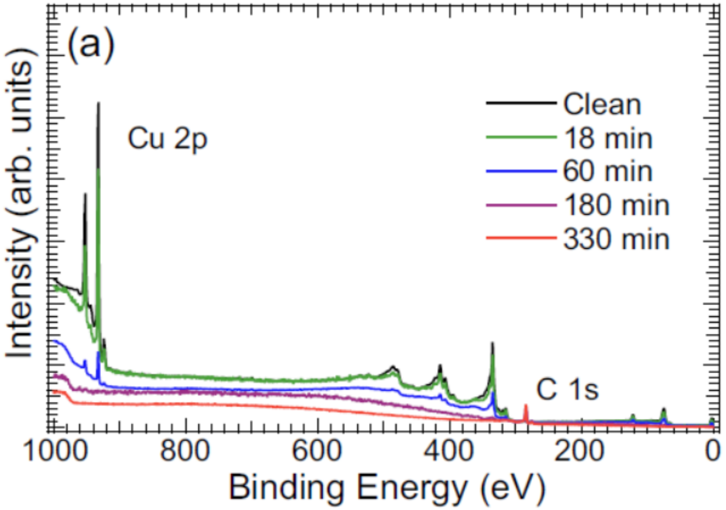


M. Ancelutti et al (Phys. Rev. Let. **2** 032030(R) 2020)



XPS

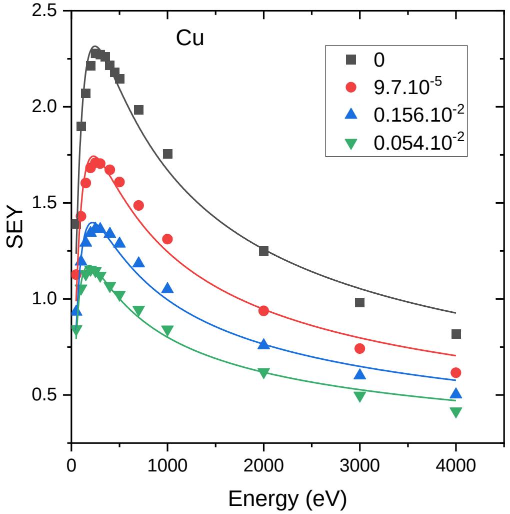




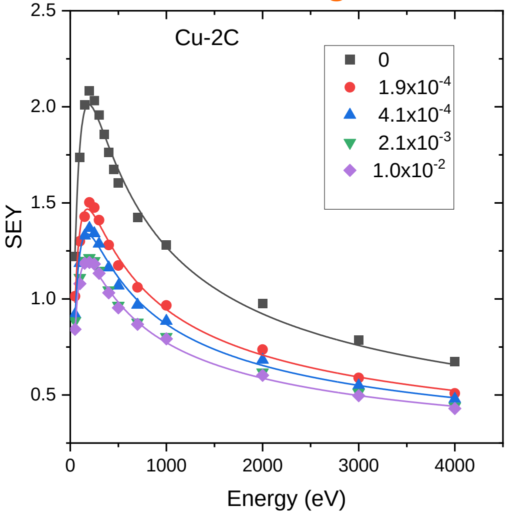
- Density of C-layers may be different
- More pollutants are present in our C-layers (dirtier than those of the Frascati team)
- H and O are incorporated in our C-coatings

C-coating on Cu : SEY and conditioning

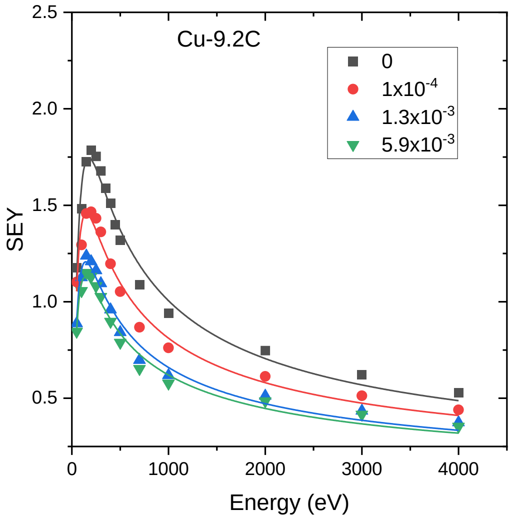
Cu



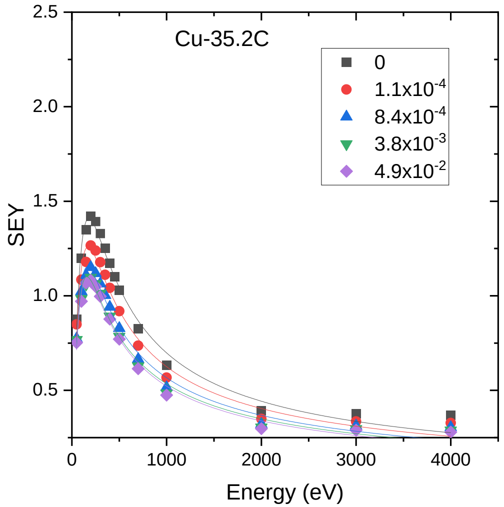
C-coating 2 nm



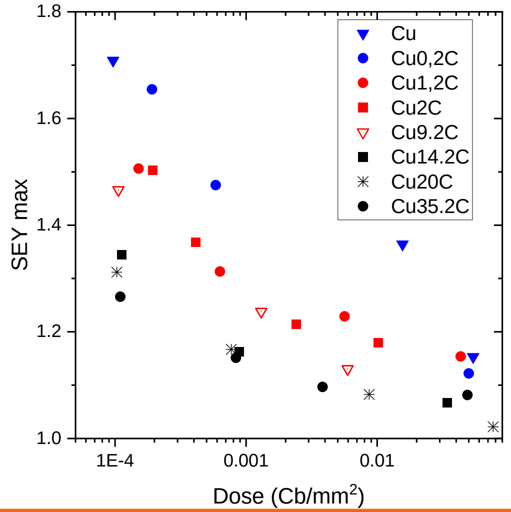
C-coating 9.2 nm



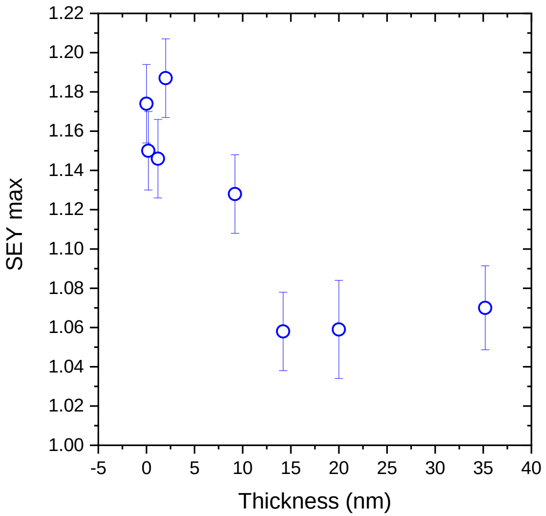
C-coating 35.2 nm



Evolution of the SEY max with electron dose (conditioning @ 500 eV)



