Progress on Copper Plating Research for Cryocooler Application

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IV InnovEEA Project Meeting

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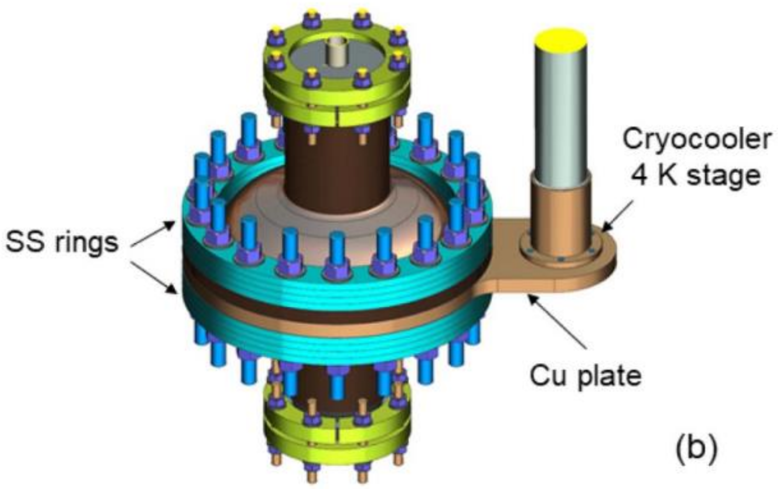
Motivation: Cryocoolers for SRF

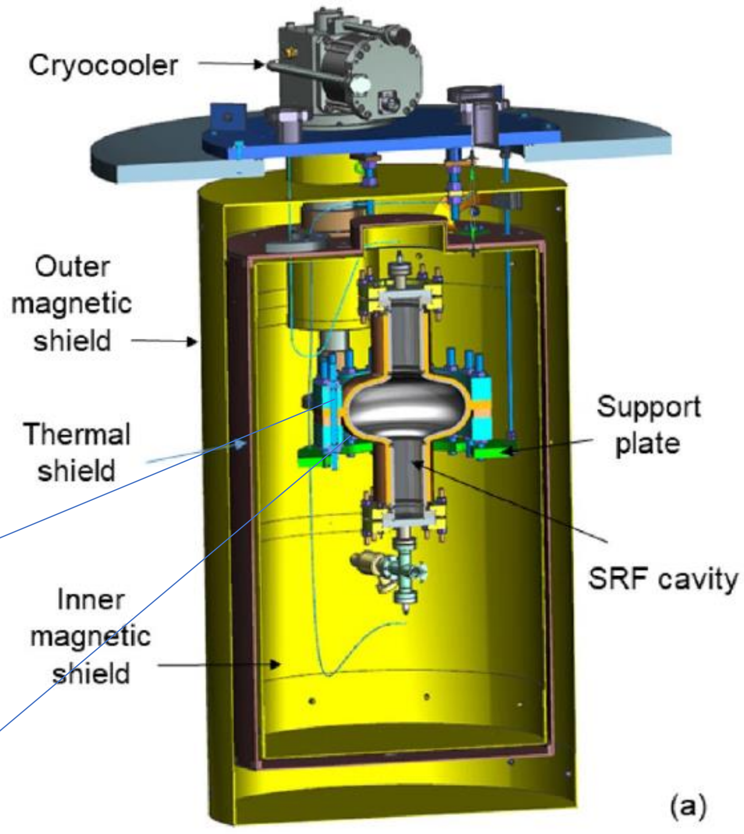
Cryocoolers: closed-cycle refrigerators

- firstly used for SRF cryomodules for **J**apan **A**tomic **E**nergy **R**esearch **I**nstitute **F**ree **E**lectron **L**aser*
- reliable, compact, easy to operate

Possible Application:

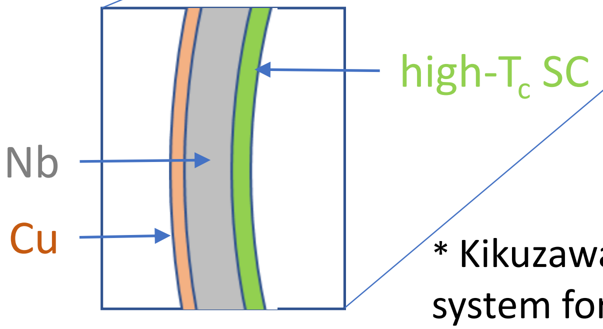
- compact low-energy electron accelerators with Nb_3Sn/Nb resonators operating at $T > 4.2$ K
- to maximize the thermal stability of the cavity: Cu-deposition onto a Cavity outer wall





from “G. Ciovati et al. *Superconductor Science and Technology* 33.7 (2020): 07LT01.”

Gifford-McMahon (GM) Cryocooler



Multi-layer Cavity

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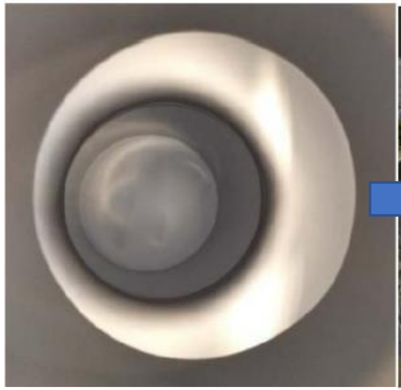
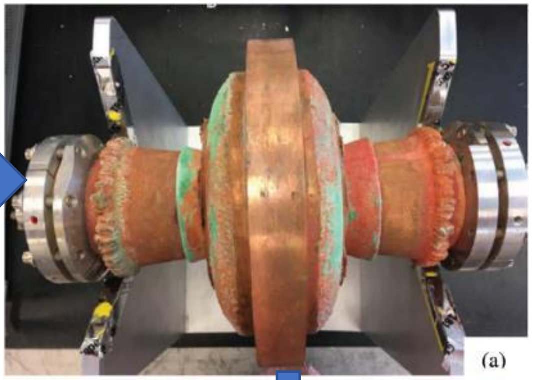
* Kikuzawa N, et al, Performance of compact refrigerators system for SRF cavities in the JAERI FEL, *SRF97C40, SRF’97, p.769*

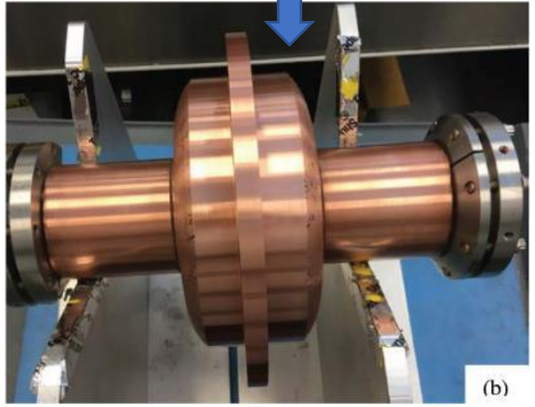
Preparing a Multi-Layer SRF Cavity

Experience of JLab: $Nb_3Sn/Nb/Cu$

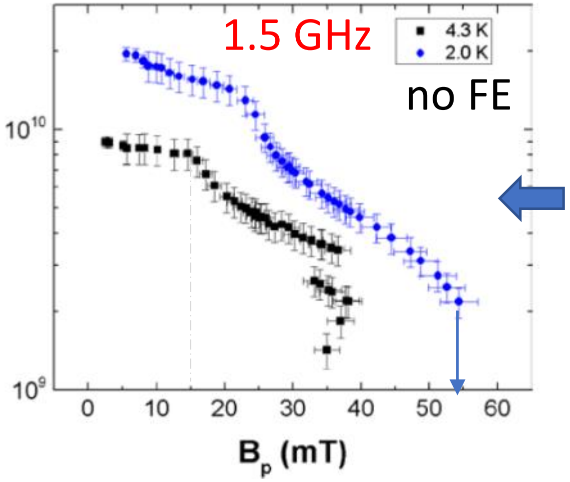


T_c=17.8K





machining



Steps:

1. Nb_3Sn by vapor diffusion
2. 1st Cu-layer by cold spraying
3. 2nd Cu-layer by electroplating in multi-steps (~90 days)

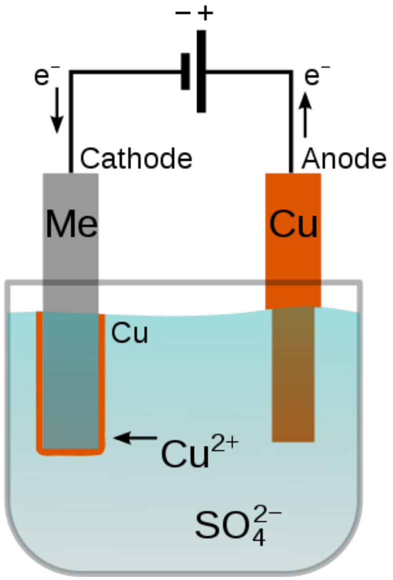
Issues:

- poor adhesion of copper directly plated onto Nb
- cold-sprayed Cu has low thermal conductivity

G. Ciovati, et al, Proceedings of SRF2019, Dresden, Germany, TUP050

Copper Electroplating onto Niobium

For Cu-plating onto most metals the water-based acidic electrolytes are commonly used



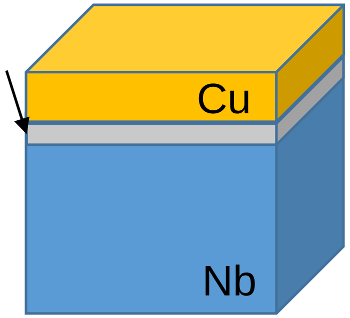
Issues:

- Niobium has a higher reactivity than Copper => galvanic displacement reaction:

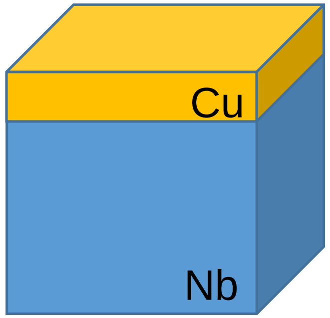
$$Nb_{(s)} + Cu^{2+} \rightarrow Cu_{(s)} + Nb^{2+}$$

➡ poor Cu-film adhesion

Experimental Approaches:



“less active” Me (Ni, Sn…)



- Two-step plating:

Step1: pre-plating with less active metal

Step 2: Standard Cu-plating

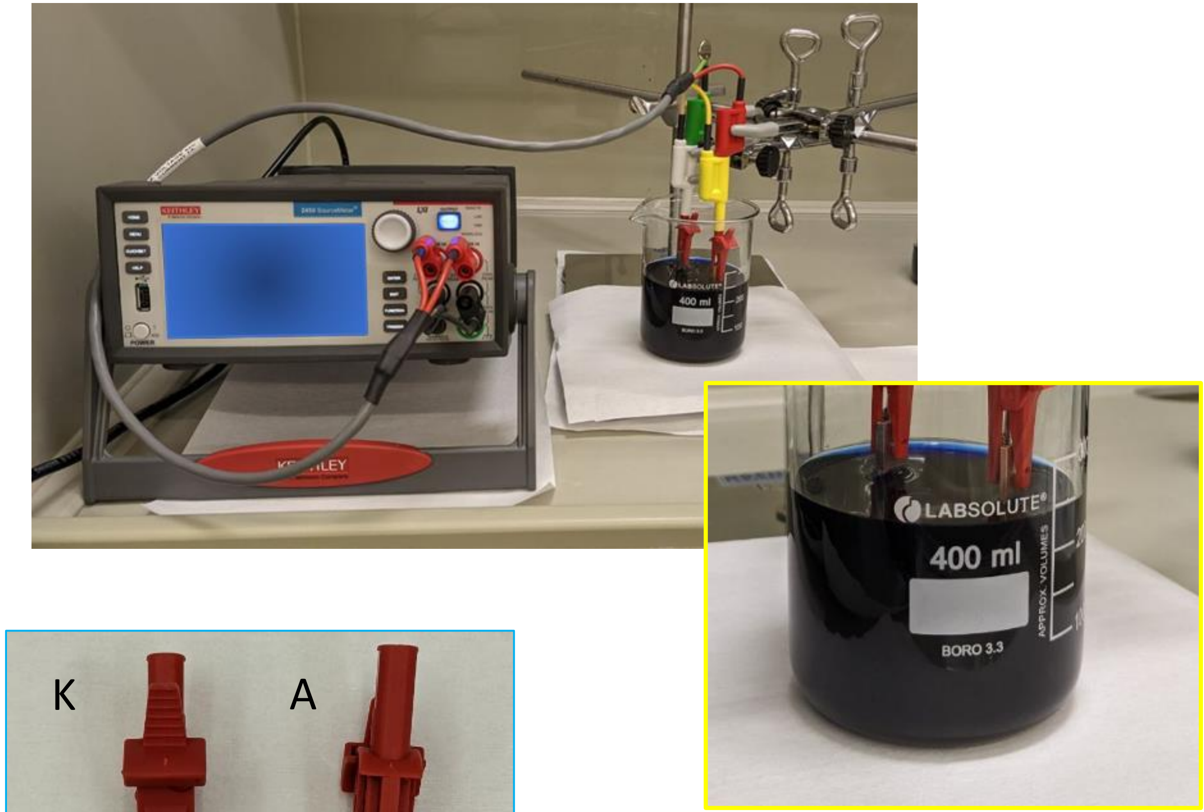
Direct Cu-plating :

- using Electrolytes for Steel (Fe has higher reactivity than Cu)
- using Complexing Agents (cyanides, glycols, surfactants etc.)
- using Non-aqueous Electrolytes (organic solvents, ionic liquids (incl. molten salts)

Electroplating onto Niobium using Electrolytes for Steel

Primary requirements to Cu-deposits:

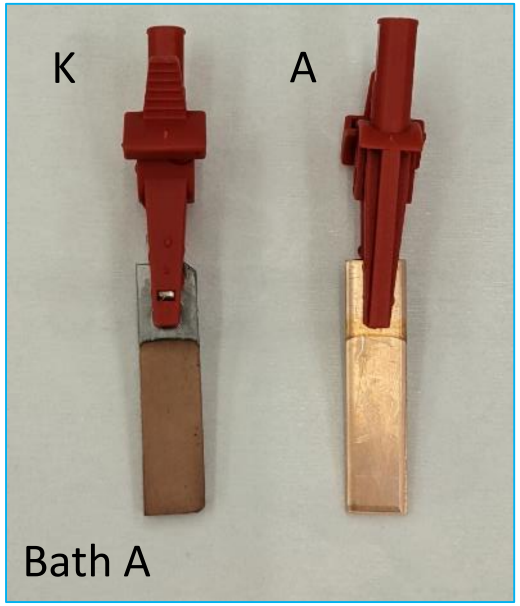
- form a continuous film;
- no easily detached from Nb (scratch-test with tweezers);
- tape test;
- thermal shock test.



Electrochemical Cell: two-electrode type (Cu used as Anode)

(1) **Alkaline Electrolyte for Steel** ($CuSO_4$+$NaC_6H_{11}O_7$+NaOH[1])

- Bath A: w/o additives
- Bath B: with additives-1 (benzotriazole)
- Bath C: with additives-2 (surfactant)



- Cu film is matt ☺
- Cu anode did not deteriorate ☺
- Cu film is not easily peeled off (but did not pass tape test ☹)

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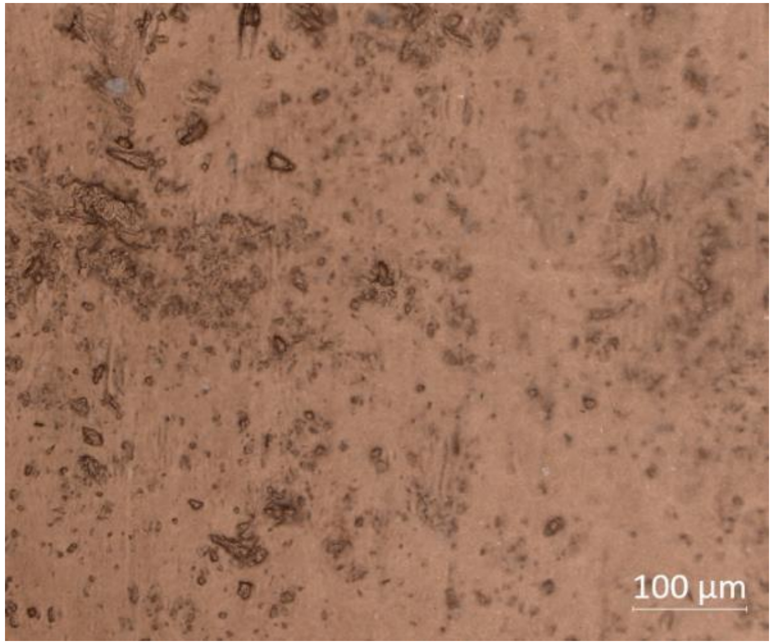
[1] R. Sekar et al, 2017

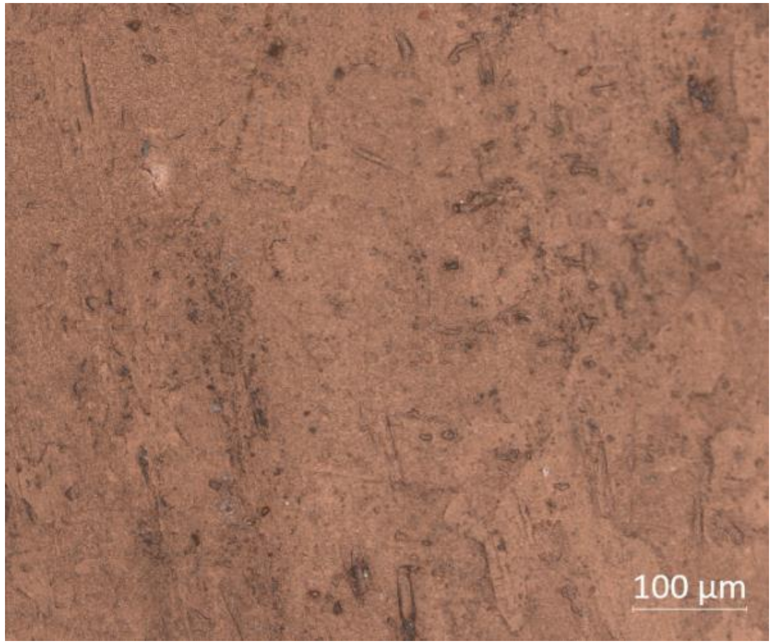
Electroplating onto Niobium using Electrolytes for Steel

Bath A

Bath B



Bath C



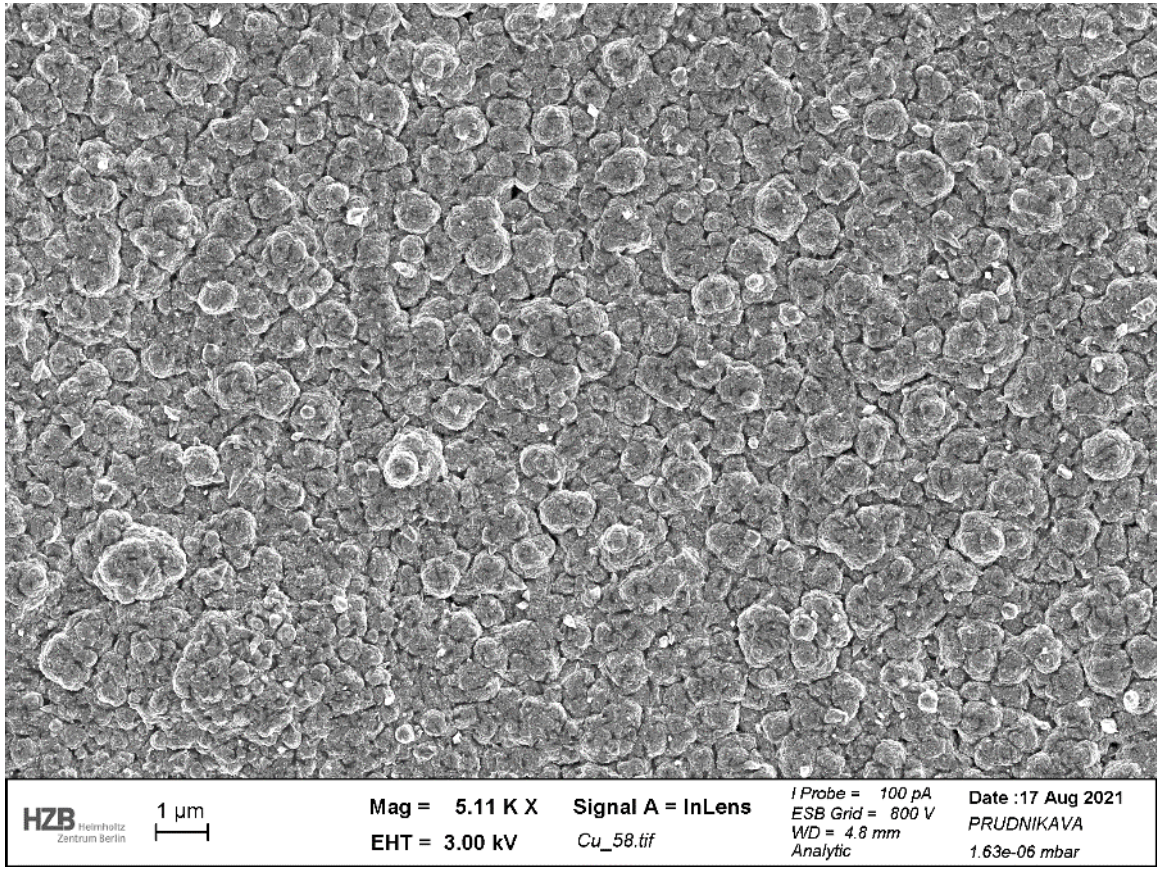
⇒ Cu-deposit thickness 0.8 µm
⇔ deposition rate 2.3 µm/h