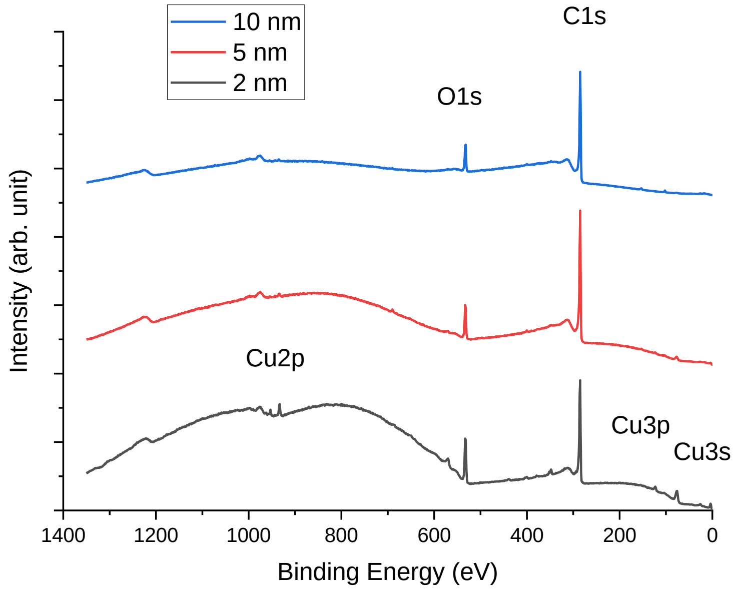
SEY of fully conditioned C-coatings

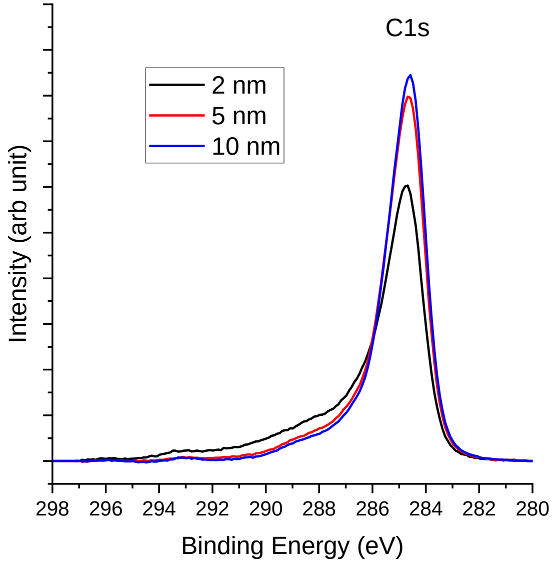


C-coating thickness has an impact on the minimum SEY value:
It is lower from a C-coating thickness > 12 nm

XPS analysis of C-coatings

Before conditioning

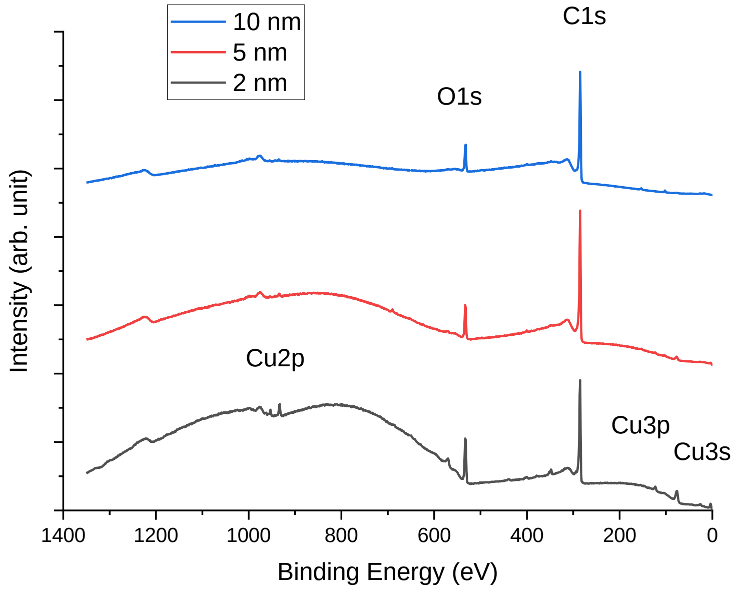


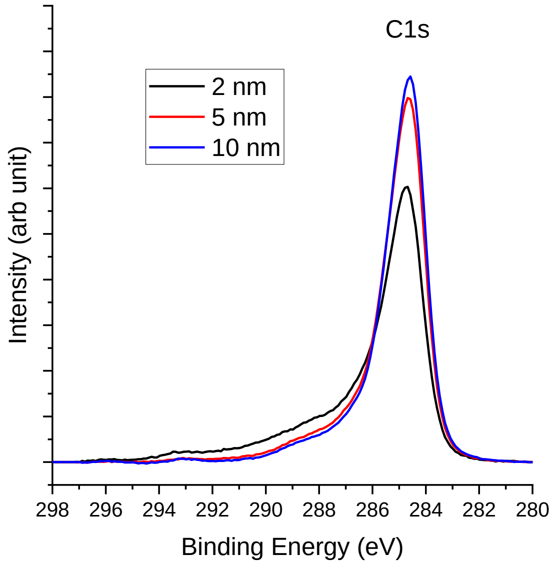


Cu signal decreases and C signal increases with the increase of C-layer thickness

XPS analysis of C-coatings

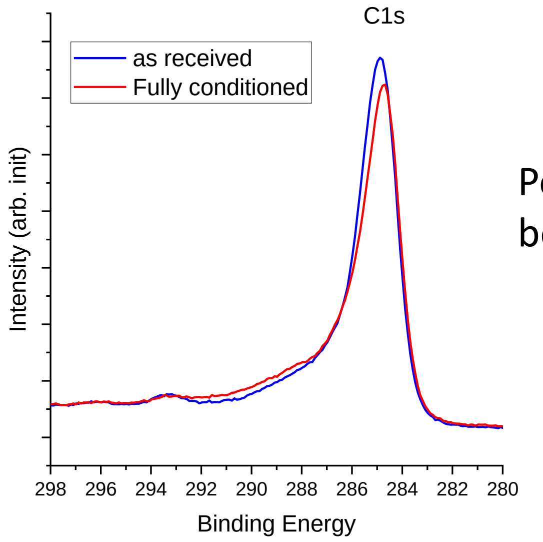
Before conditioning





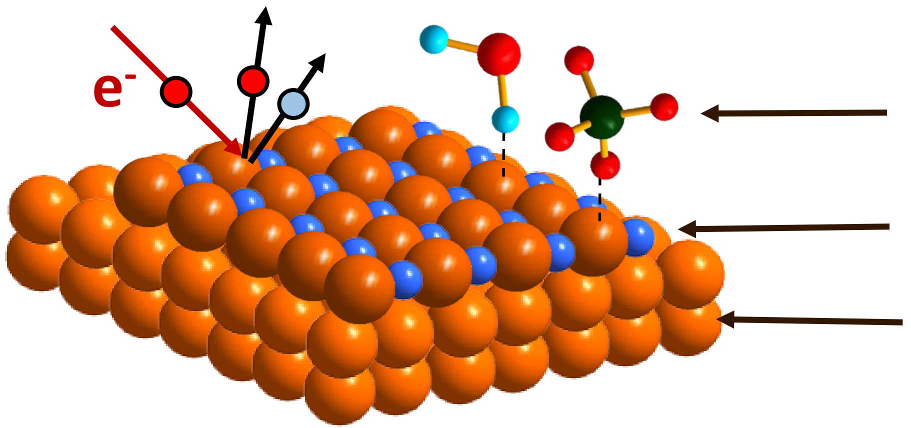
Cu signal decreases and C signal increases with the increase of C-layer thickness

Fully conditioned C-coating
Thickness = 2 nm



Peak shift correspondingto the C transformation from C-C bonds (sp3) to C=C bonds (sp2)

Materials for accelerators → technical surfaces



- surfaces in accelerators are **technical surfaces** (and not pure Cu surfaces in the case of Cu LHC Beam Screen)
- there are **always contaminants** deposited on the surface + native oxide layers (Cu_2O et $Cu(OH)_2$)

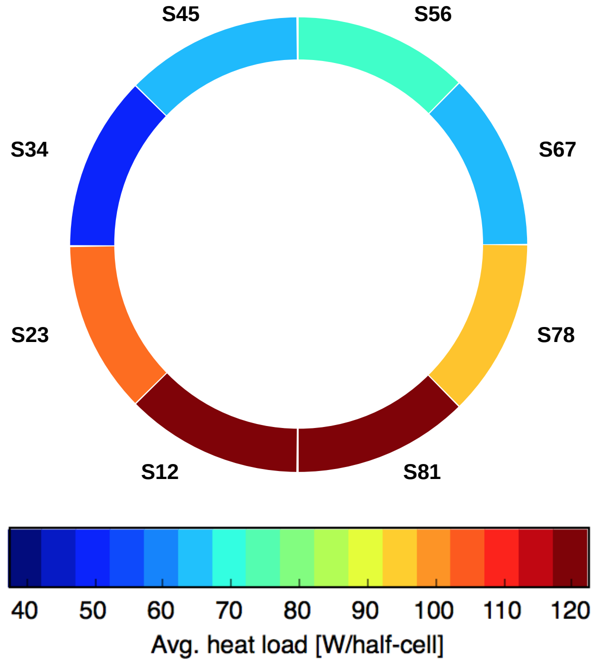
- Solution to reduce SEY : thin film deposition (a-C coating or LASE surface)
- But only the extreme surface (below 10 nm) is involved in the secondary electron emission process

OUTLINE

- **What is the minimum C-layer thickness to decrease SEY?**
- **What is the role played by the native oxides of the metal?**
- **Comparison of SEY for several conditioned materials**

Copper oxides : a "hot topic" at CERN !