optical microscopy x20

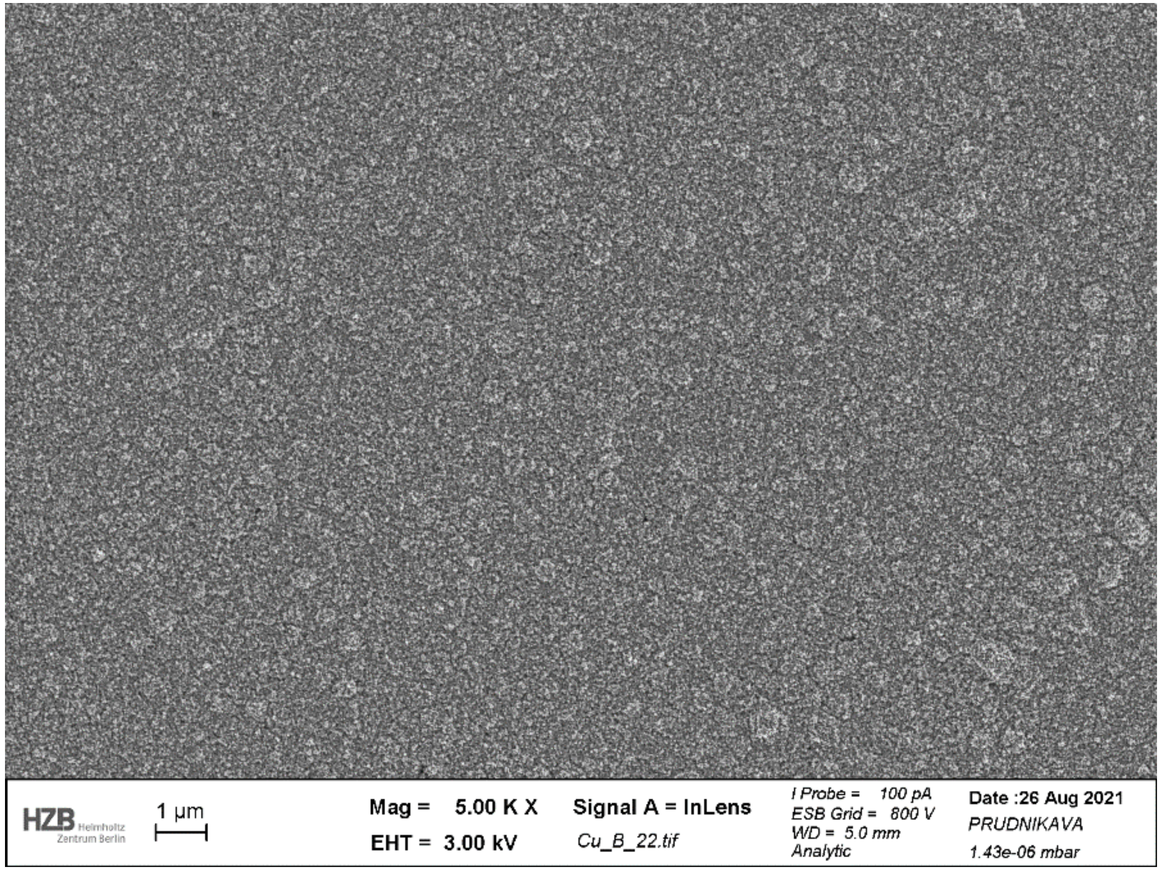
Electroplating onto Niobium using Electrolytes for Steel

SEM images

Bath A



Bath B (with additives)



*Bath C looks alike

Electroplating onto Niobium using Electrolytes for Steel

Primary requirements to Cu-deposits:

- form a continuous film;
- no easily detached from Nb (scratch-test with tweezers) .
- scotch-tape test;
- thermal shock test.

Commercial Acidic Electrolytes:

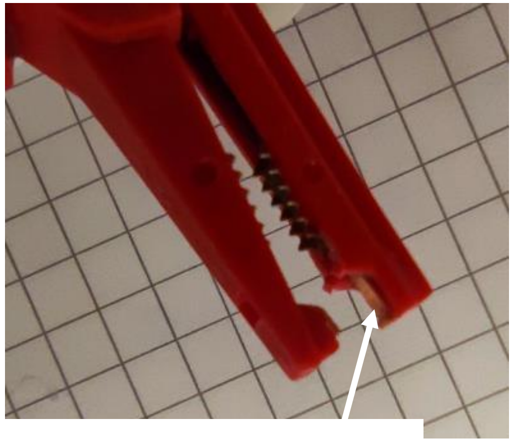
(2) **µChem 520** (copper (2-30 g/l), sulfuric acid (200-250g/l), chloride (50-70 g/l));

(3) **High speed bright copper electroplating solution by Sigma-Aldrich:**

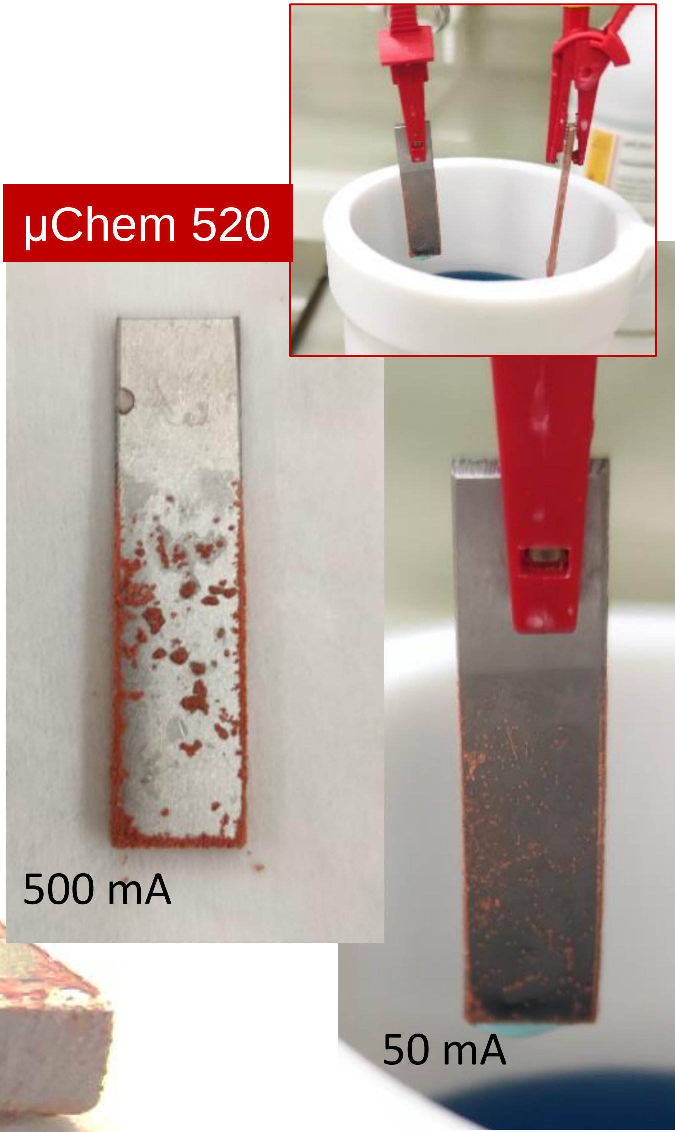
40 mg/L chloride basis
600 mg/L (organic additives)
65.0 g/L Cu basis
8.0 g/L H_2SO_4 basis

=> no continuous Cu-film obtained

Electroplating at:
varied *T* °C, *j mA/cm²*, with and w/o solution agitation



continuous Cu-film at steel components



Modified Alkaline Electrolyte for Steel: Cu/Nb Film

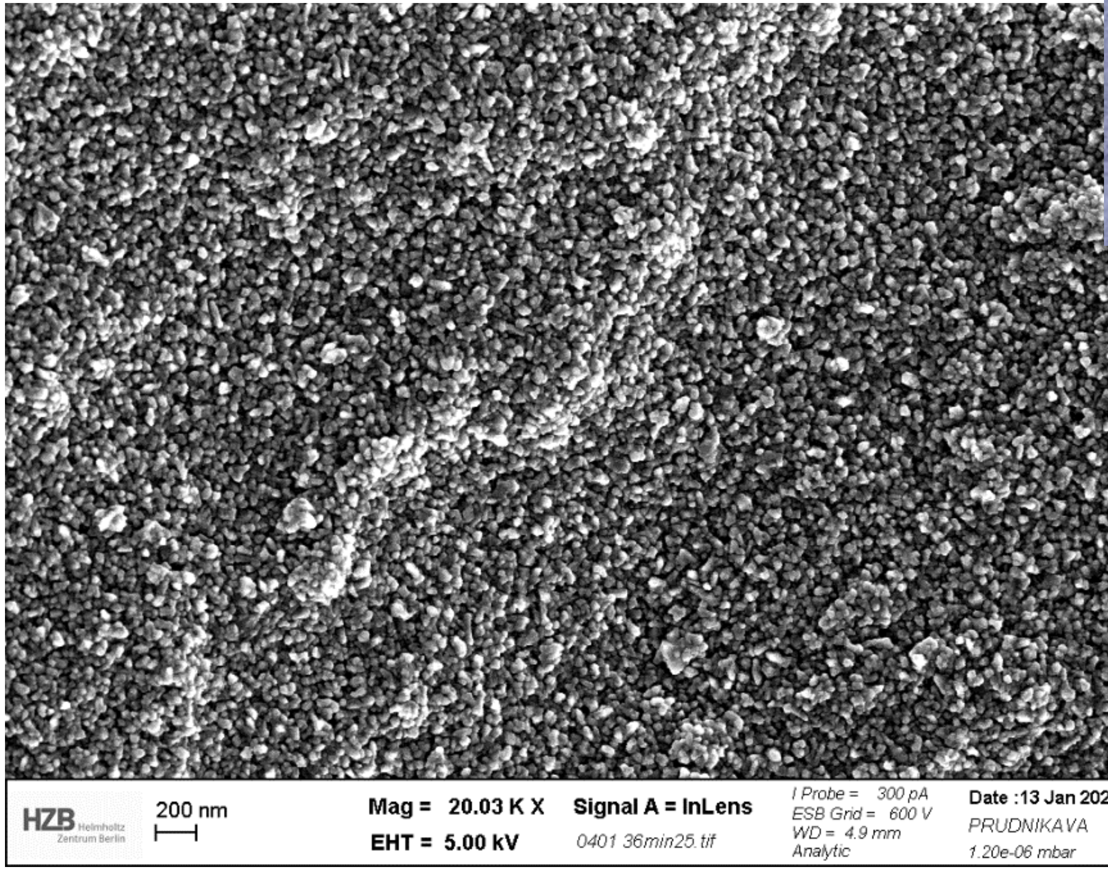
By modifying composition, concentration, plating parameters for alkaline electrolyte

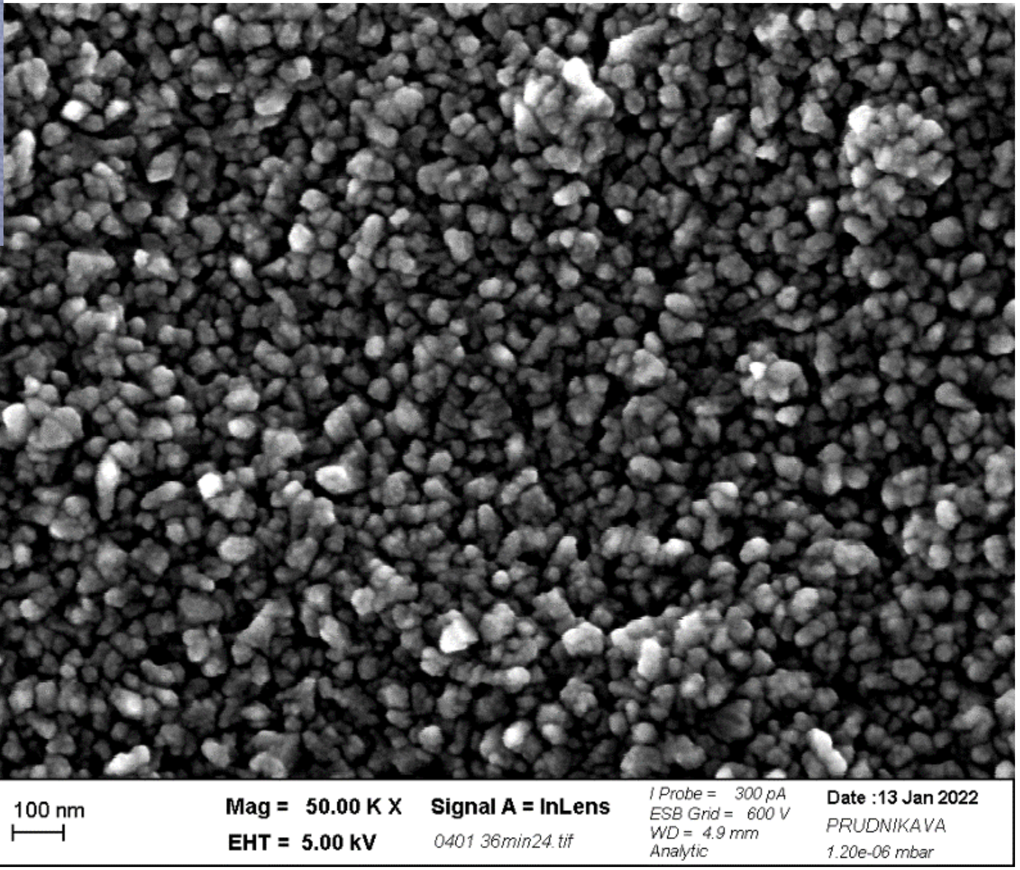
- obtained a continuous Cu-film on Nb ☺

- Cu-film thickness: ~170 nm ☹;
- low deposition rate (0.28 um/h) ☹

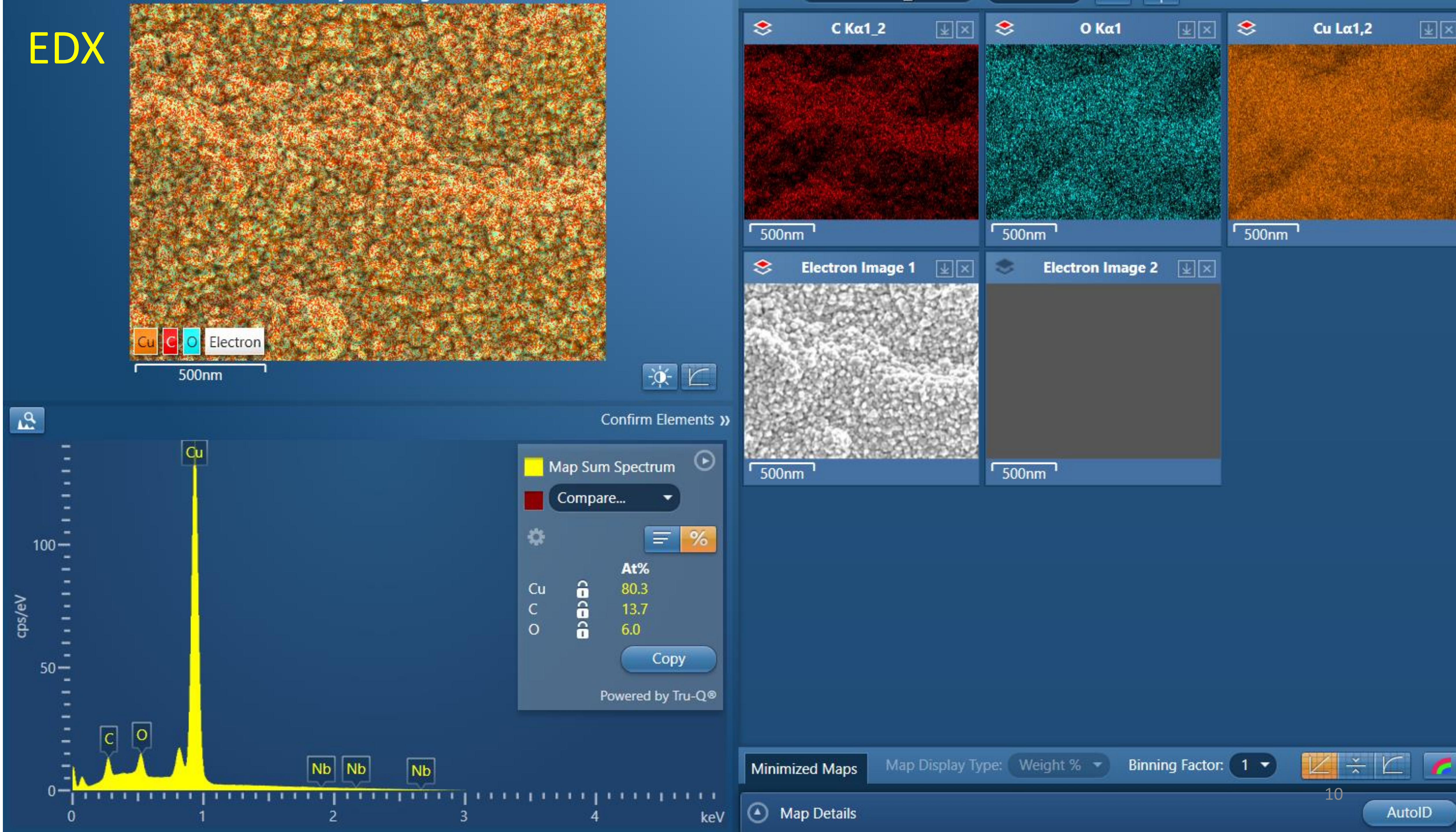
- Stable solution ☺ ;
- reproducible results ☺

SEM





EDX

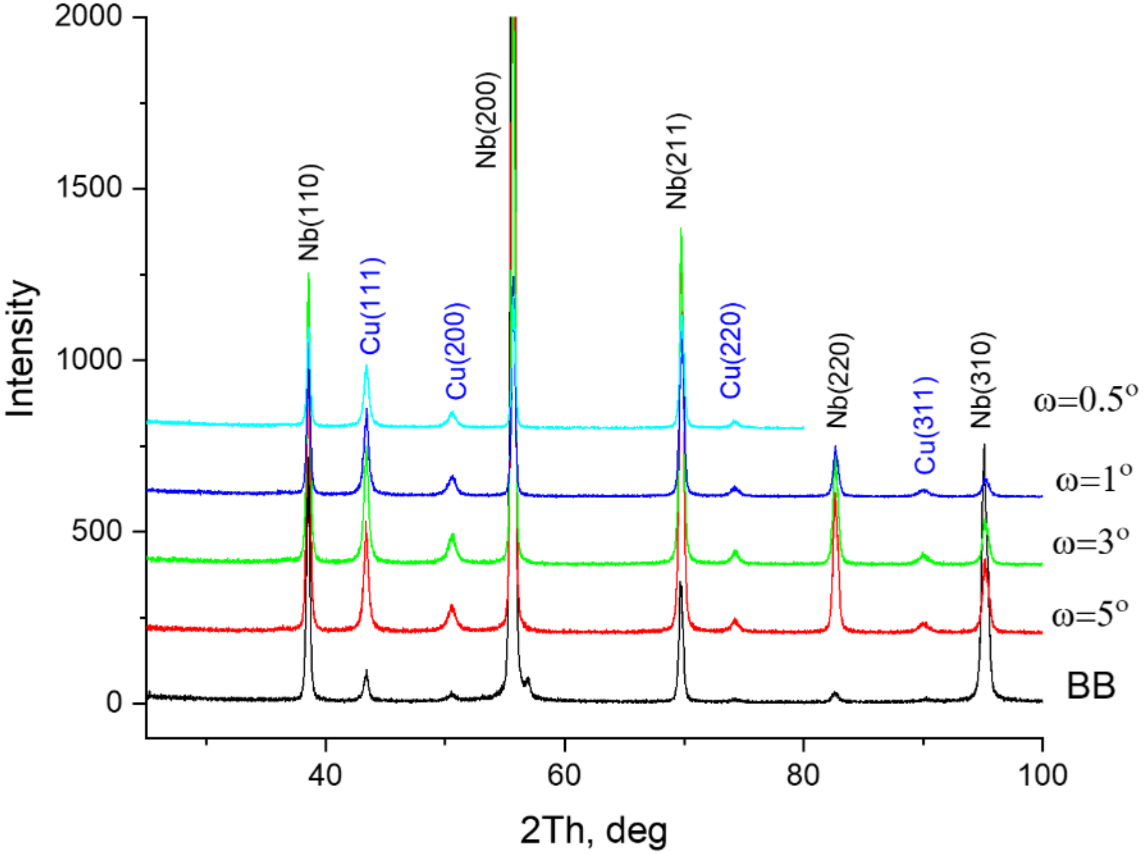


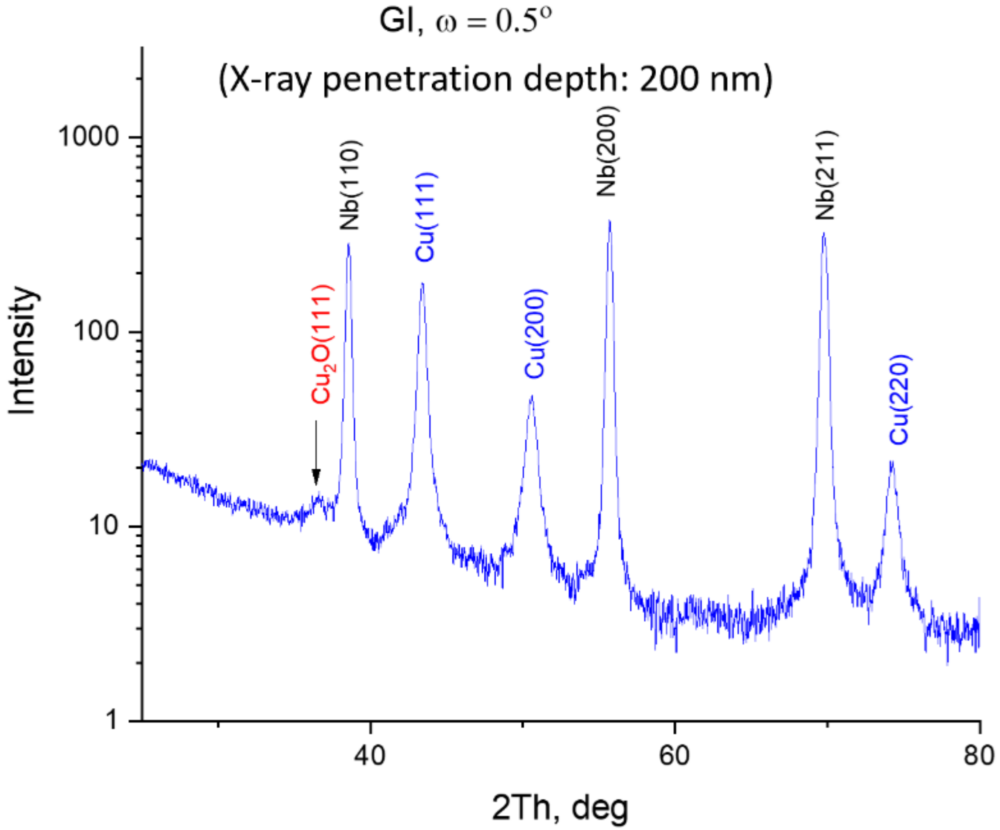
	At%
Cu	80.3
C	13.7
O	6.0

Cu/Nb Film: XRD

XRD measured in Bragg-Brentano (BB) geometry and in Grazing-Incidence geometry (GI) at various incidence angles

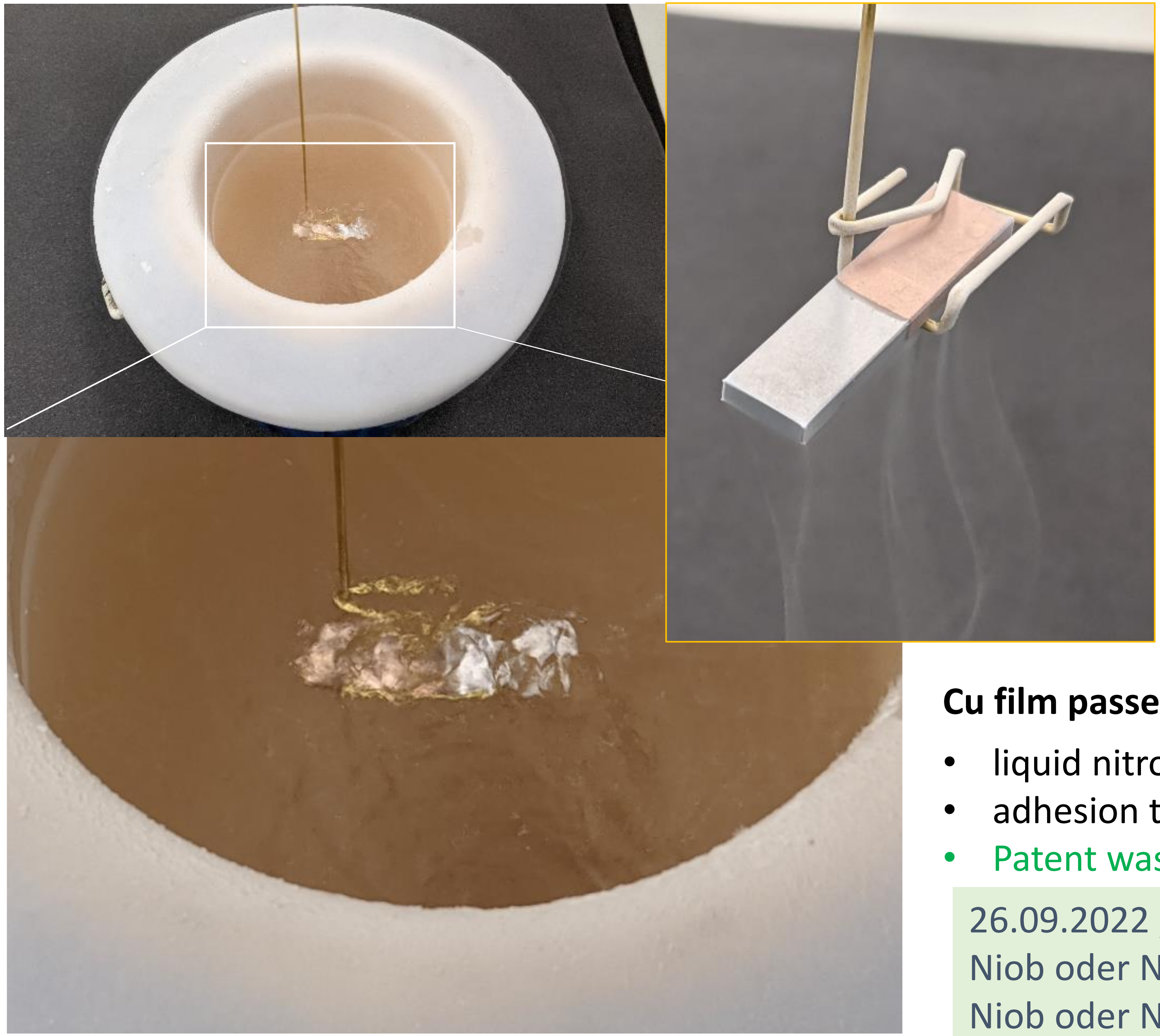
Calculated average crystallite size of Cu film is 22.70 nm





In BB geometry only Cu reflexes were observed

Cu/Nb Film: Liquid Nitrogen Test, Adhesion Tape Test



Designation: D3359 – 09$^{\varepsilon 2}$

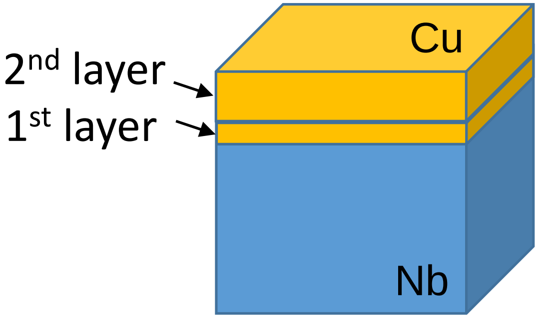
Standard Test Methods for
Measuring Adhesion by Tape Test

Cu film passed:

- liquid nitrogen test ☺
- adhesion tape test ASTM D3359, Test Method A (X-cut Tape Test) ☺
- Patent was filed ☺

26.09.2022 „Verfahren zum Elektroplattieren von Kupfer auf Niob oder Nioblegierungen und Werkstück aus Niob oder Nioblegierung mit Kupferbeschichtung“

Cu/Nb Film for Cryomodule Application



Strategy:

1st Cu-layer (alkaline electrolyte): to be used as a buffer layer

2nd layer (acidic electrolyte): Cu-film of required thickness n·100 μm

Studying Cu-plating with Acidic Electrolyte (Cu/Cu plating)

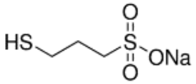
Electrolytes:

1. “Standard” $CuSO_4/H_2SO_4/H_2O$
2. “Standard” $CuSO_4/H_2SO_4/H_2O$ with various additives (polyethylene glycol, sodium lauryl sulphate, benzotriazole)
3. “Modified” $CuSO_4/H_2SO_4/Cl^-$/Janus Green B/(w/MPS or w/a MPS*)
4. Commercial S. Aldrich Cu-plating solution

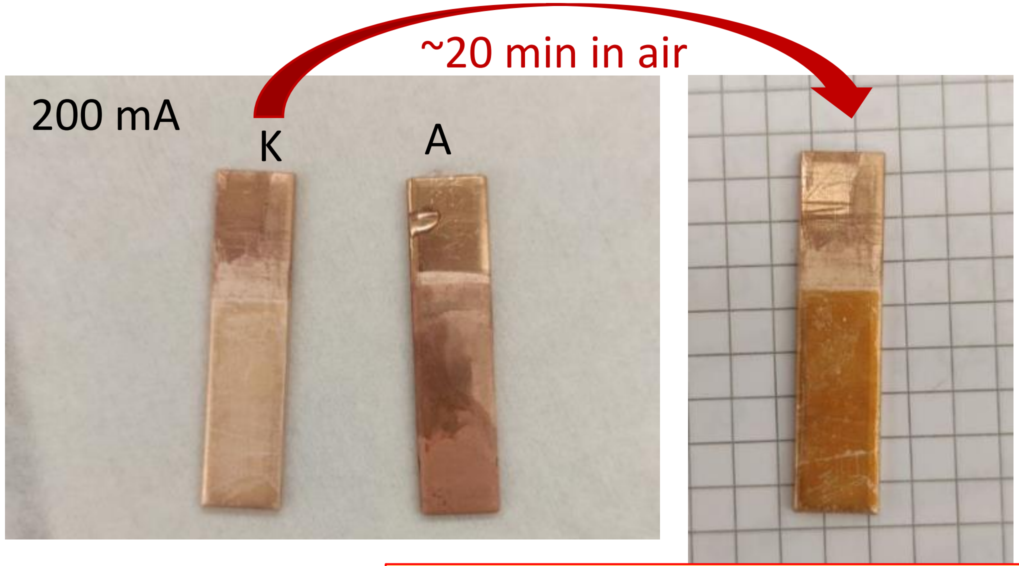
What was Studied:

1. Quality of Cu-films obtained using **standard** Cupric Electrolyte (deposition rate: current density, temperature)
2. **Influence of additives** onto Cu-film oxidation (SEM/EDX, XRD)
3. Quality of films obtained using **modified** Cupric Electrolytes (deposition rate, uniformity, CuO_x)
4. Quality of films obtained using **S.Aldrich Electrolyte**

*MPS: Sodium 3-mercapto-1-propanesulfonate



Testing Acidic Electrolytes (1): Cu plating onto Copper



Electrolyte:

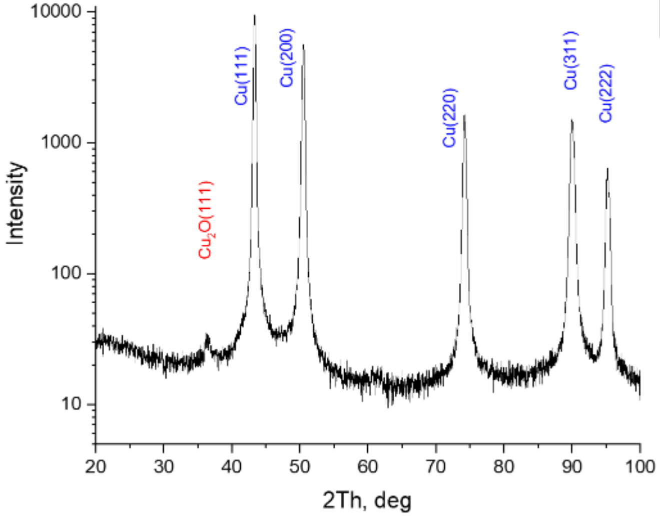
$CuSO_4 \cdot 5H_2O$
H_2SO_4
H_2O

Plating parameters:

j=2.7 A/dm^2
T=27°C
t=5 min

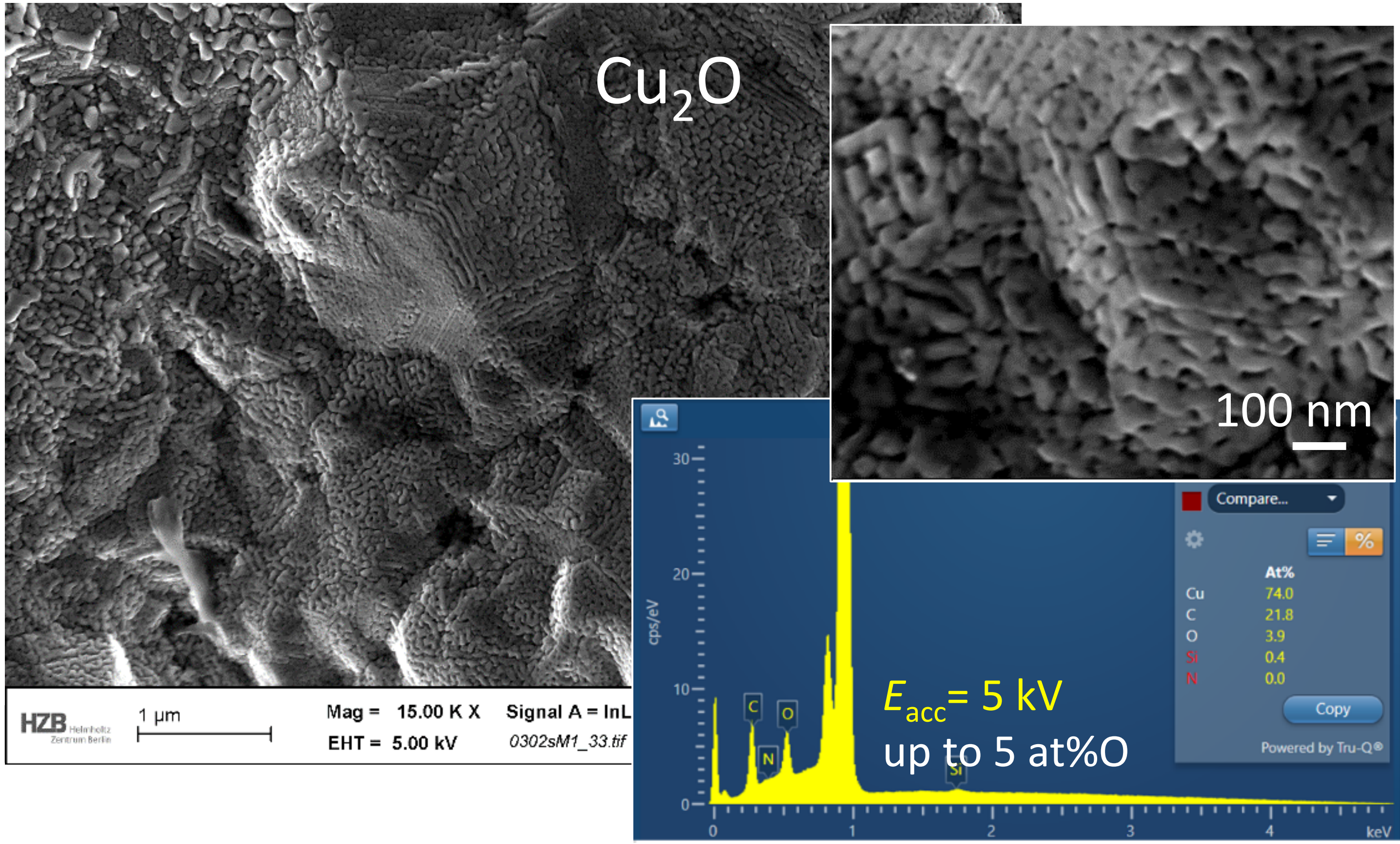
- Visible Cu-film post-oxidation

XRD, EDX: Cu_2O agglomerates



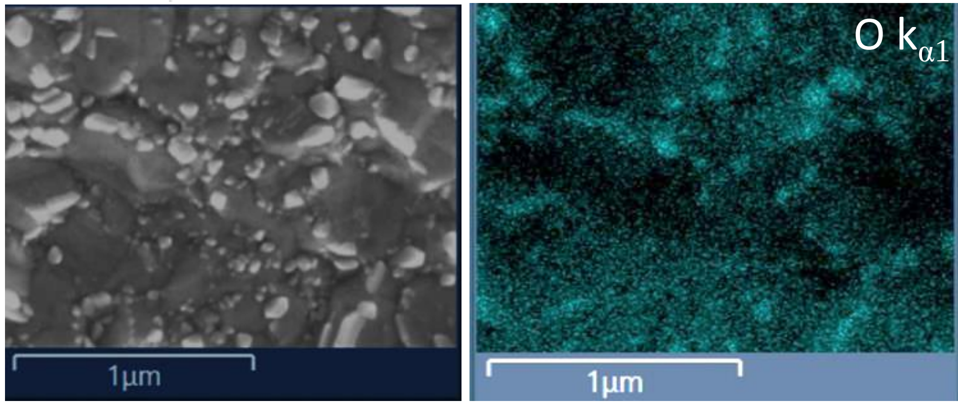
GI, ω=5°

Cryst. Size
Cu(111): 30.18 nm
Cu_2O(111): 10.89 nm

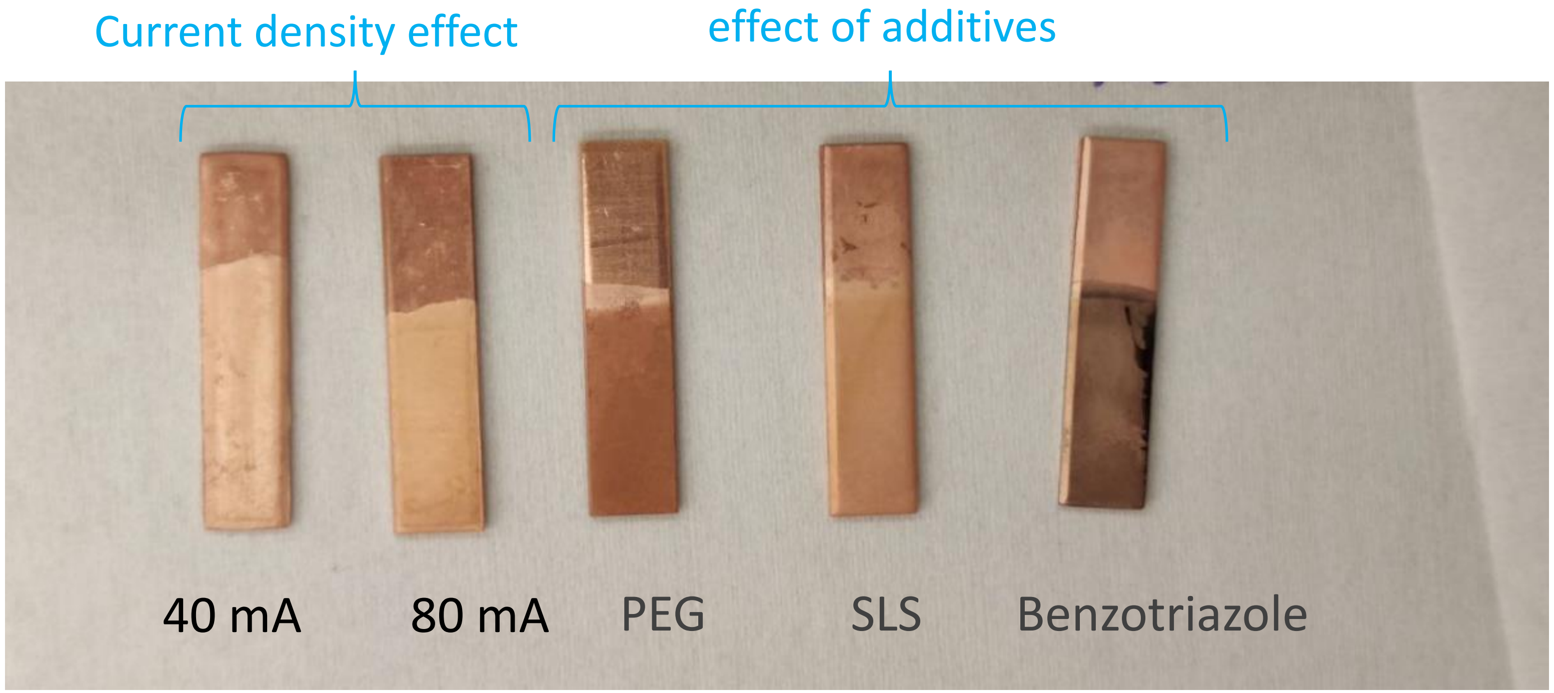


	At%
Cu	74.0
C	21.8
O	3.9
Si	0.4
N	0.0

E_{acc}= 5 kV
up to 5 at%O



Testing Acidic Electrolytes (2): Cu plating onto Copper



Samples 1-2
$CuSO_4 \cdot 5H_2O$ (0.64M)
H_2SO_4 (0.2 mM)
H_2O

Samples 3-5
$CuSO_4 \cdot 5H_2O$
H_2SO_4
H_2O
and various additives:

- polyethylene glycol (PEG)
- sodium lauryl sulphate (SLS)
- benzotriazole

	I, mA	j, mA/cm^2	deposition rate, µm/h	at% O at 5kV	O/Cu at 5 kV	Cryst. Size Cu(111), nm
$CuSO_4$+H_2SO_4	200	27.8	-	3.9	0.05	30.18
$CuSO_4$+H_2SO_4	40	5.7	7.9	-	-	-
$CuSO_4$+H_2SO_4	80	13.2	17.4	4.5	0.06	32.76
$CuSO_4$+H_2SO_4+PEG	80	13.2	17.5	5.5-5.9	0.07-0.08	29.86
$CuSO_4$+H_2SO_4+SLS	80	13.2	17.4	3.6	0.05	32.84
$CuSO_4$+H_2SO_4 + benzotriazole	80	14	19.2	2-4.3	0.03-0.06	23.9