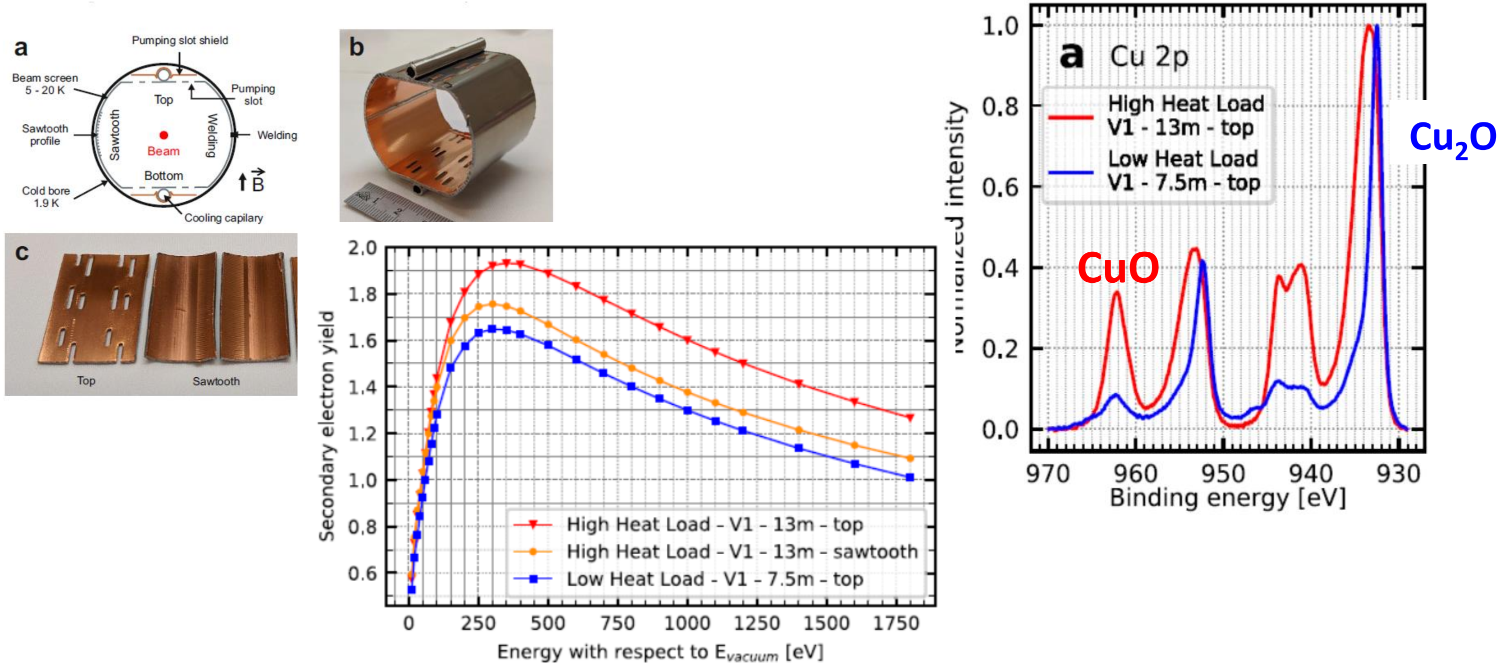
Heat load from the EC in the LHC



Giovanni Iadarola, CERN
E-CLOUD workshop 2018

- heat load is inhomogeneous along the ring
- machine appears to be splitted into two parts:
Blue arcs average heat load are lower (so less EC) that other arcs (with an important EC activity)

V. Petit PhD Thesis (CERN, 2020) / V. Petit et al COMMUNICATIONS PHYSICS



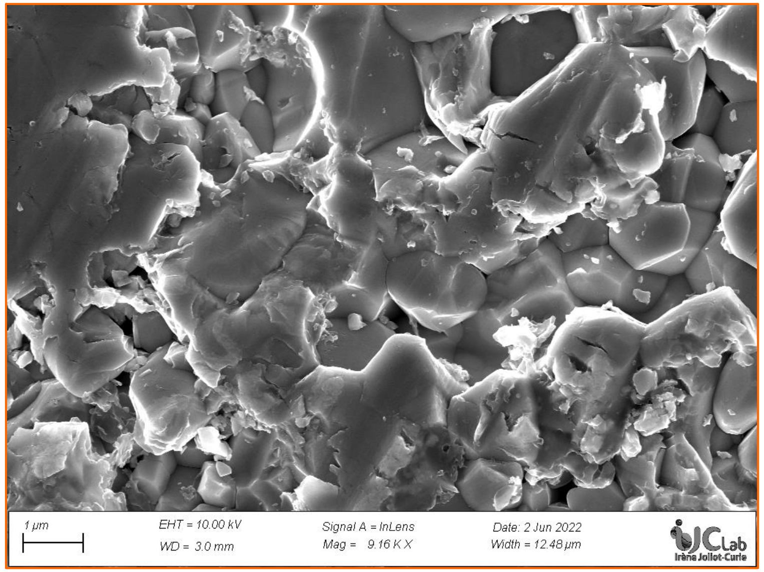
- Beam screen extracted from the LHC beam pipe
- High Heat Load parts exhibit a higher SEY than the Low Load parts
- **CuO was detected (and not the native oxide Cu_2O) in High Heat Load parts** (high EC activity because more e- produced) **!**

CuO is responsible for the higher SEY observed on this sample (responsible for the high heat loads measured in some arcs)