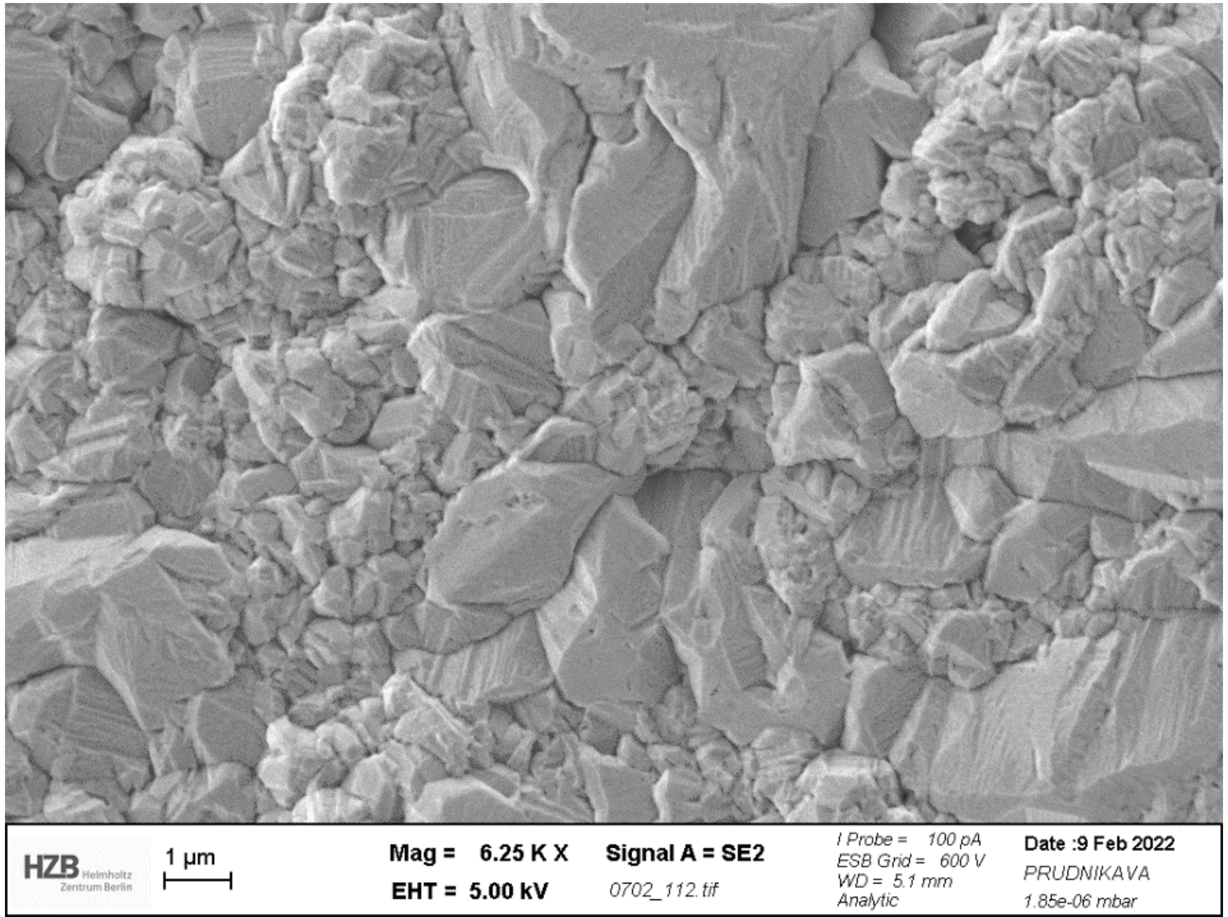
Testing Acidic Electrolytes (2): Cu plating onto Copper

Cu-film morphology: General view (SEM)

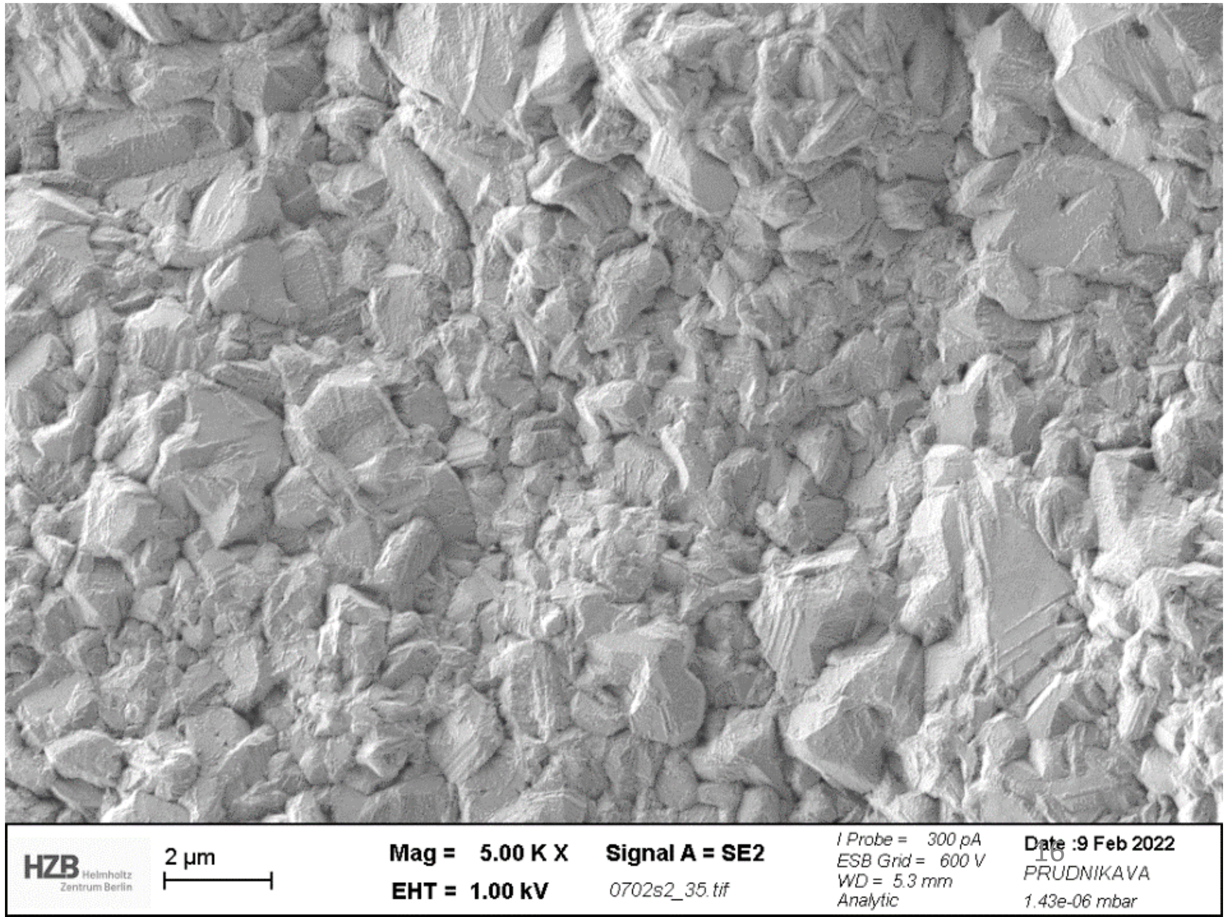
Current density effect

- Higher current => smaller Cu-grains

40 mA



80 mA

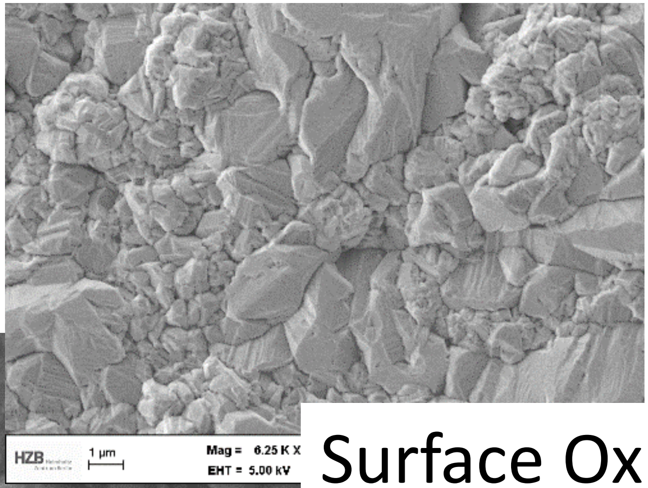


Testing Acidic Electrolytes (2): Cu plating onto Copper

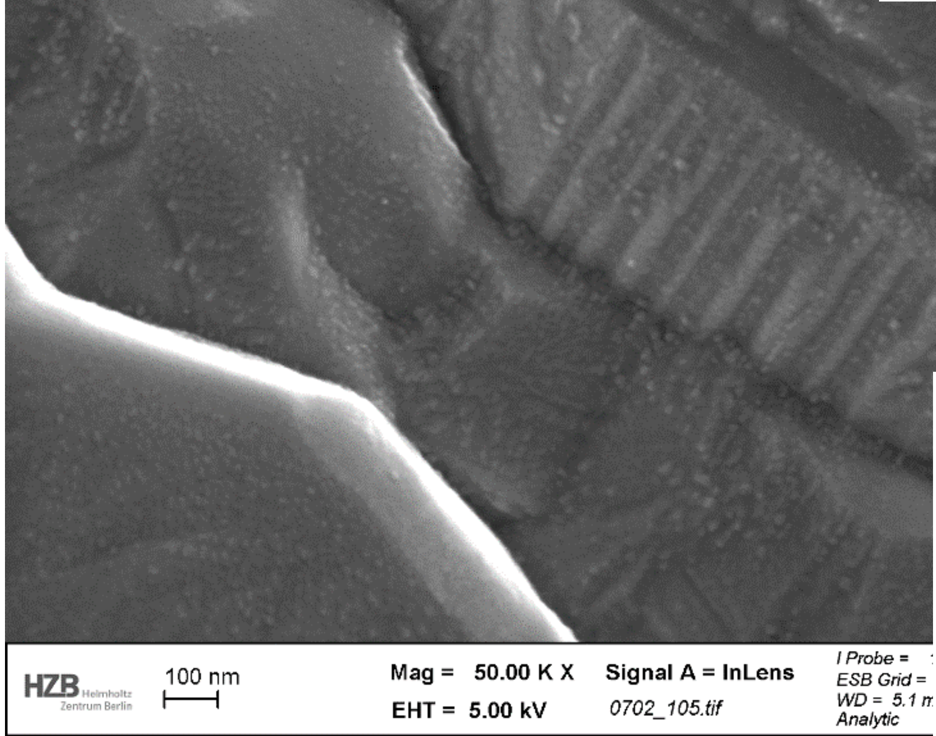
- Higher current => larger Cu_2O precipitates

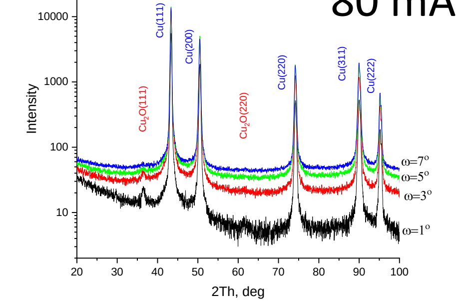
40 mA

80 mA

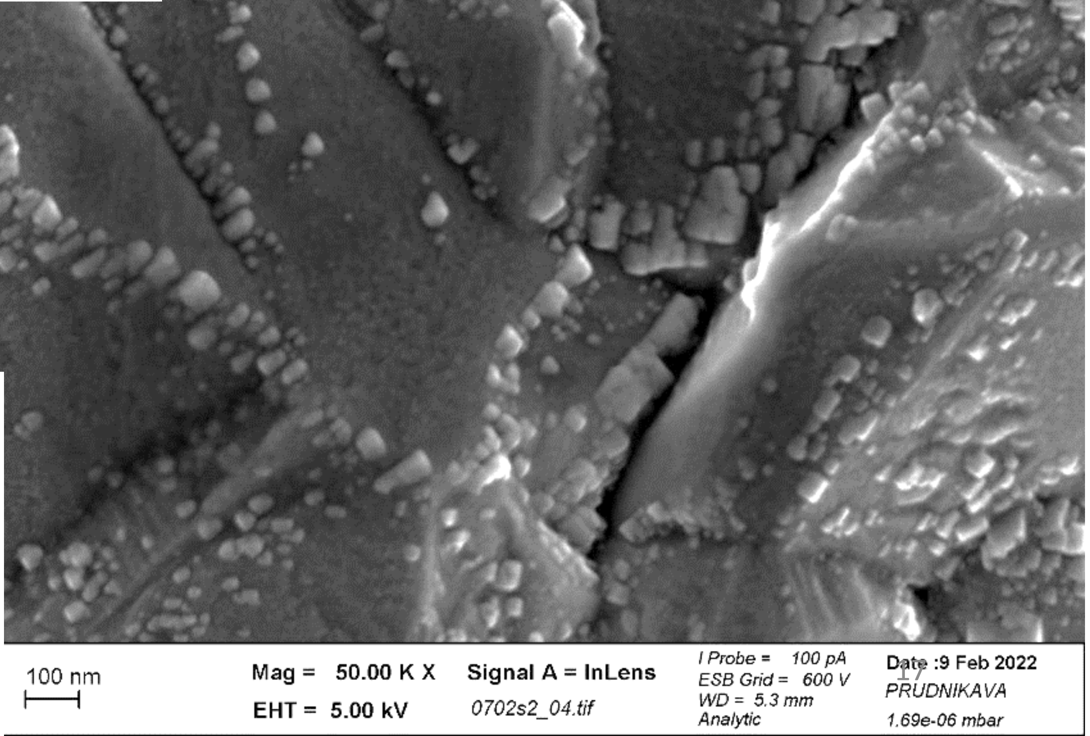


Surface Oxides (SEM)



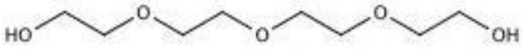


80 mA



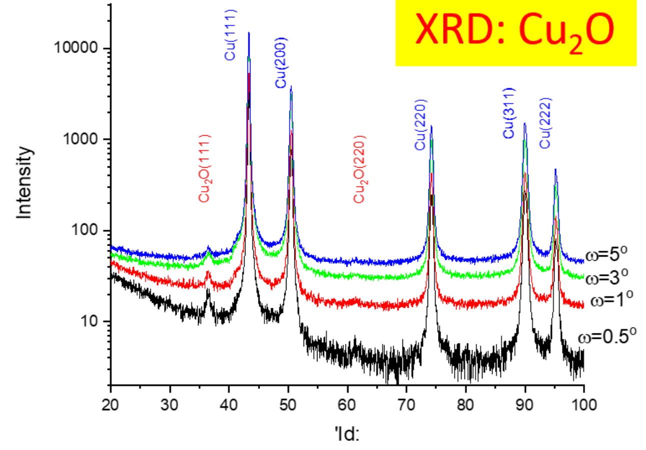
Testing Acidic Electrolytes (2): Cu plating onto Copper

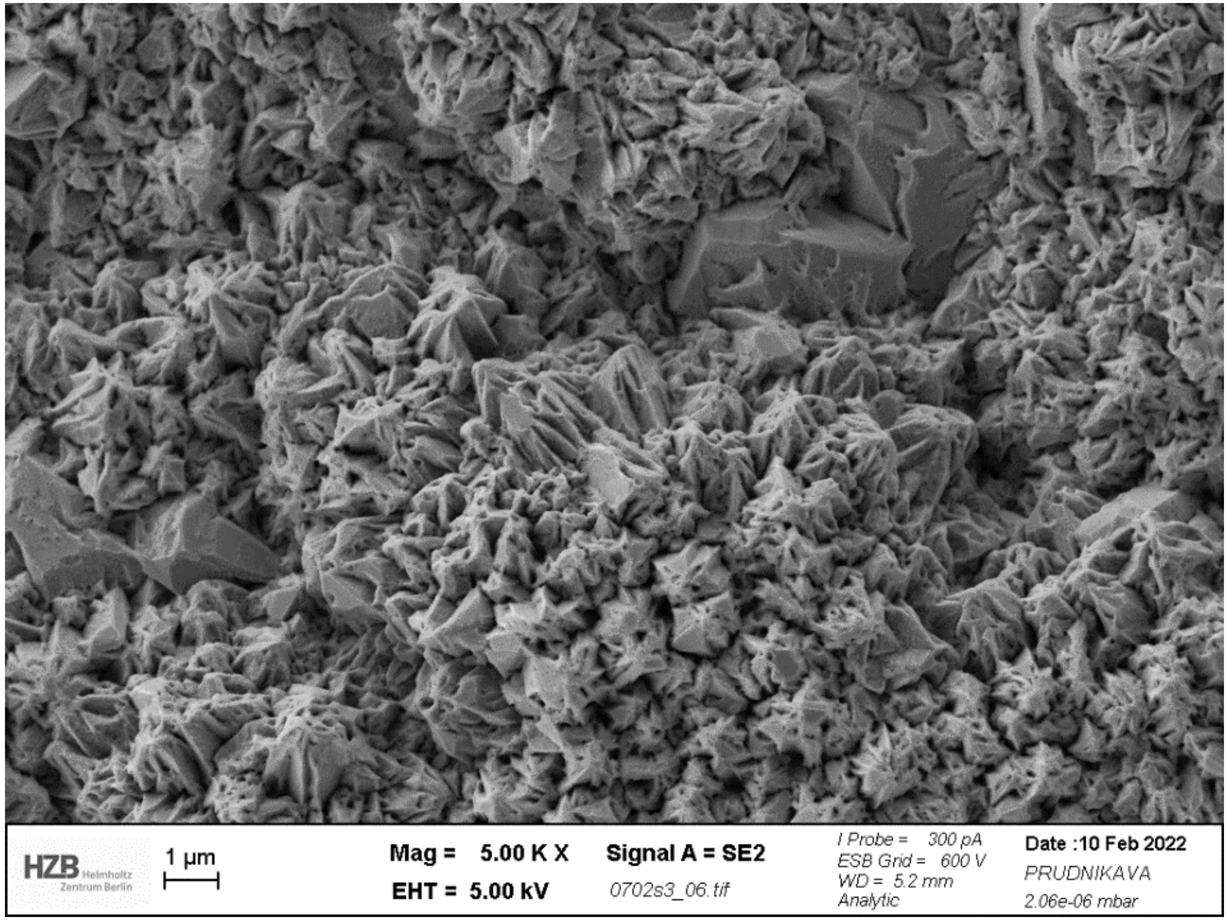
with Polyethyleneglycol $C_{2n}H_{4n+2}O_{n+1}$

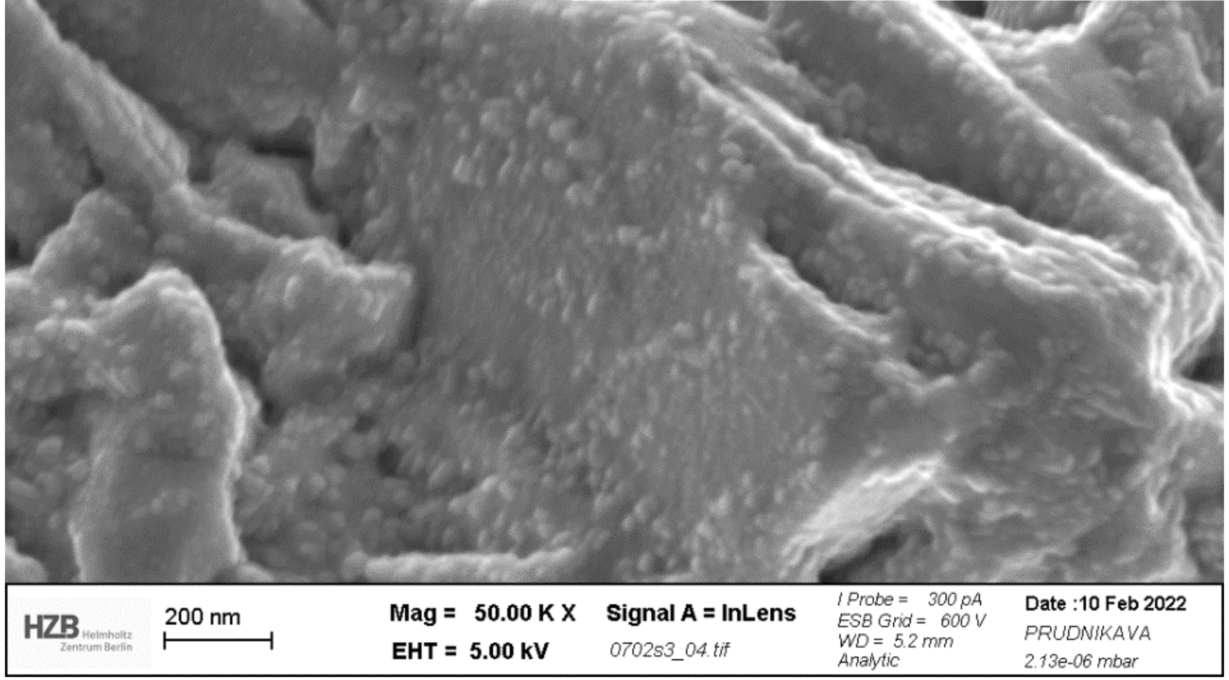


- Cu_2O is still present <=> no effect on film oxidation

XRD: Cu_2O





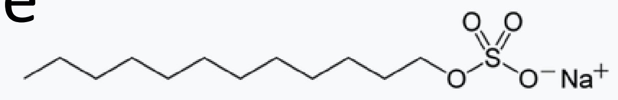


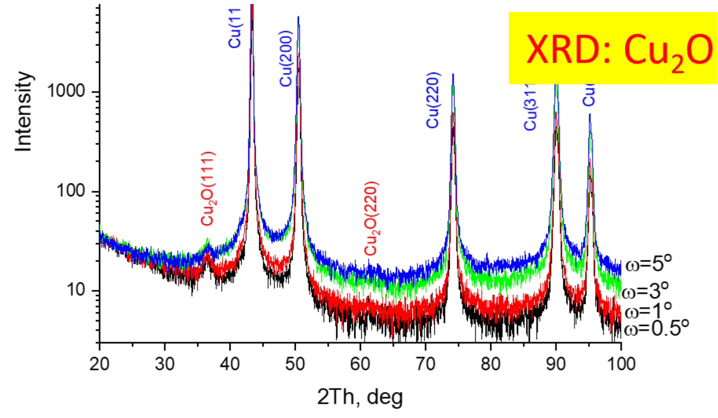
Testing Acidic Electrolytes (2): Cu plating onto Copper