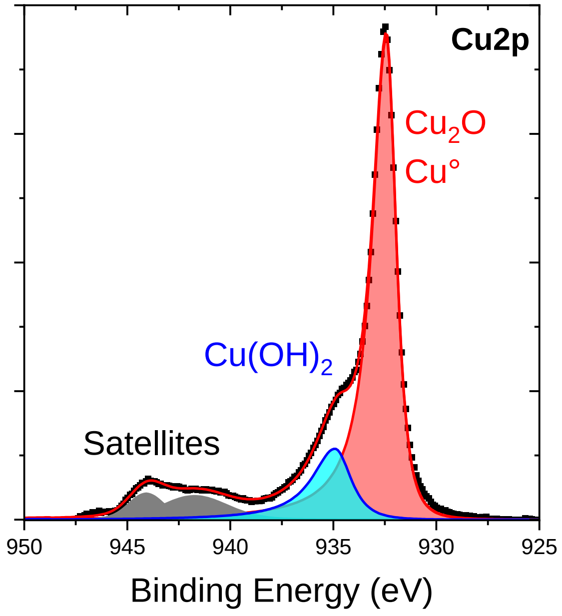
Cu_2O – cuprite : SEY and conditioning

Provided by the NEYCO company

SEM

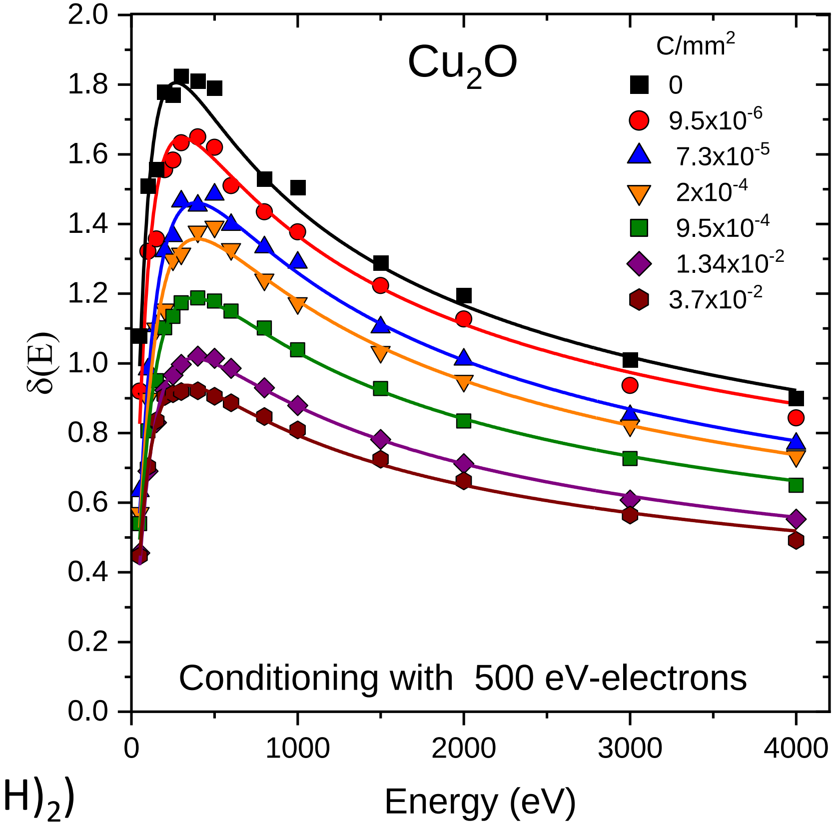


XPS



Typical XPS spectrum of Cu_2O (+ $Cu(OH)_2$)

SEY



After conditioning SEY ≈ 0.9

Elaboration of CuO - tenorite

CuO layer was produced by a chemical route on a Cu substrate :

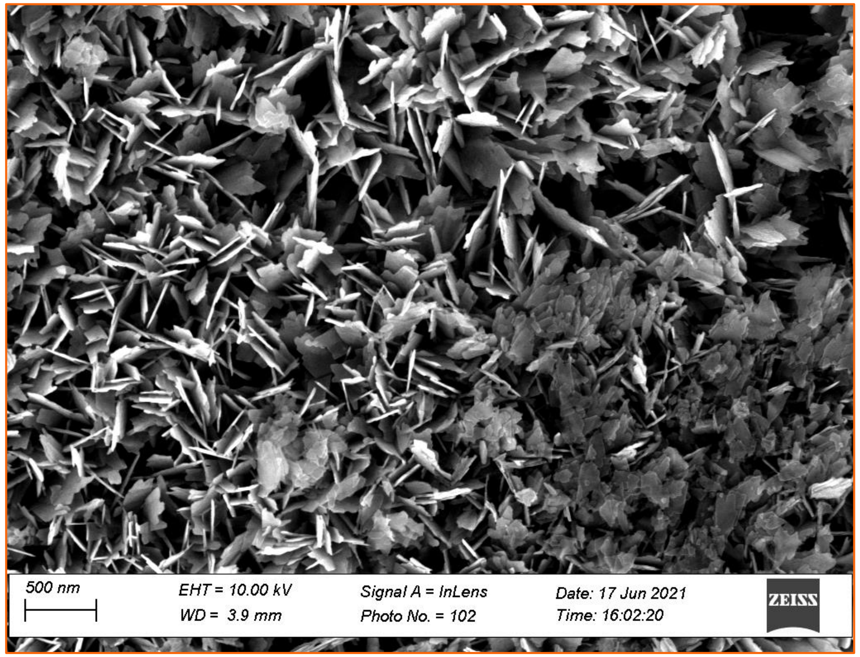
$Cu + 2KOH + K_2S_2O_8 \rightarrow 2K_2SO_4 + Cu(OH)_2$

$Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$

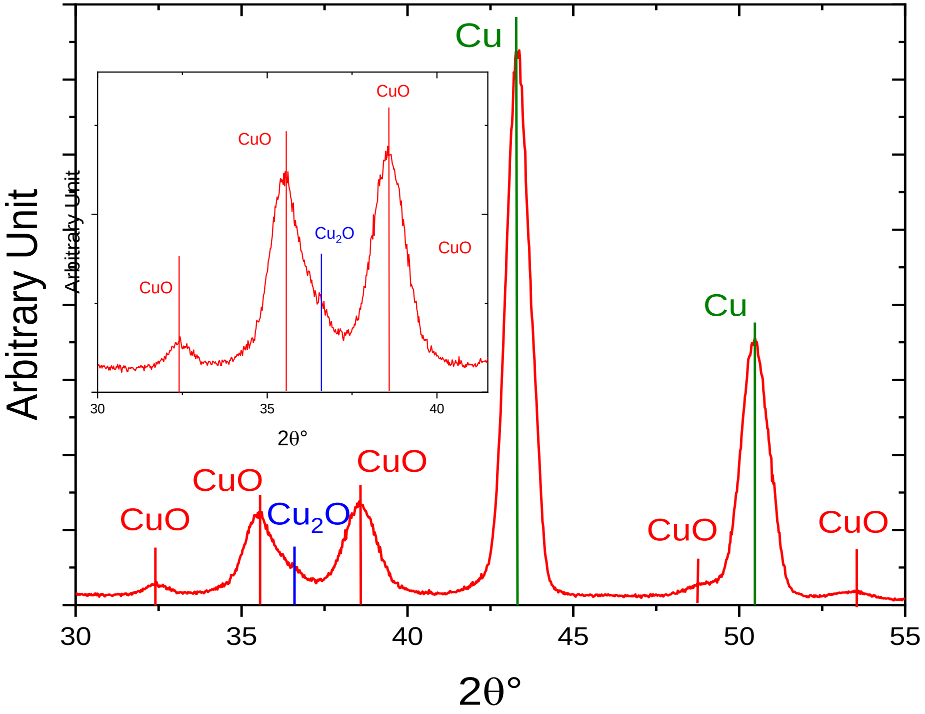
$Cu^{2+}(aq) + 2OH^- \rightarrow Cu(OH)_2(aq)$

$Cu(OH)_2(aq) \rightarrow$ **CuO** $+ H_2O$ at 60°C

SEM

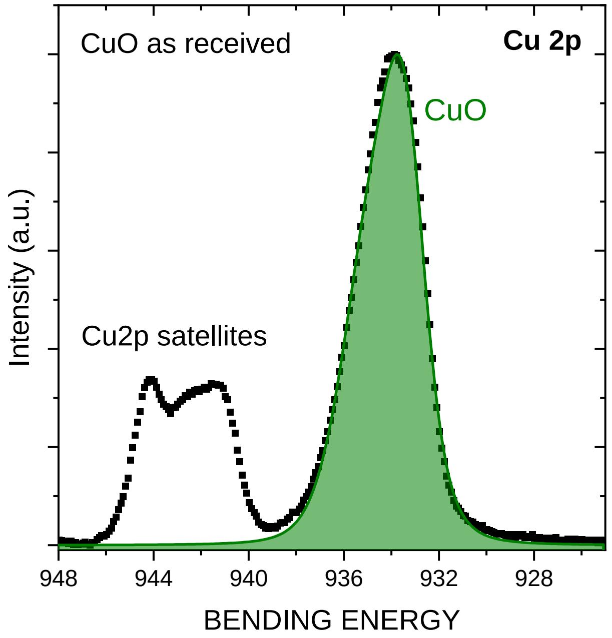


X-ray diffraction



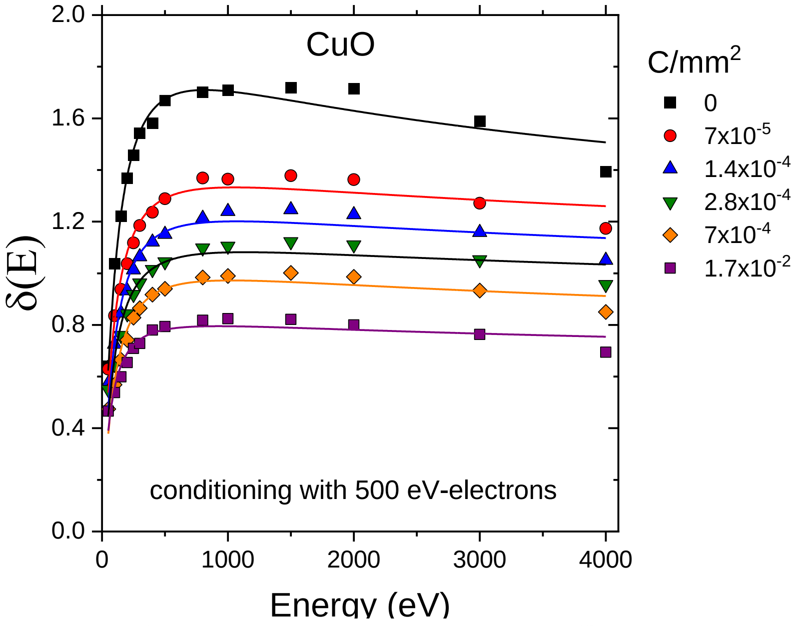
mainly CuO with a small amount of Cu_2O (5%)