- Cu_2O is present

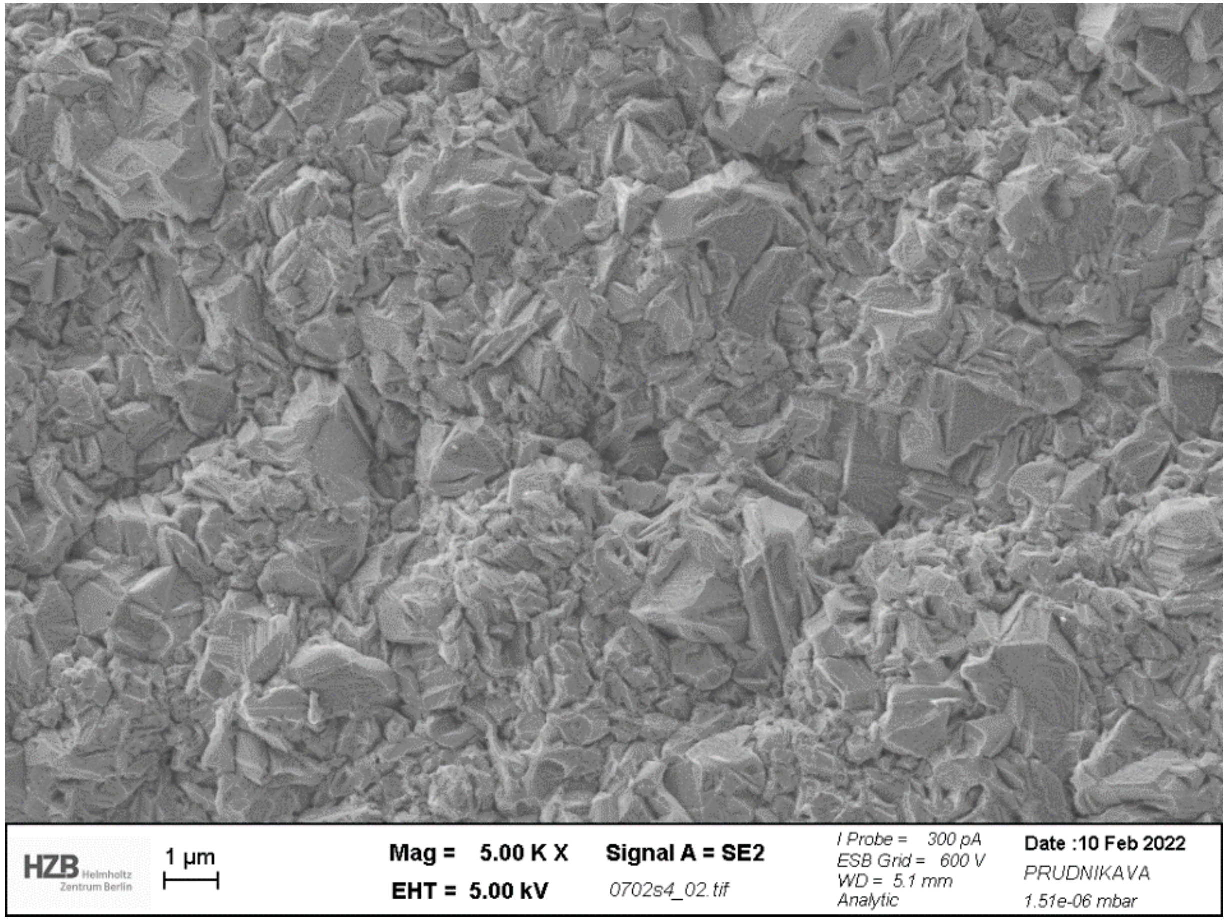
=> no effect on film oxidation

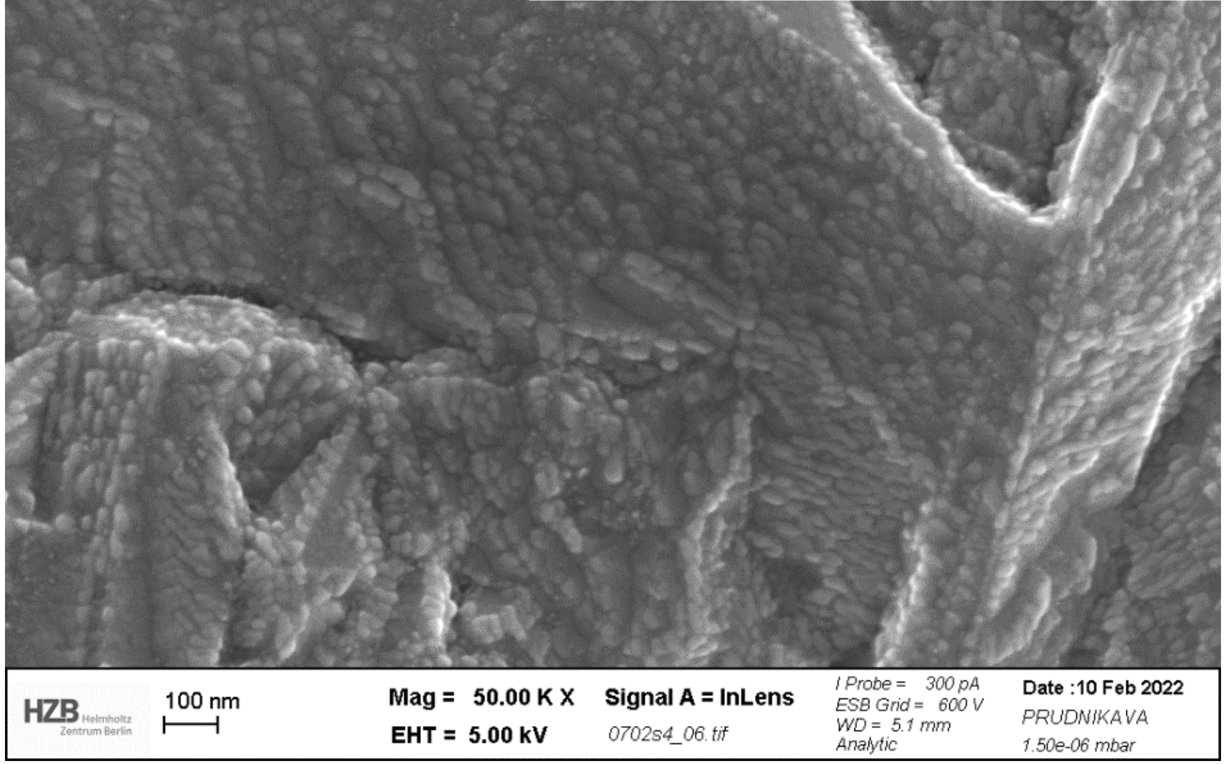
with Sodium Lauryl Sulphate





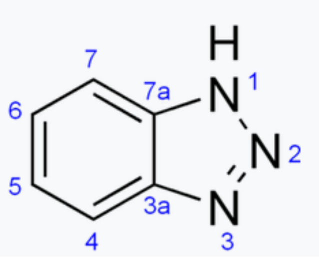
XRD: Cu_2O

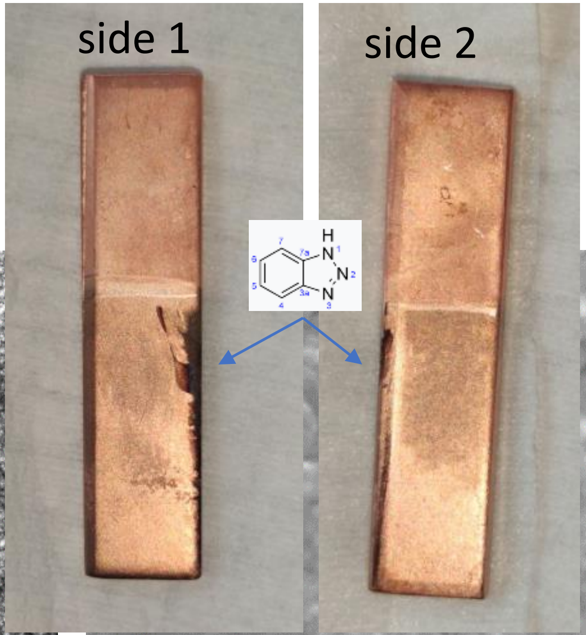


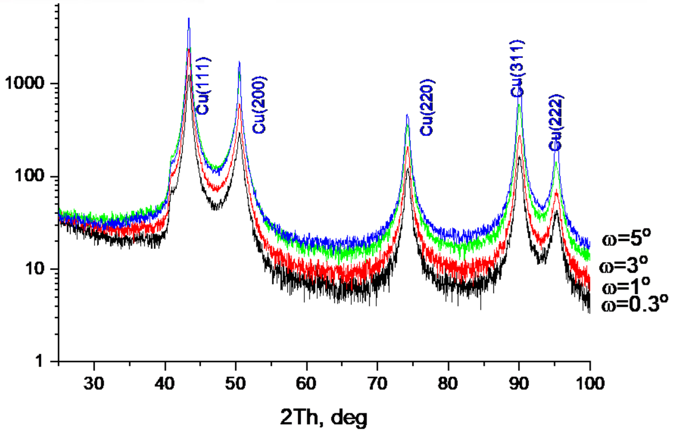


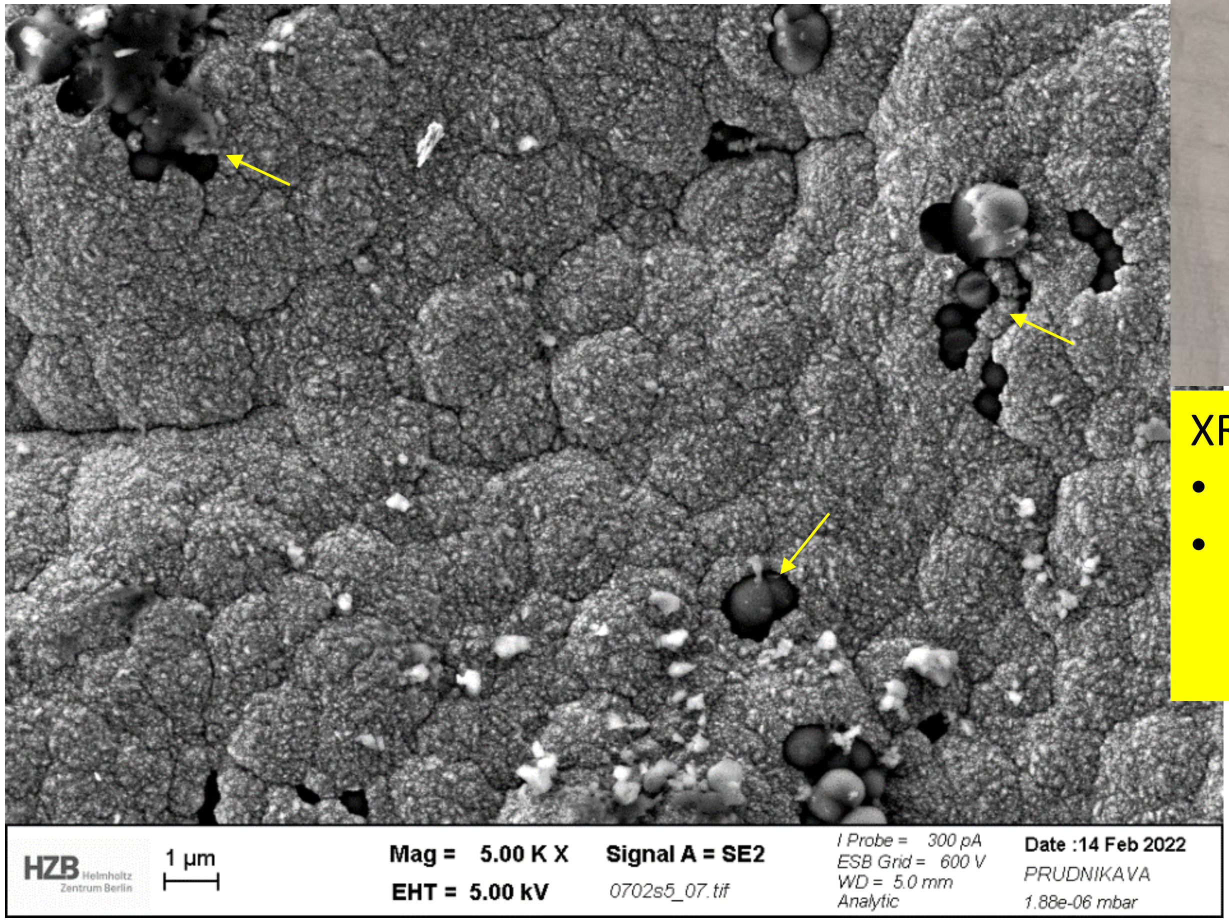
Testing Acidic Electrolytes (2): Cu plating onto Copper

with benzotriazole



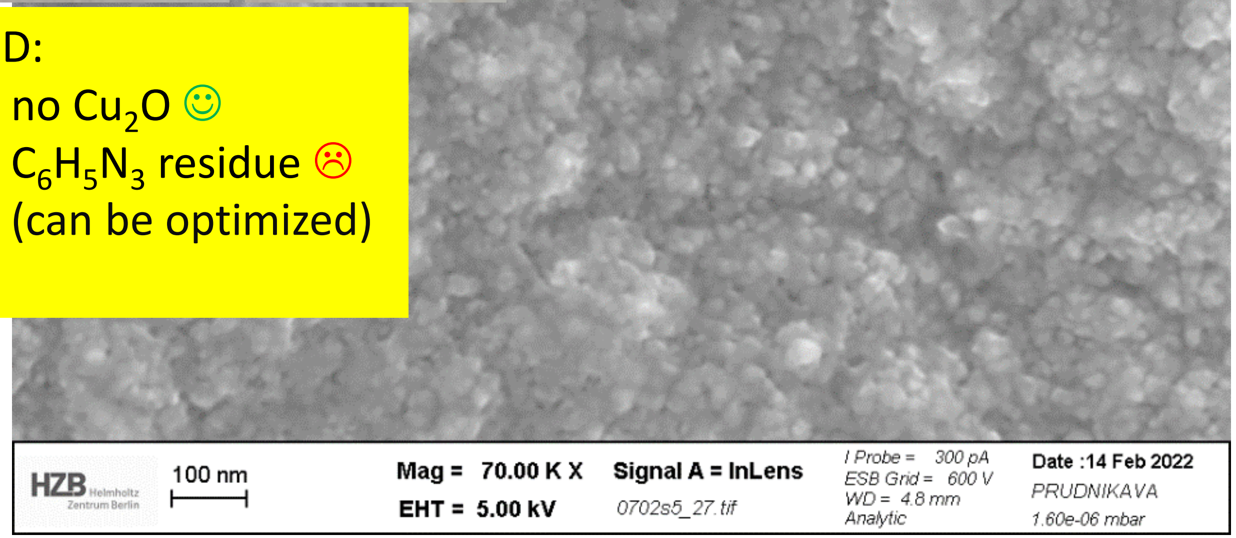




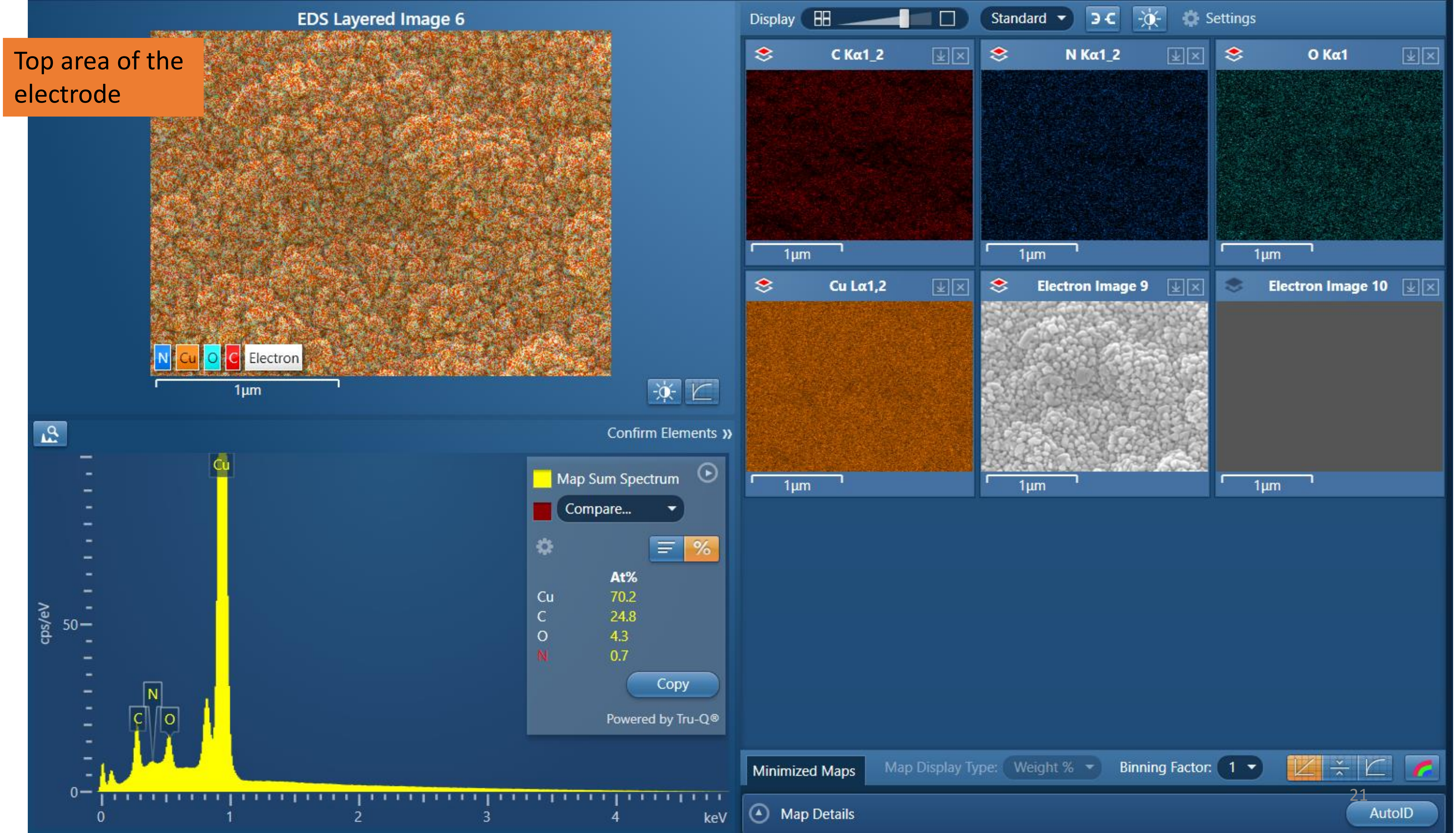


XRD:

- no Cu_2O ☺
- $C_6H_5N_3$ residue ☹ (can be optimized)