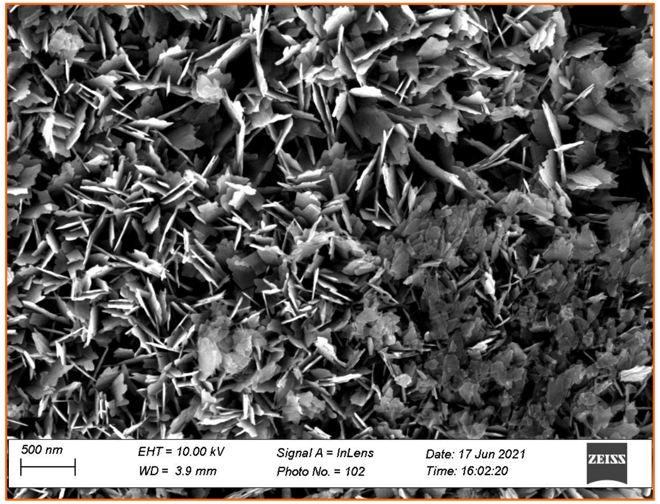
XPS



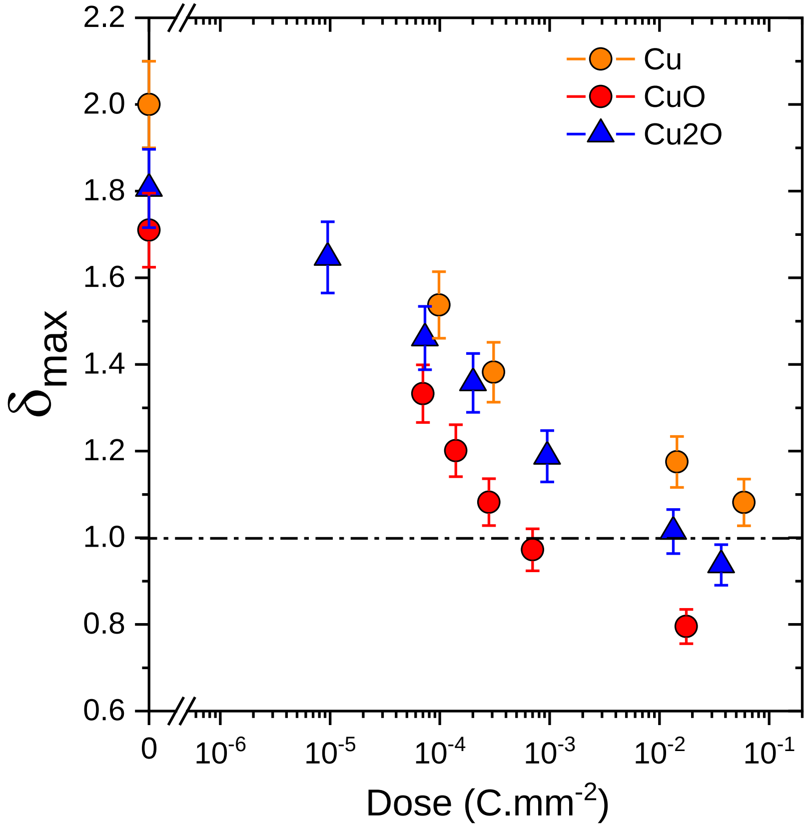
Typical XPS spectrum of CuO

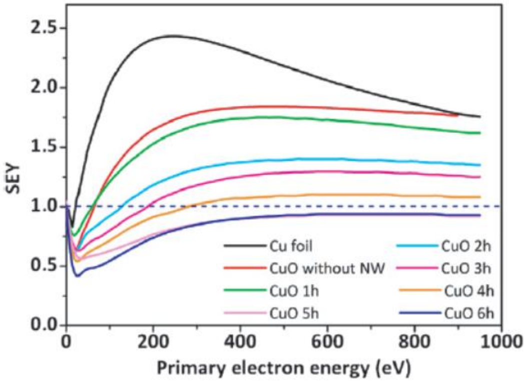
CuO : SEY and conditioning

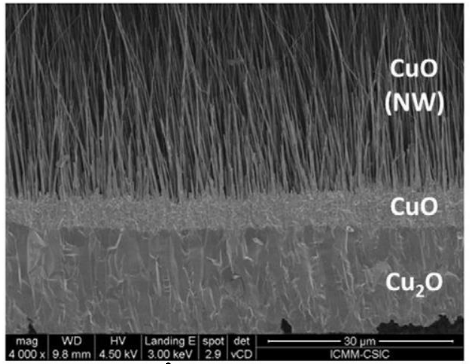




nanoflake-like structure







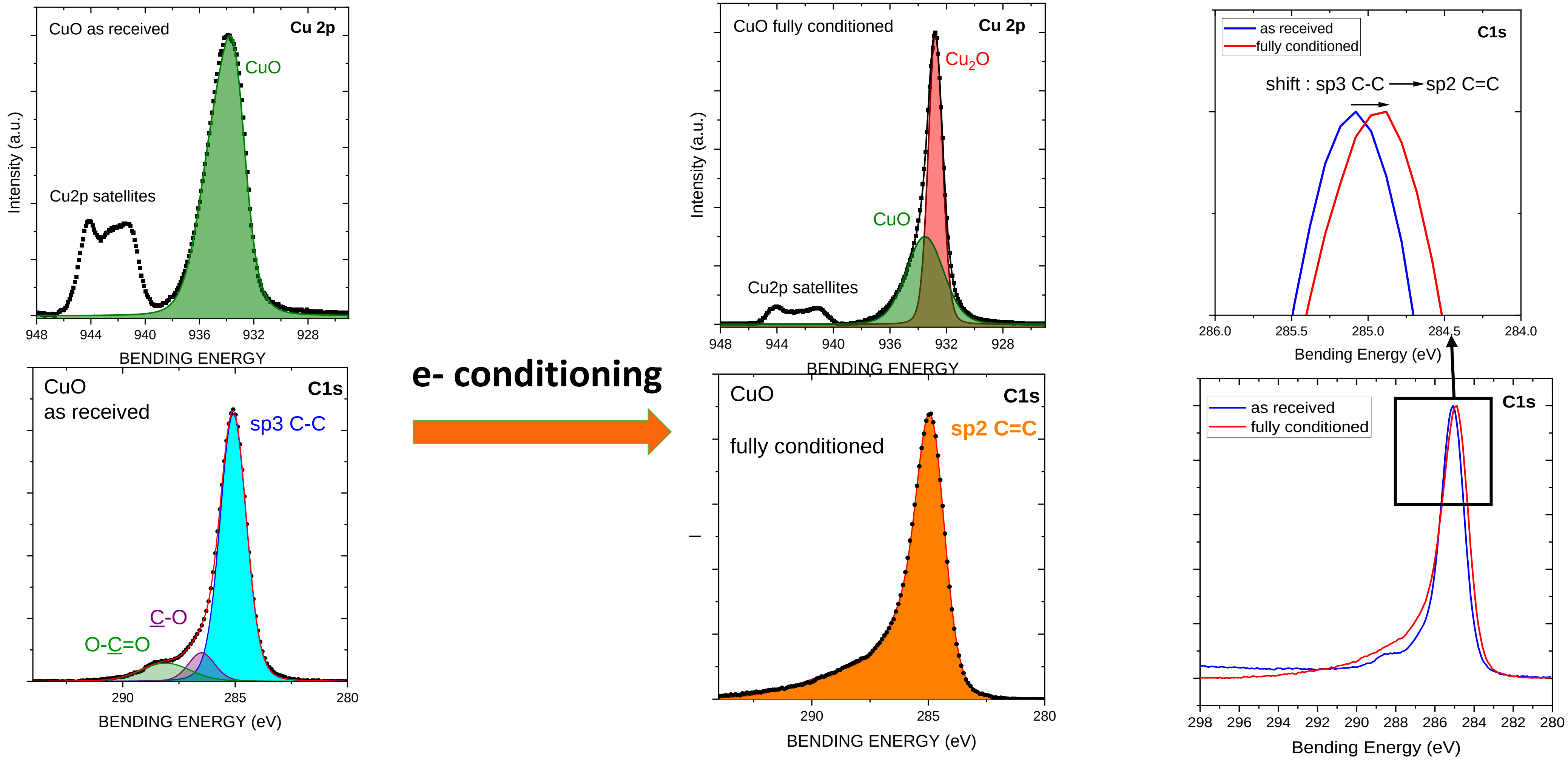
nanowire structure

L Aguilera *et al* J. Phys. D: Appl. Phys. **46** (2013) 165104

The shape of the SEY curve is different from that of Cu_2O (or Cu) : due to a nanostructured surface (see also the SEY of a laser treated surface of copper)

$\delta_{max} \approx 0.79$ in the fully conditioned state and the conditioning rate of CuO seems higher than that of Cu or Cu_2O

XPS analysis of CuO

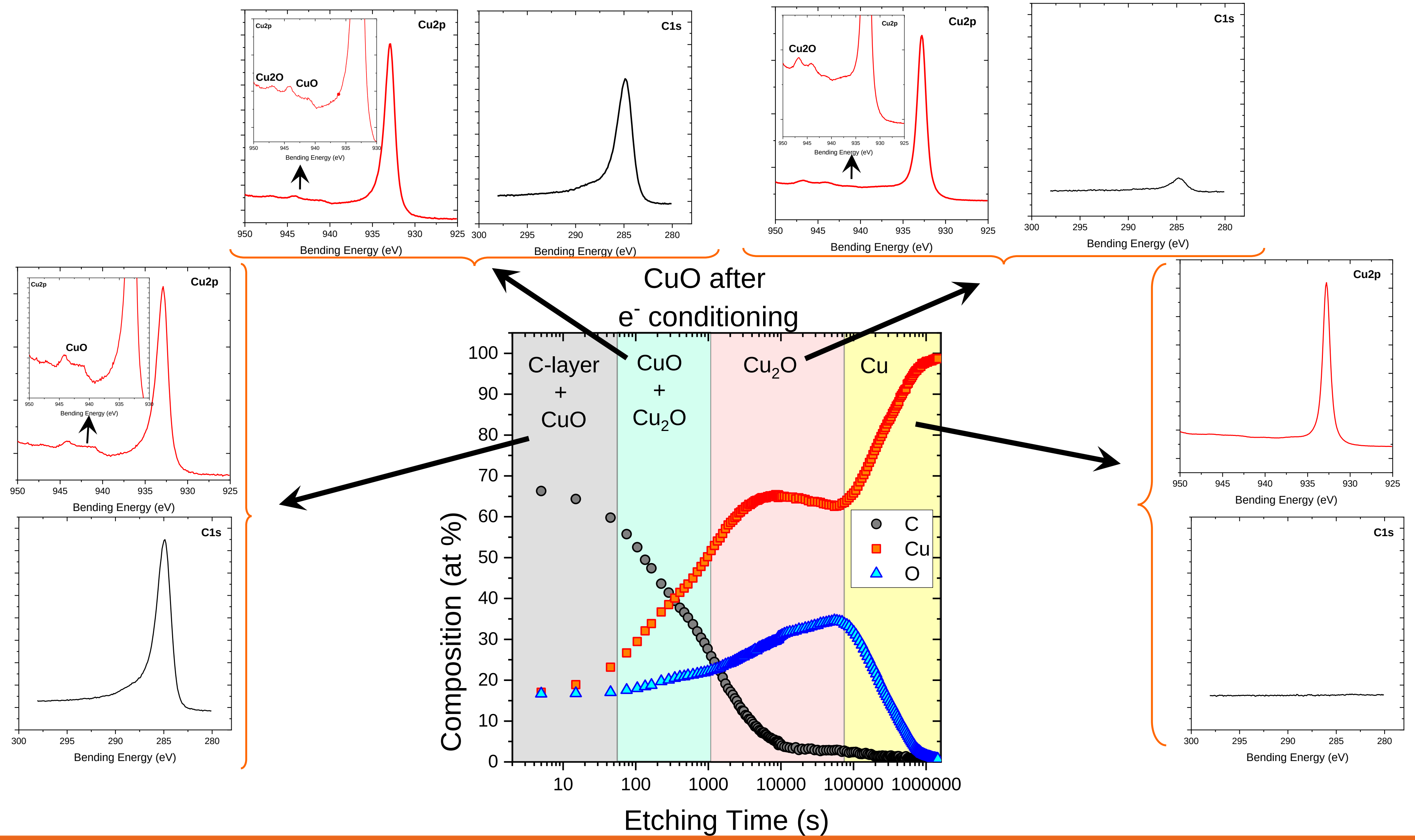


Adventitious carbon (C-O, O-C=O) is removed by electron irradiation

Modification of the C hybridization : from C-C bonds (sp3) to C=C bonds (sp2) compatible with a graphite structure

CuO is partially reduced into Cu_2O

Depth profiles of elements in a fully conditioned CuO by XPS analysis



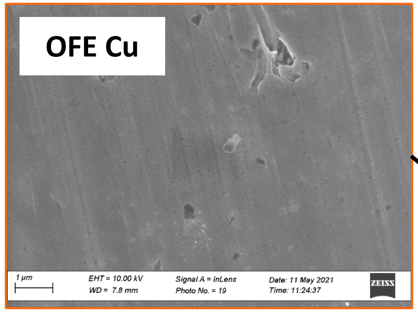
1- A graphitic carbon layer is first detected at the extreme surface with CuO.

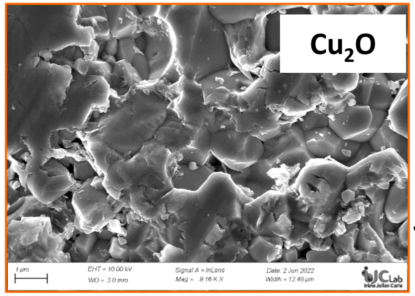
2- At a larger depth, an oxide layer (CuO+Cu_2O) is seen

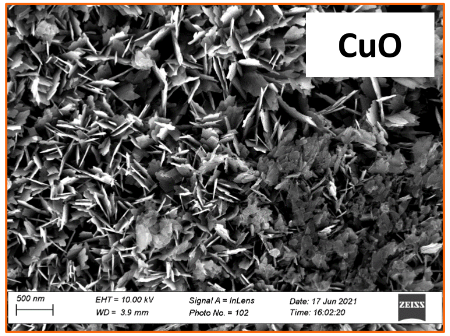
3- Cu_2O alone is then observed at a larger depth

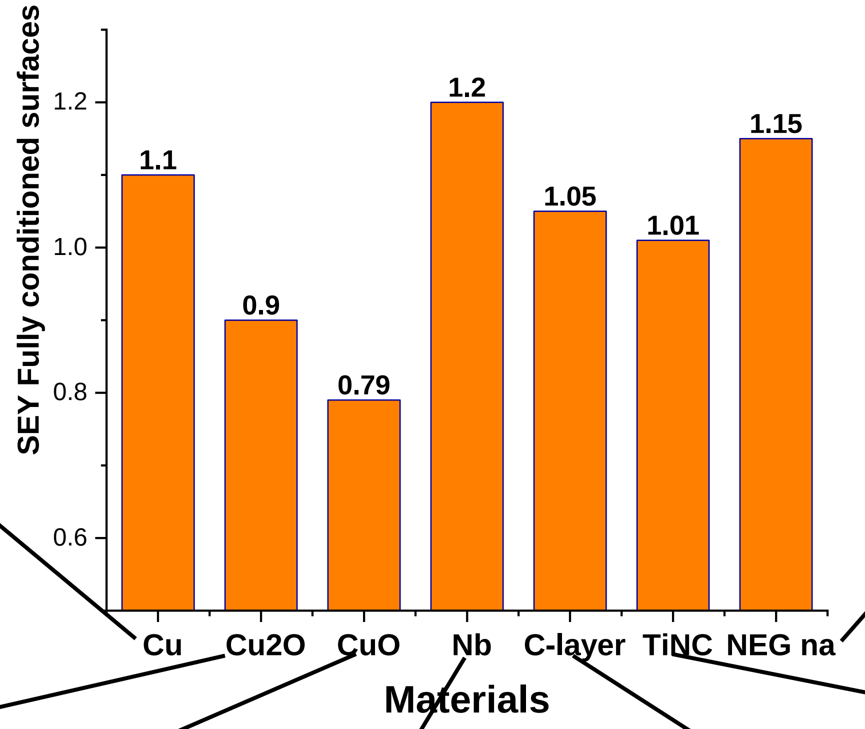
4- Copper oxide disappeared and only metallic Cu is detected at the largest depths

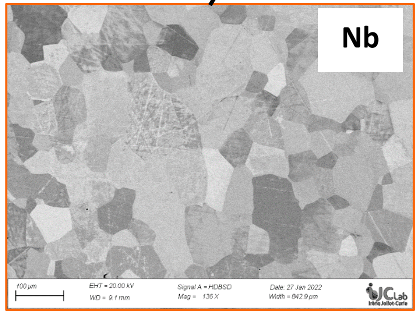
Comparison of SEY for several conditioned materials

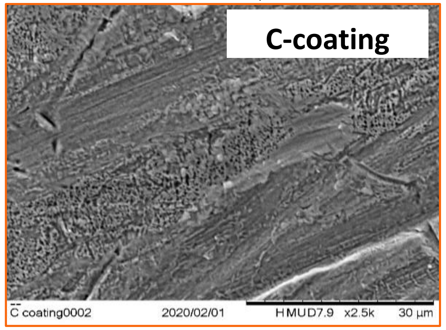


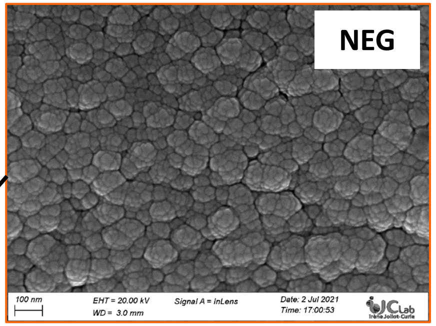


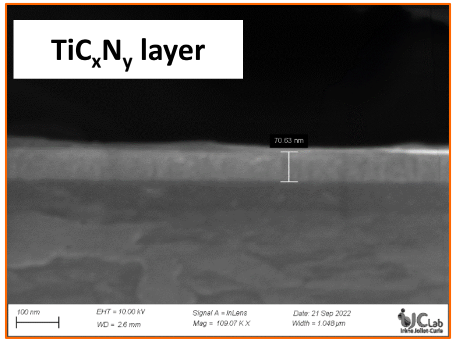












Conclusion and perspectives

- **For a better understanding of conditioning phenomena it is essential to perform surface chemistry analysis** :
  (i) EC formation in accelerators due to materials properties
  (ii) evolution of surfaces submitted to different type of irradiation

- **Coatings with a very low thickness layer (≈10 nm for a-C) are efficient to decrease the SEY**

- **CuO (and Cu_2O) has not necessary a detrimental effect on the SEY of Cu (depends on roughness?)**

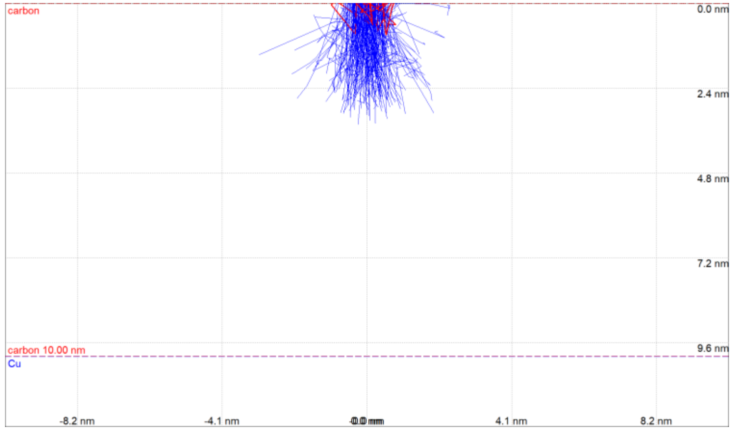
- **Perspectives R&D**:
  (i) influence of cryogenic temperature on the SEY (a new multitechnic setup will join our characterization platform in 2023)

  (ii) investigation of the stimulated desorption at RT and cryogenic temperature
  (a new facility called TANCREDE is built to investigate ISD in a large energy range (from 500 eV to MeV) on the ANDROMEDE platform at IJCLAB)