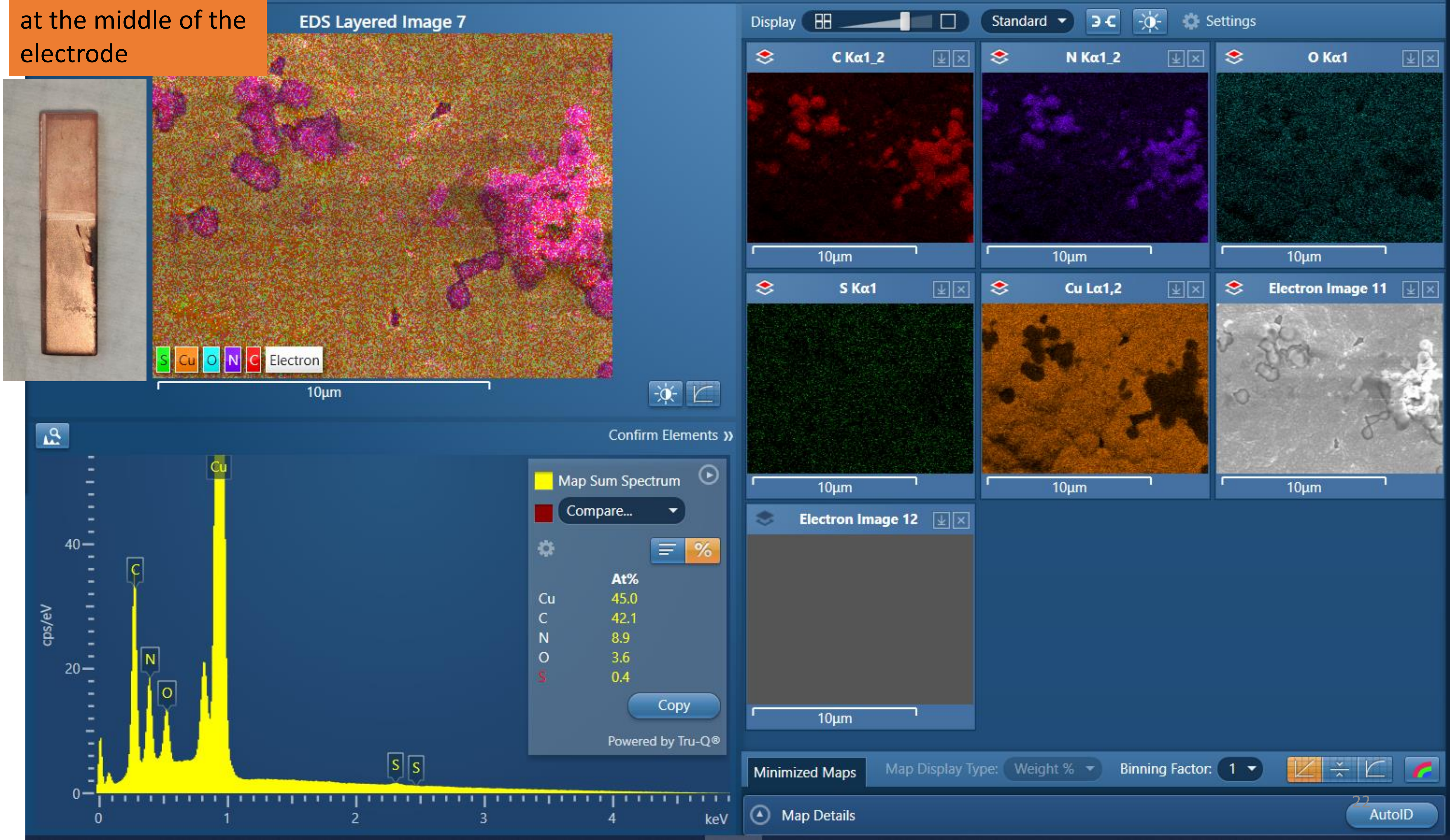


Top area of the electrode



	At%
Cu	70.2
C	24.8
O	4.3
N	0.7

at the middle of the electrode



	At%
Cu	45.0
C	42.1
N	8.9
O	3.6
S	0.4

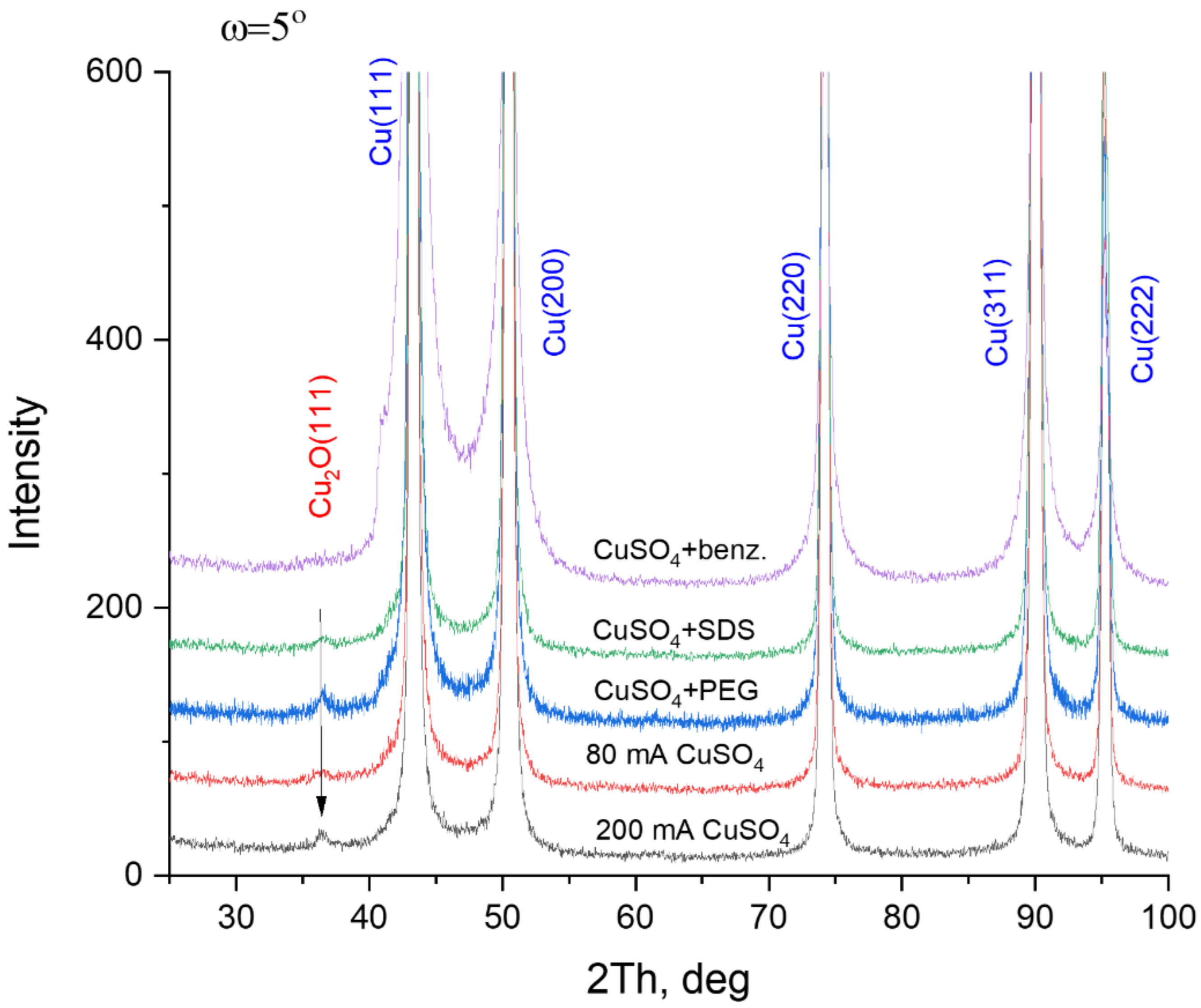
Testing Acidic Electrolytes (2): Cu plating onto Copper

HZB Helmholtz Zentrum Berlin

XRD

comparison at ω=5°

- ✓ only benzotriazole additive affects the Cu_2O formation

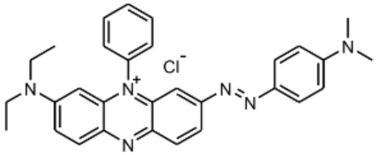


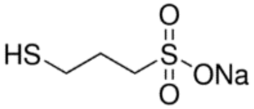
Testing Acidic Electrolytes (3): Cu plating onto Copper

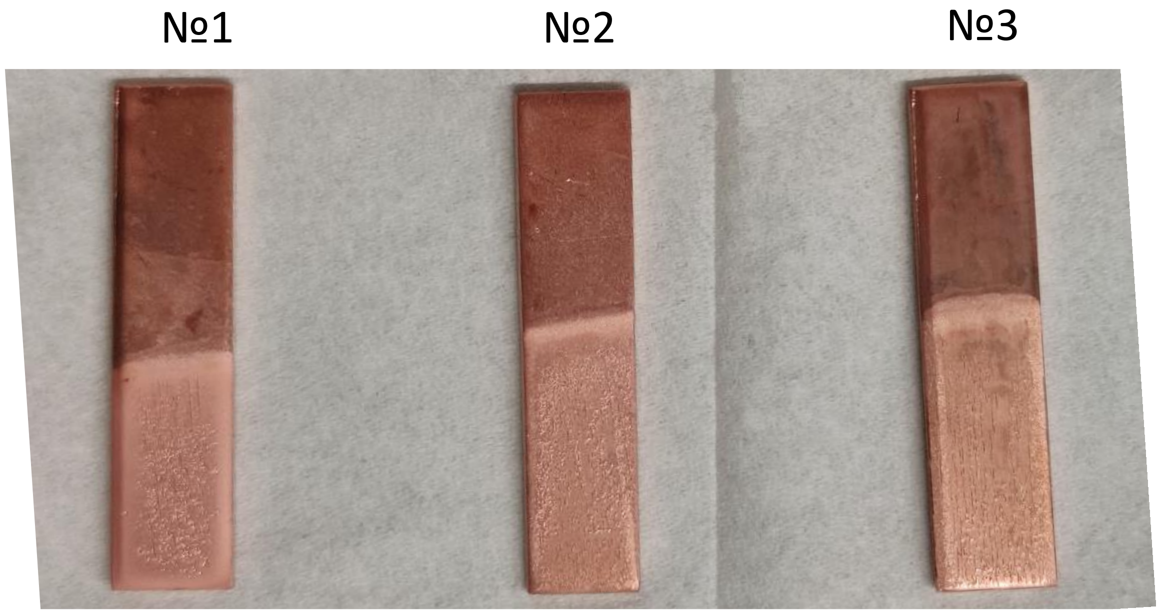
Modified Electrolyte:

$CuSO_4 \cdot 5H_2O$
H_2SO_4
H_2O
with the additives:

- NaCl + Janus Green B
- NaCl + Janus Green B + MPS







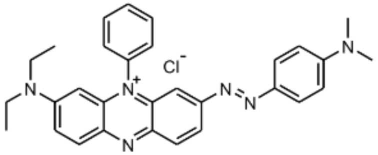
		I, mA	j, mA/cm²	deposition rate, um/h	at% O at 5kV	O/Cu at 5kV	Cryst. Size Cu(111), nm
№1	$CuSO_4$+H_2SO_4+NaCl +Janus Green B	80	17.6	24.5	2.1-3.6	0.02-0.04	29.64
№2	$CuSO_4$+H_2SO_4+NaCl +Janus Green B	50	13.2	13.5	2.7	0.03	33.28
№3	$CuSO_4$+H_2SO_4+NaCl +Janus Green B+MPS	50	13.2	12.9	3.5-4	0.04-0.05	33.40

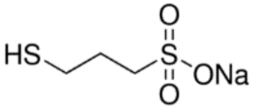
Testing Acidic Electrolytes (3): Cu plating onto Copper

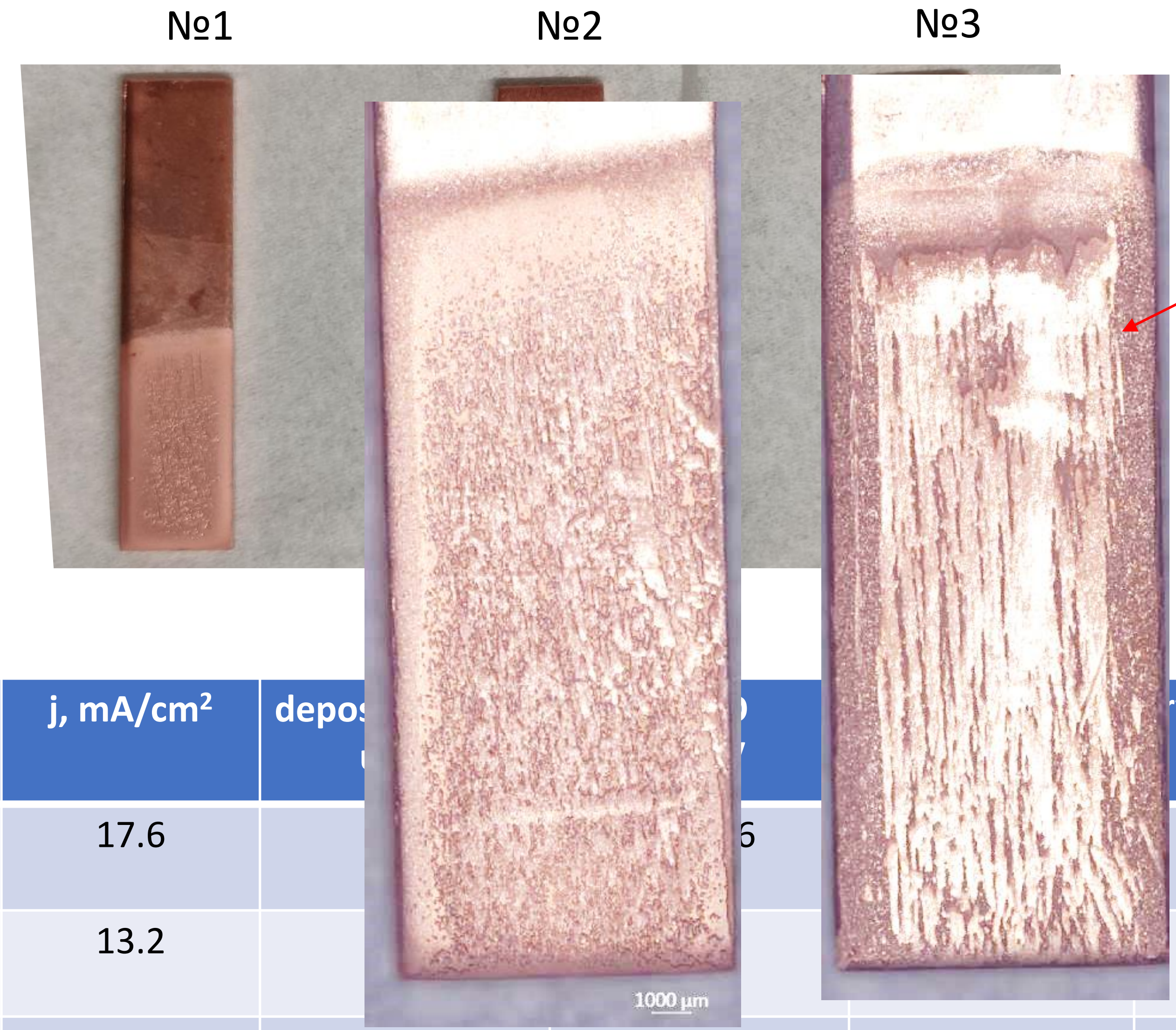
Modified Electrolyte:

$CuSO_4 \cdot 5H_2O$
H_2SO_4
H_2O
with the additives:

- NaCl + Janus Green B
- NaCl + Janus Green B + MPS





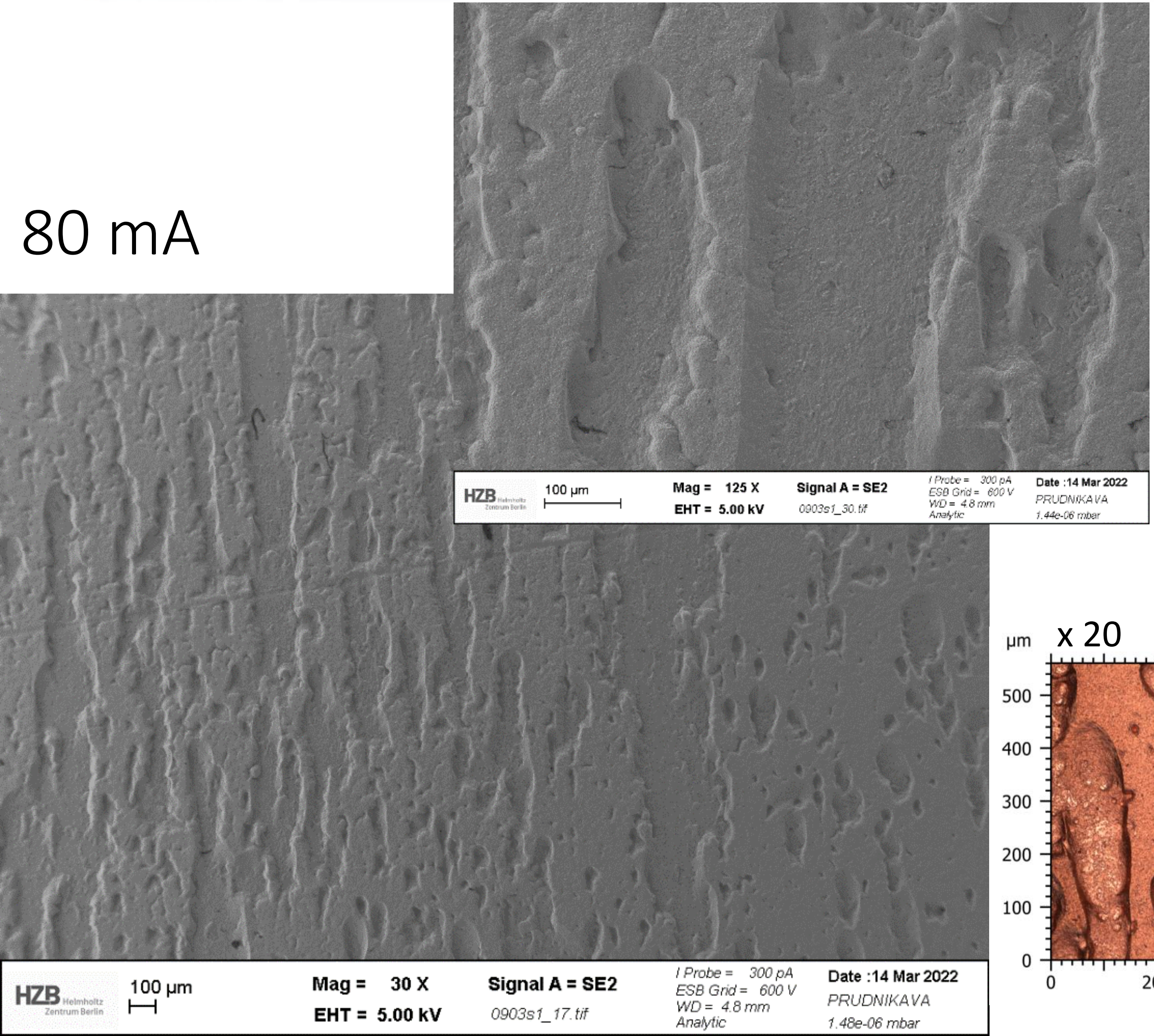


Cu-film grooving (channeling)

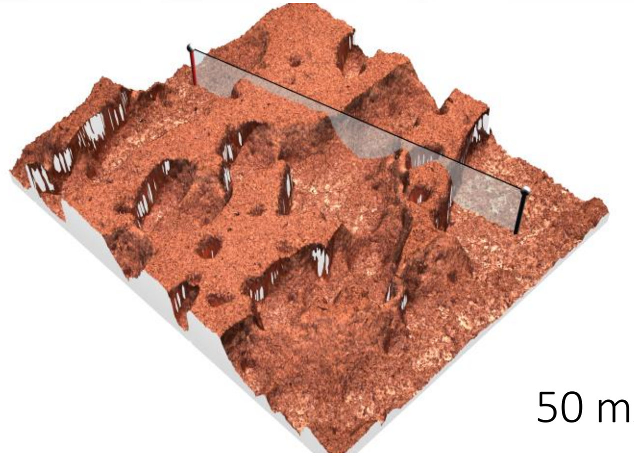
		I, mA	j, mA/cm²	depos	)		ryst. Size Cu(111), nm
№1	$CuSO_4$+H_2SO_4+NaCl +Janus Green B	80	17.6		6		29.64
№2	$CuSO_4$+H_2SO_4+NaCl +Janus Green B	50	13.2				33.28
№3	$CuSO_4$+H_2SO_4+NaCl +Janus Green B+MPS	50	13.2	12.9	3.5-4	0.04-0.05	33.40

Testing Acidic Electrolytes (3): Cu plating onto Copper

80 mA

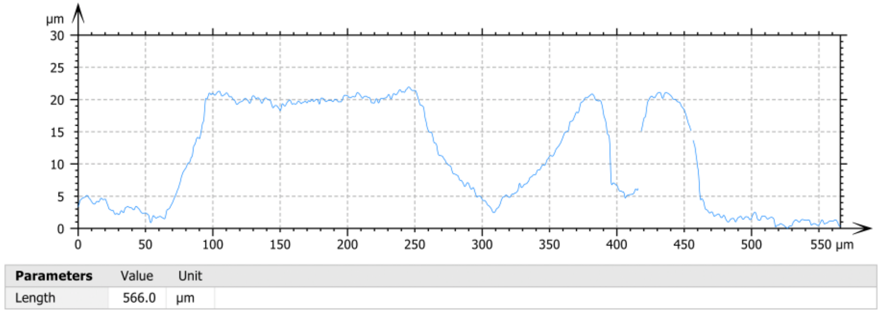

HZB Helmholtz Zentrum Berlin
100 µm
Mag = 125 X
EHT = 5.00 kV
Signal A = SE2
0903s1_30.tif
I Probe = 300 pA
ESB Grid = 600 V
WD = 4.8 mm
Analytic
Date :14 Mar 2022
PRUDNIKAVA
1.44e-06 mbar

HZB Helmholtz Zentrum Berlin
100 µm
Mag = 30 X
EHT = 5.00 kV
Signal A = SE2
0903s1_17.tif
I Probe = 300 pA
ESB Grid = 600 V
WD = 4.8 mm
Analytic
Date :14 Mar 2022
PRUDNIKAVA
1.48e-06 mbar



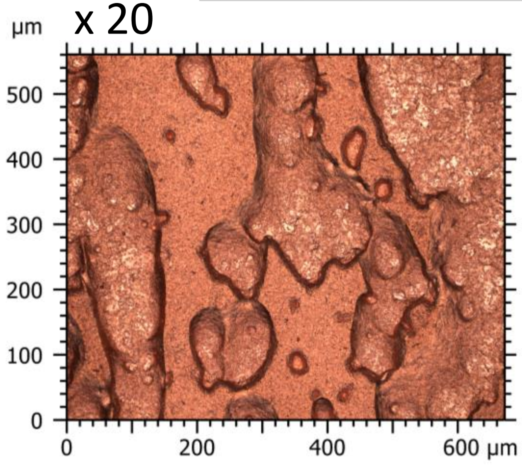
Cu-film grooving (channeling)

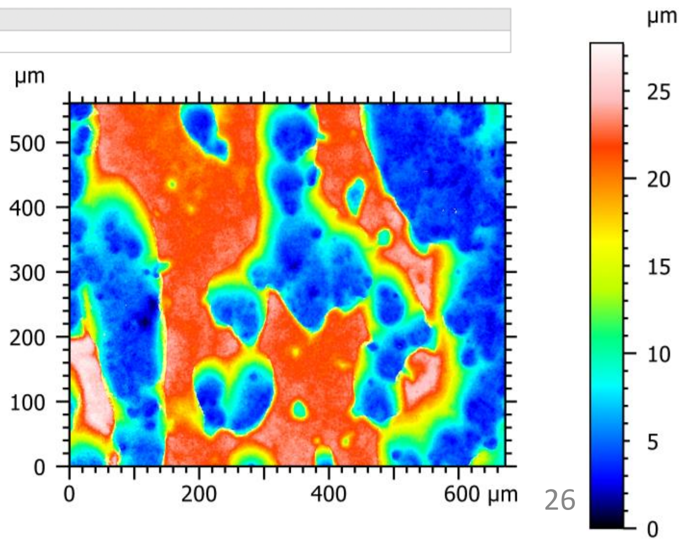
50 mA



Parameters	Value	Unit
Length	566.0	µm

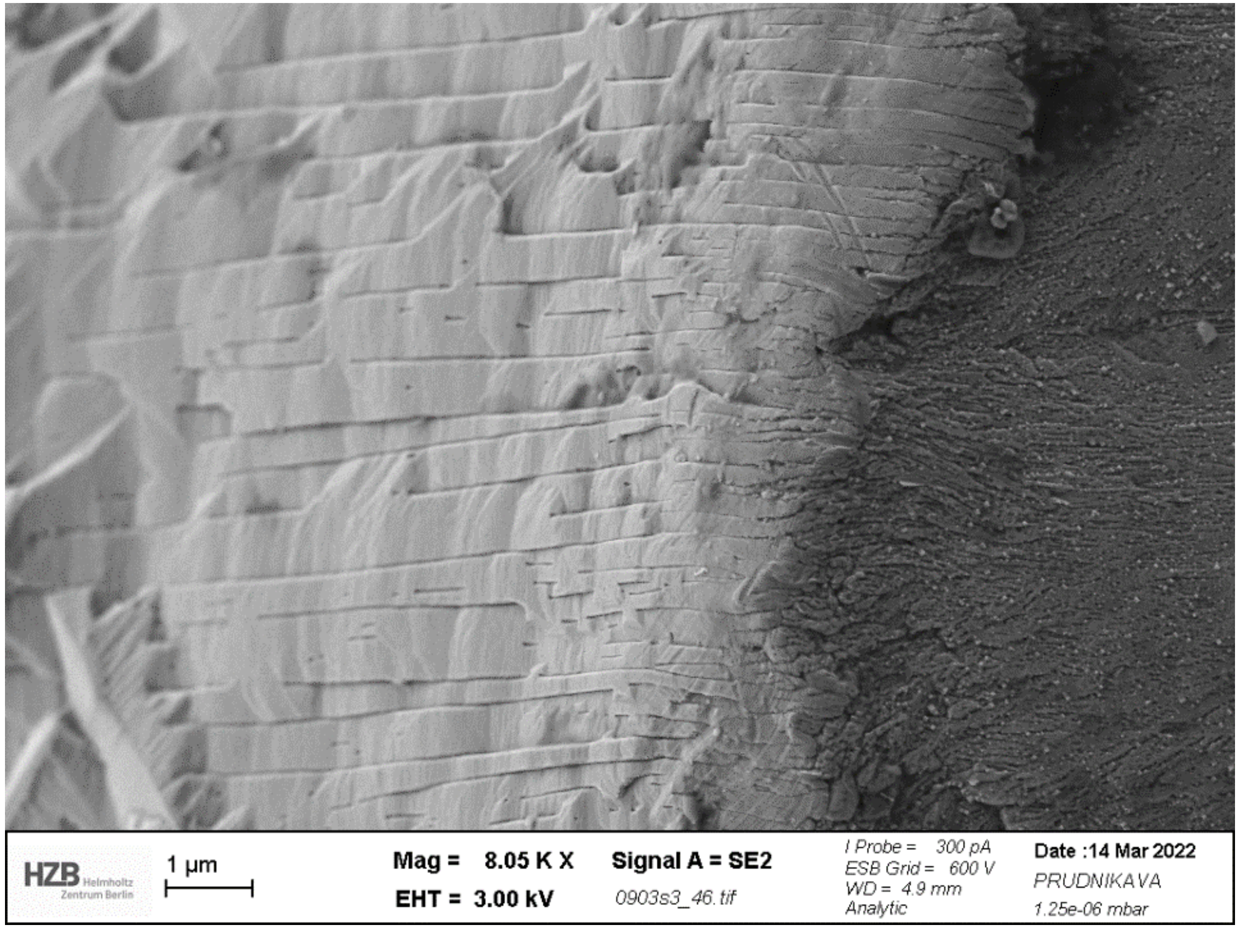
x 20

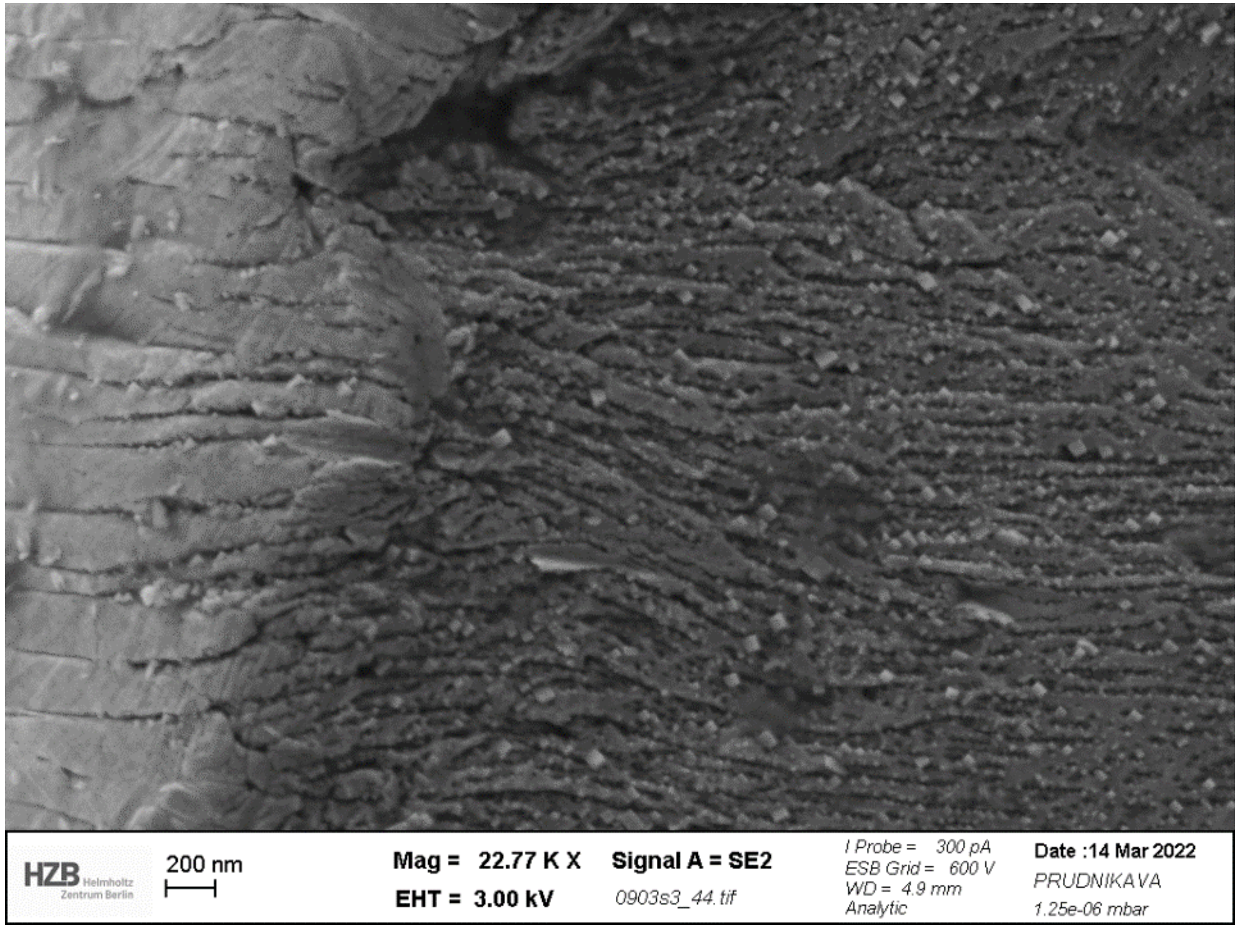




Testing Acidic Electrolytes (3): Cu plating onto Copper

Grooving is owing to preferential growth of the Cu seed along one crystallographic direction

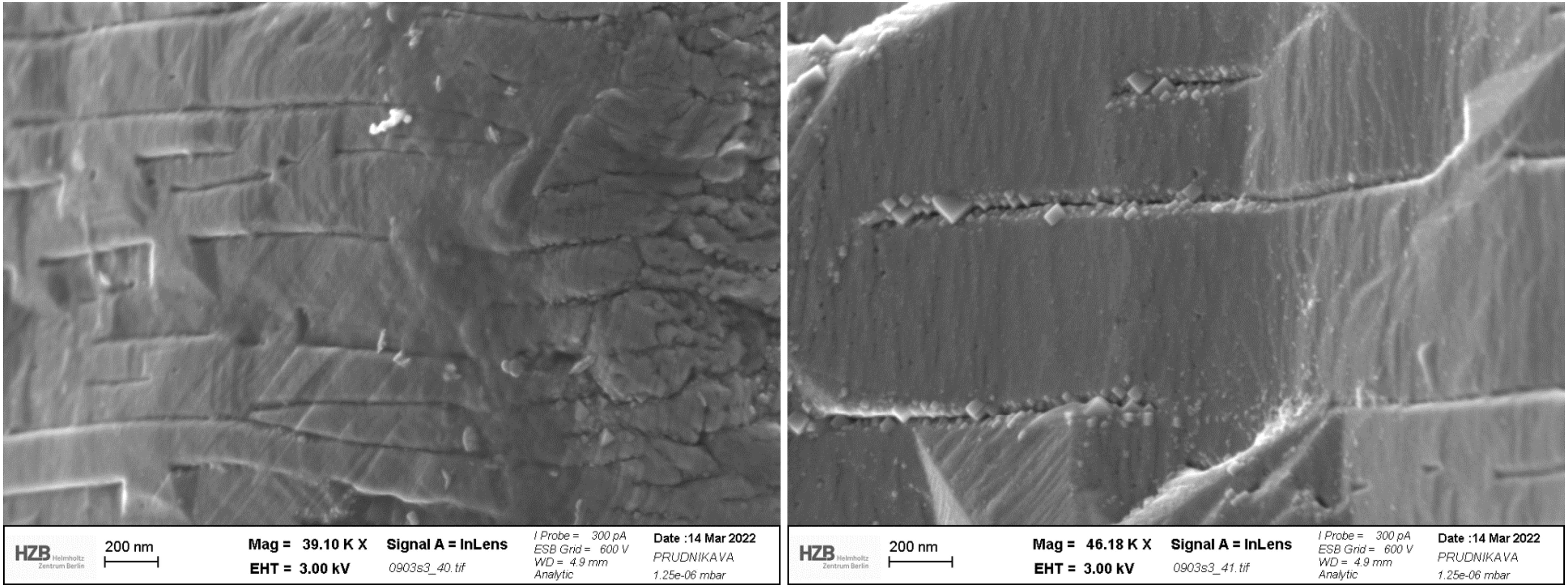




№3 (50 mA, MPS)

Testing Acidic Electrolytes (3): Cu plating onto Copper

Grooving is owing to preferential growth of the Cu seed along one crystallographic direction



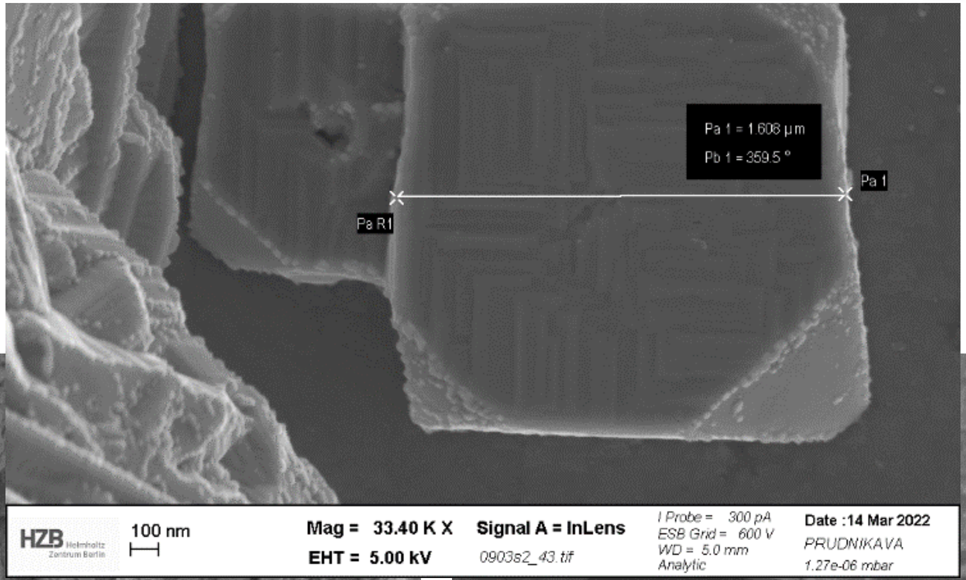
№3 (50 mA, MPS)

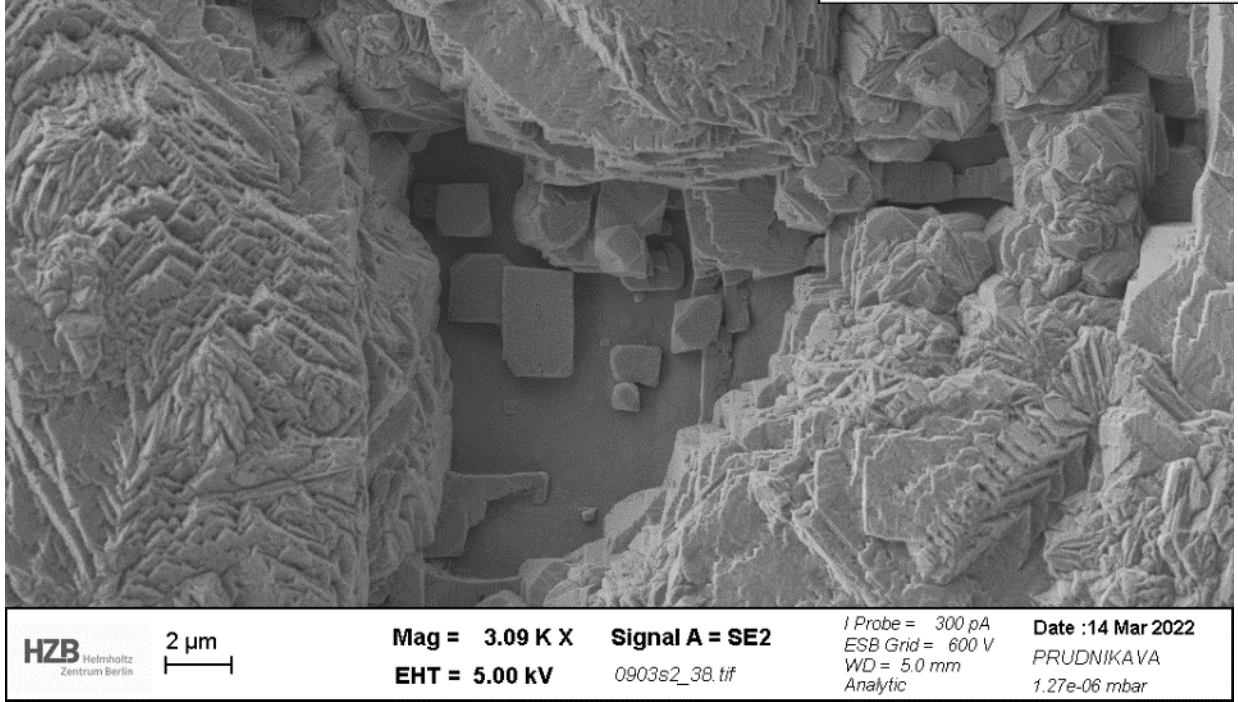
Testing Acidic Electrolytes (3): Cu plating onto Copper

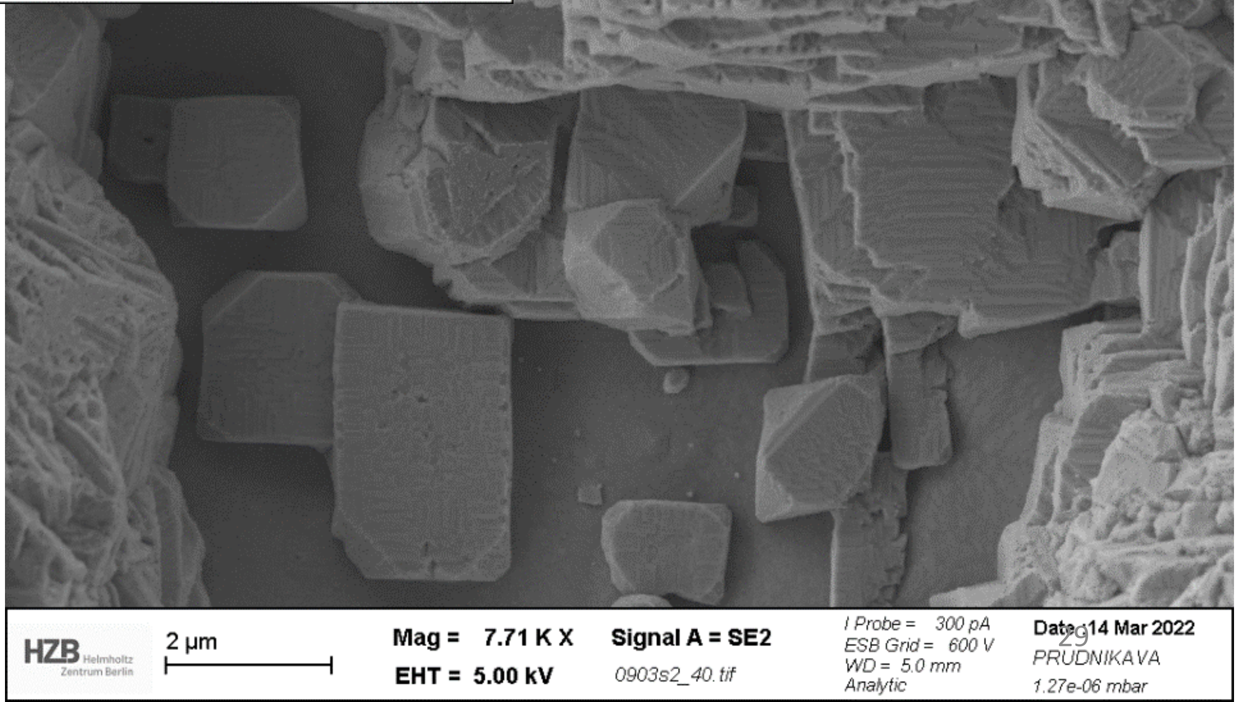
Grooving was not affected by

- initial surface roughness of the electrode;
- bath temperature;
- MPS presence

- Cu-film evens off as film thickness builds up (by increasing current density or/and electroplating duration)