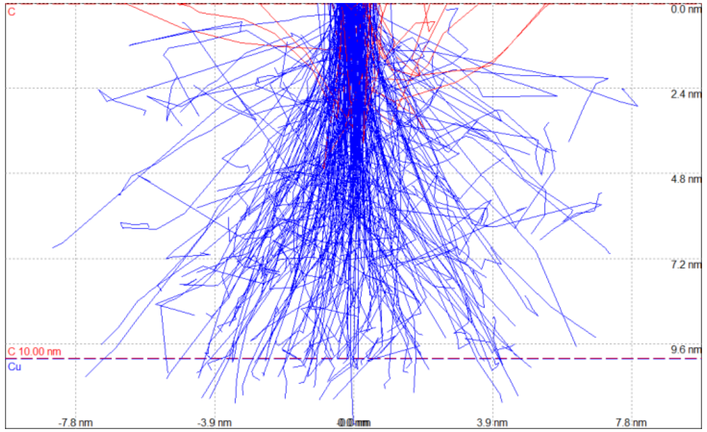
Thanks for your attention

Penetration depth of electrons in carbon

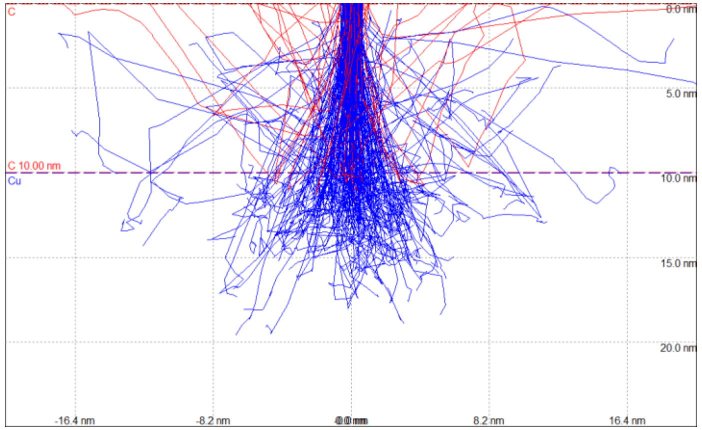
E=200eV



E=500eV

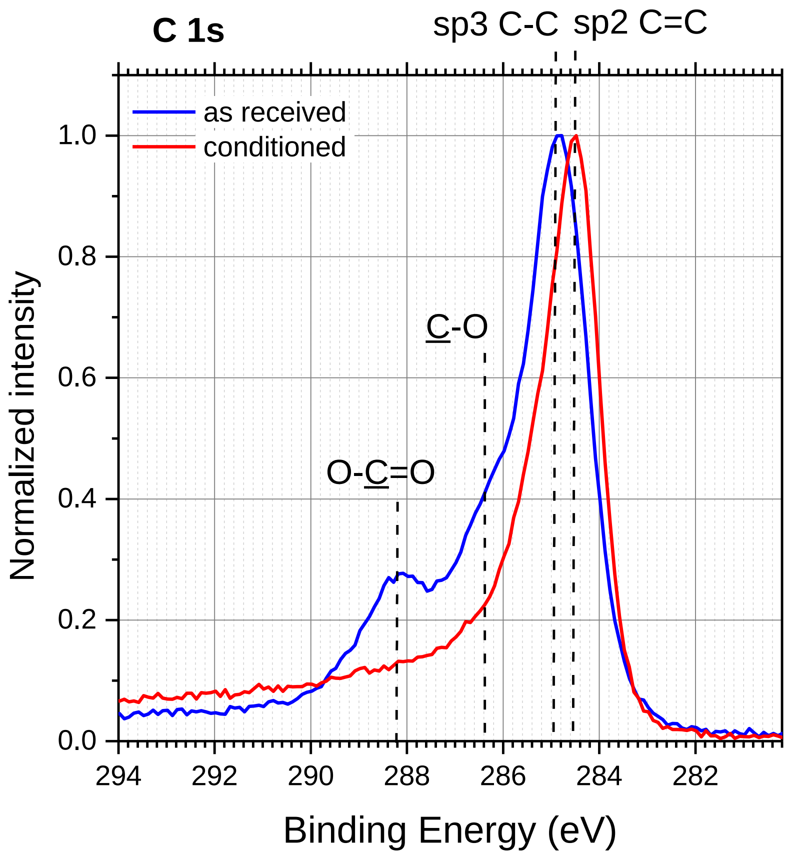


E=1000eV



Nature of C present on the conditioned sample? TOF-SIMS analysis

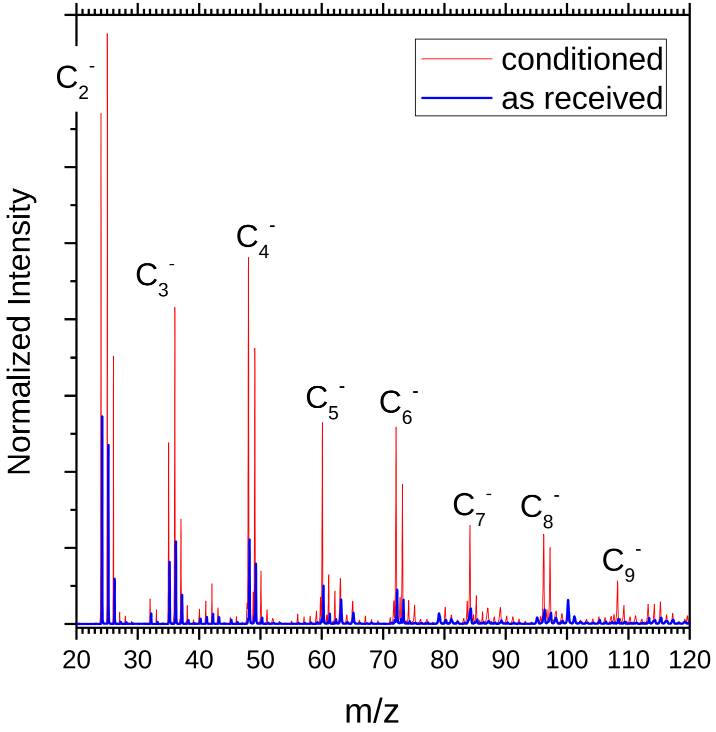
XPS



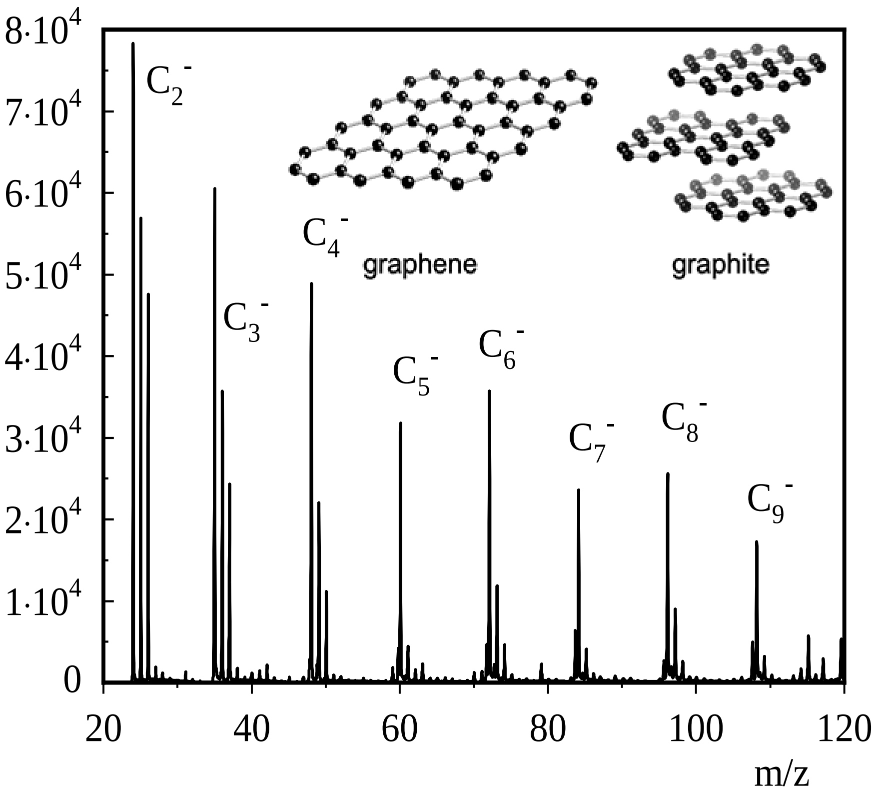
XPS : Modification of the C hybridization : from C-C bonds (sp3) to C=C bonds (sp2) compatible with a graphite structure.

MeV-Time Of Flight –Spectrometry – ANDROMEDE Platform

Carbon on the surface of a fully conditioned Cu



Graphene reference sample



TOF-SIMS : a graphitic (graphene) carbon layer is formed on the surface of the fully conditioned sample (with a large amount of H).

→ **Carbon from organic compounds initially present on the surface is transformed into a graphite layer (0.5 nm) by e- irradiation.**