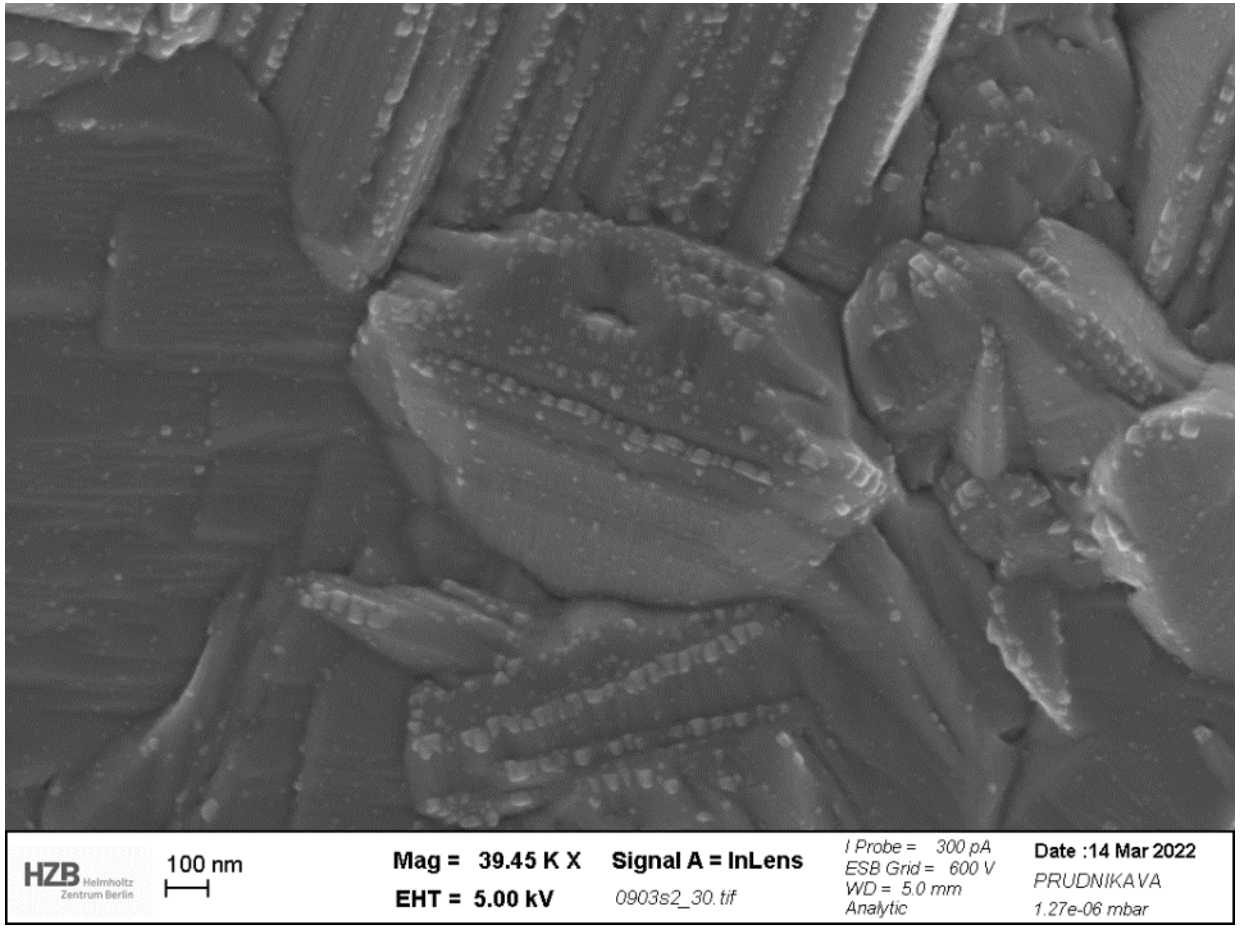


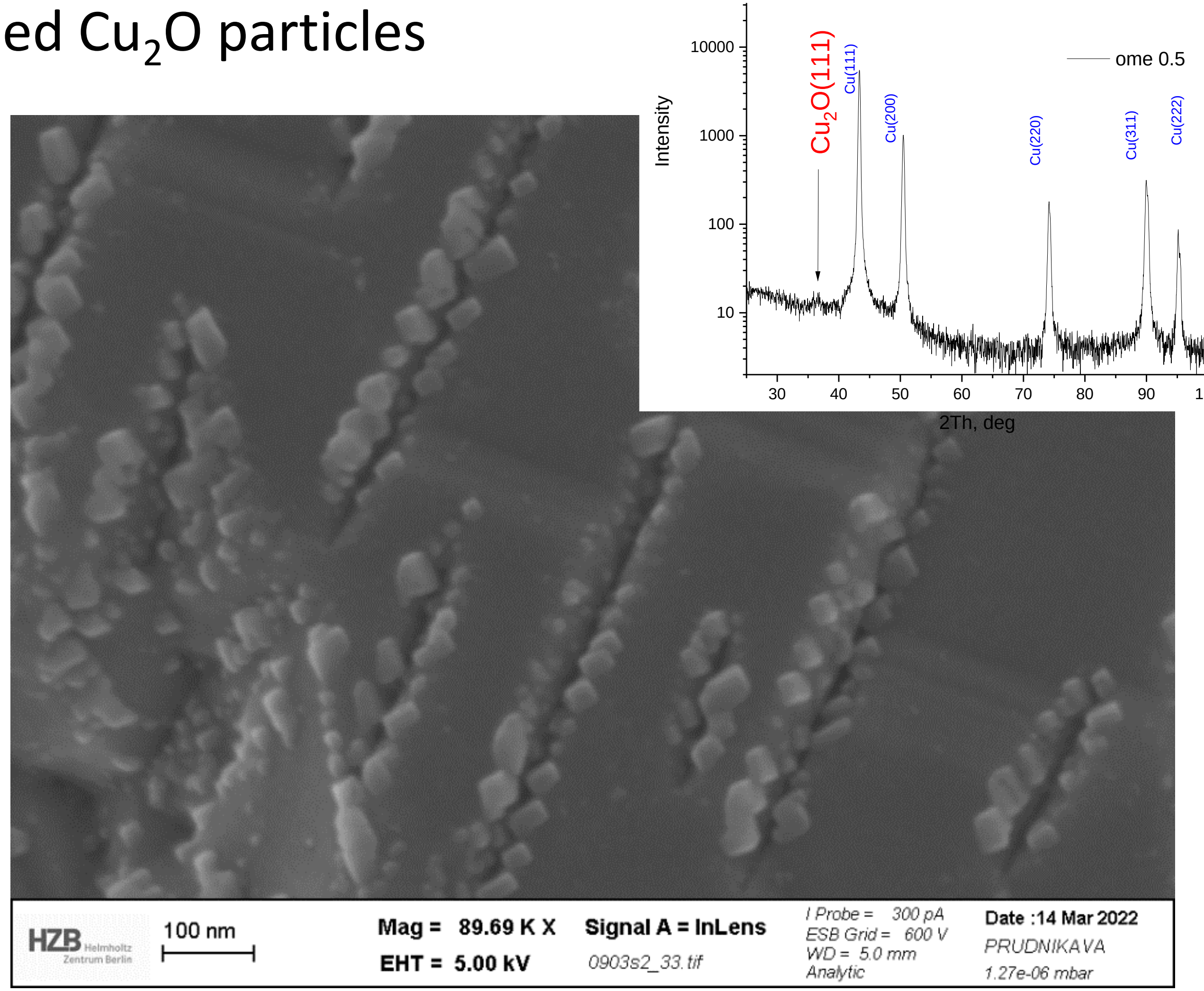




Testing Acidic Electrolytes (3): Cu plating onto Copper

Cu-film oxidation? Some crystal planes revealed Cu_2O particles

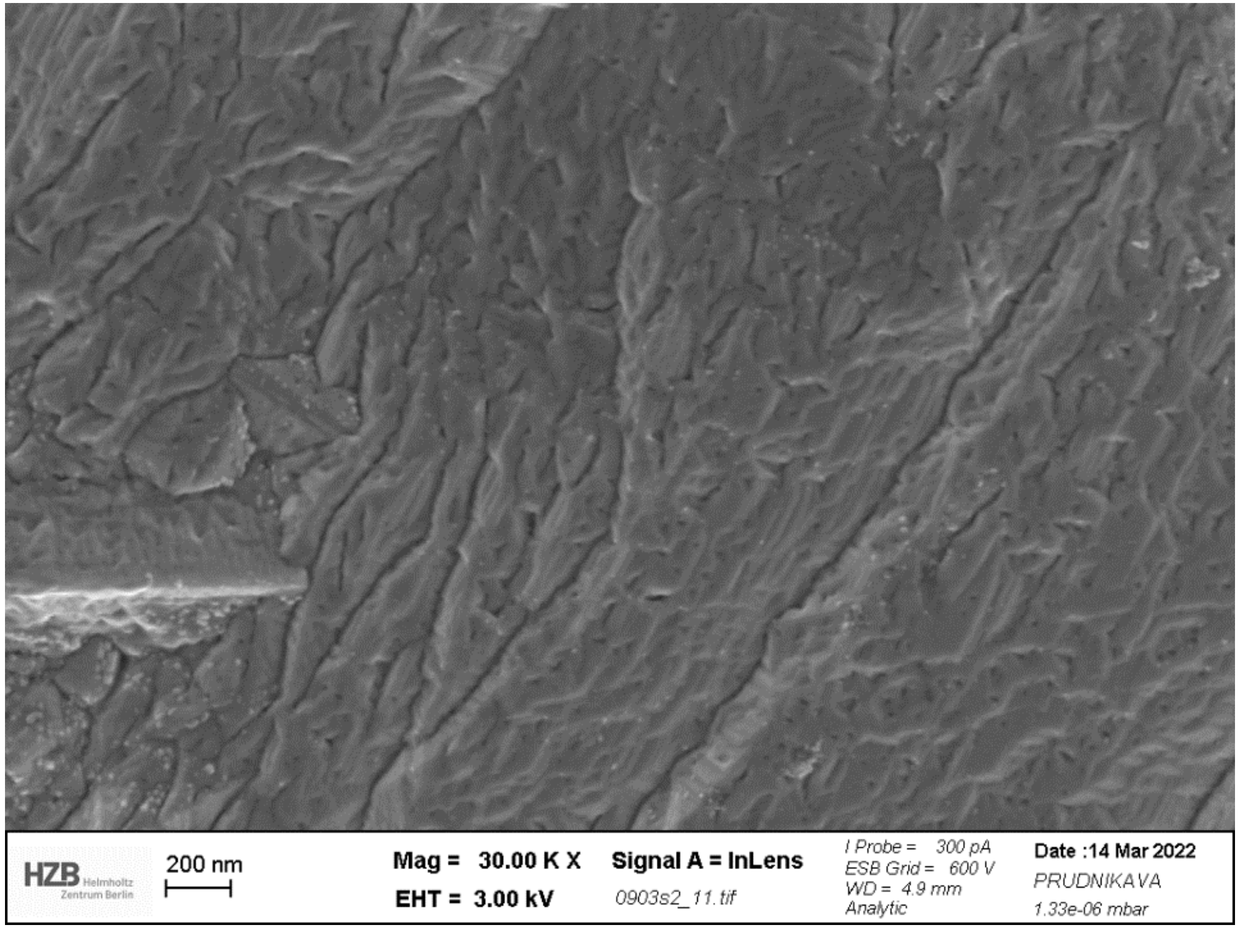


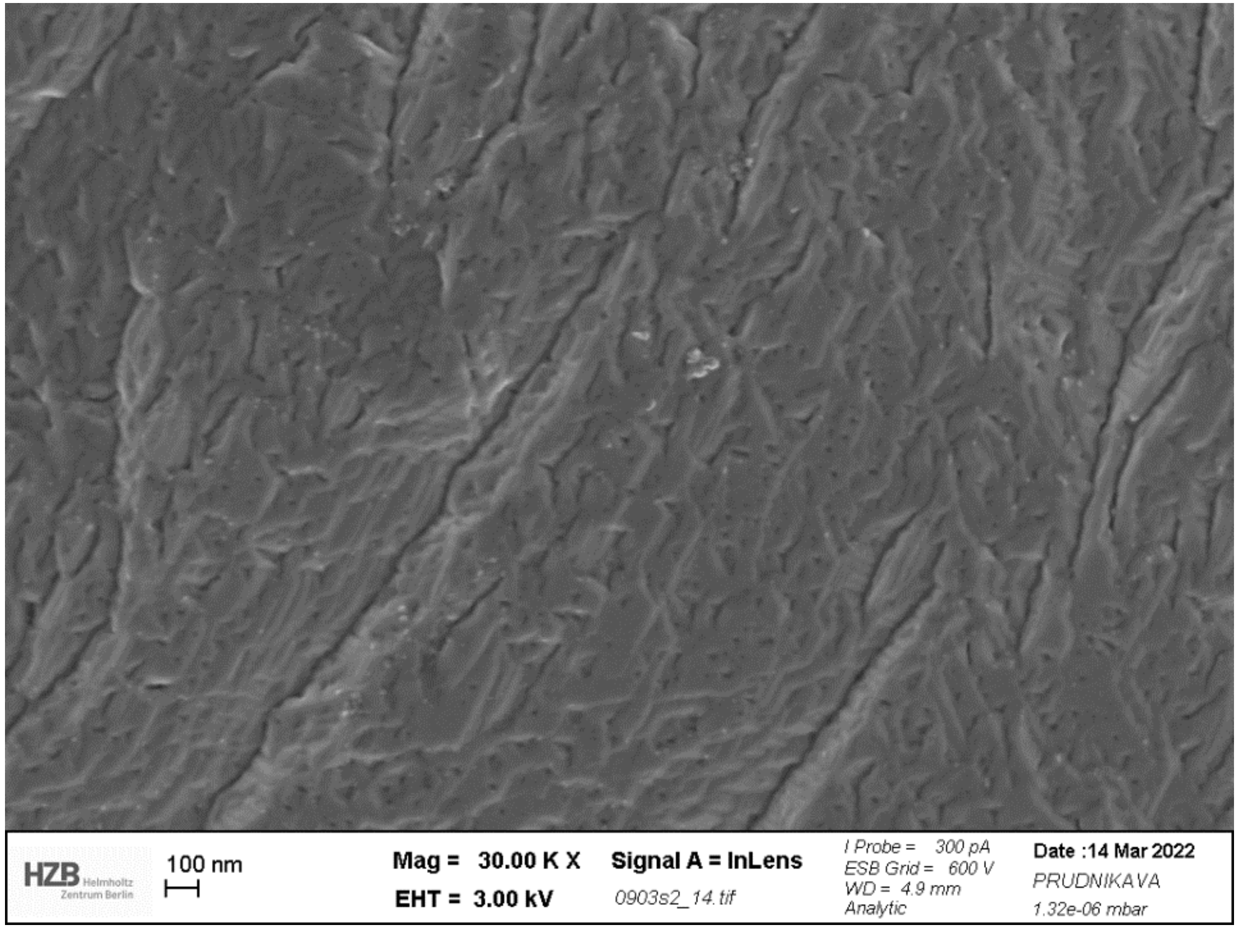


№2 (50 mA, no MPS)

Testing Acidic Electrolytes (3): Cu plating onto Copper

some - did not (and is valid for recipes №1-3)

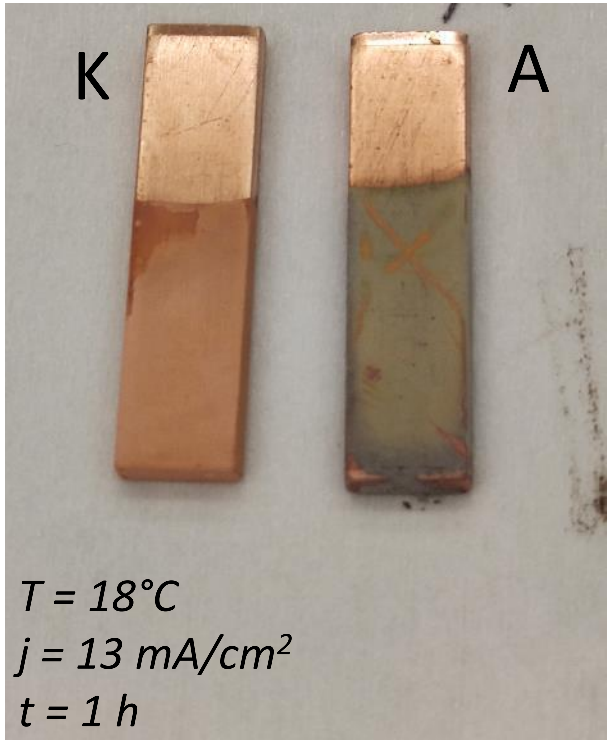




№2 (50 mA, no MPS)

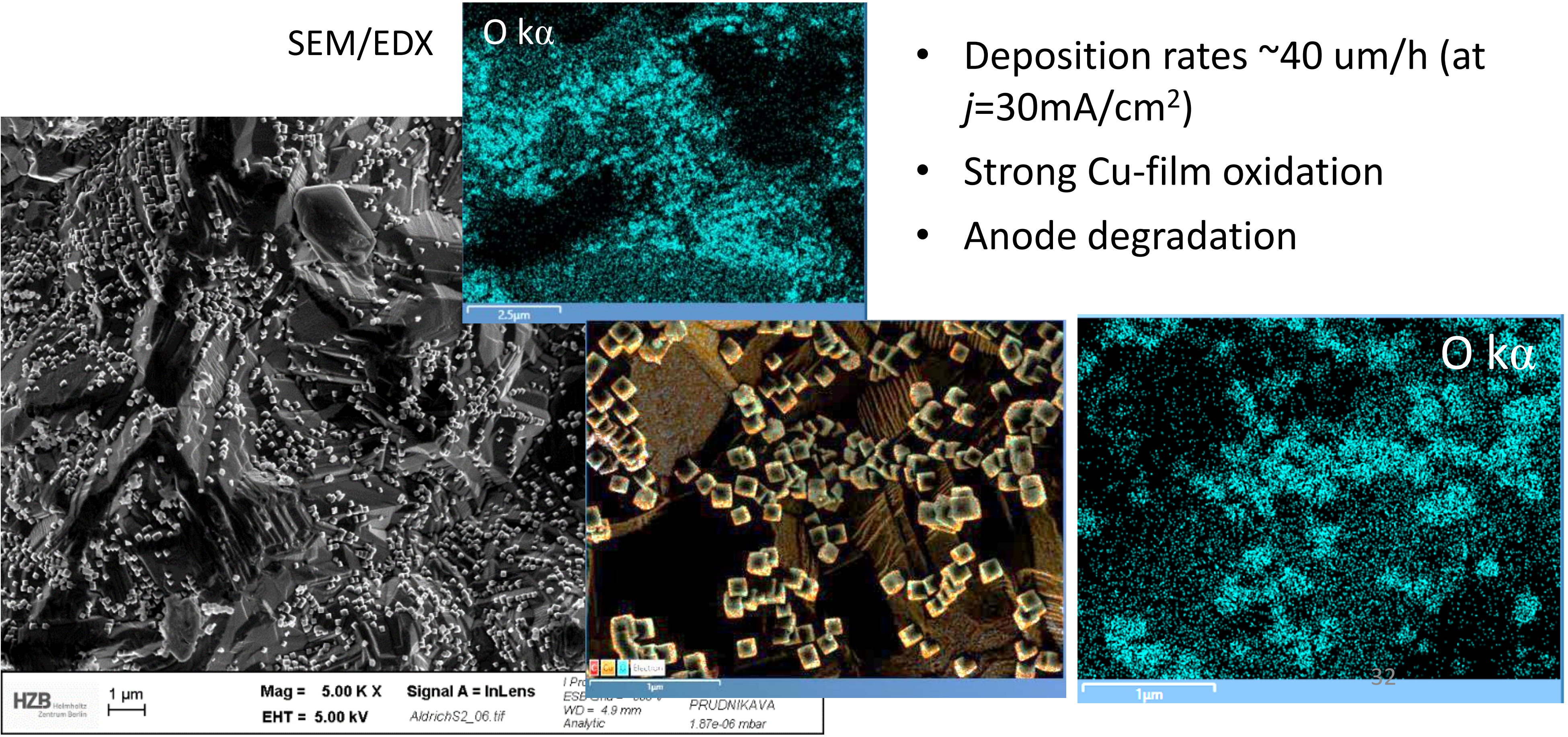
Testing Acidic Electrolytes (4): Cu plating onto Copper

Electrolyte: High speed bright copper electroplating solution by Sigma Aldrich (deposition rate declared: up to 5 µm/min)



T = 18°C
j = 13 mA/cm^2
t = 1 h

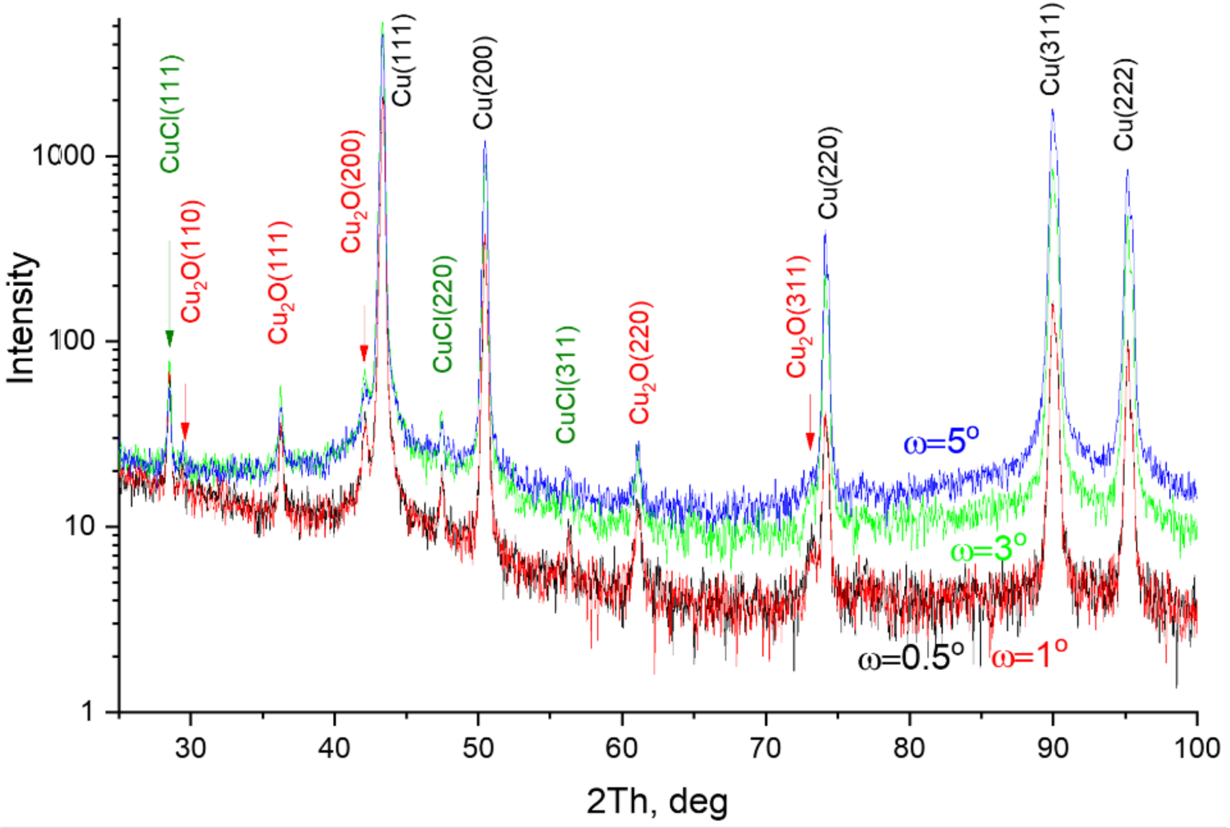
SEM/EDX



- Deposition rates ~40 um/h (at j=30mA/cm^2)
- Strong Cu-film oxidation
- Anode degradation

Testing Acidic Electrolytes (4): Cu plating onto Copper

XRD: Cu films

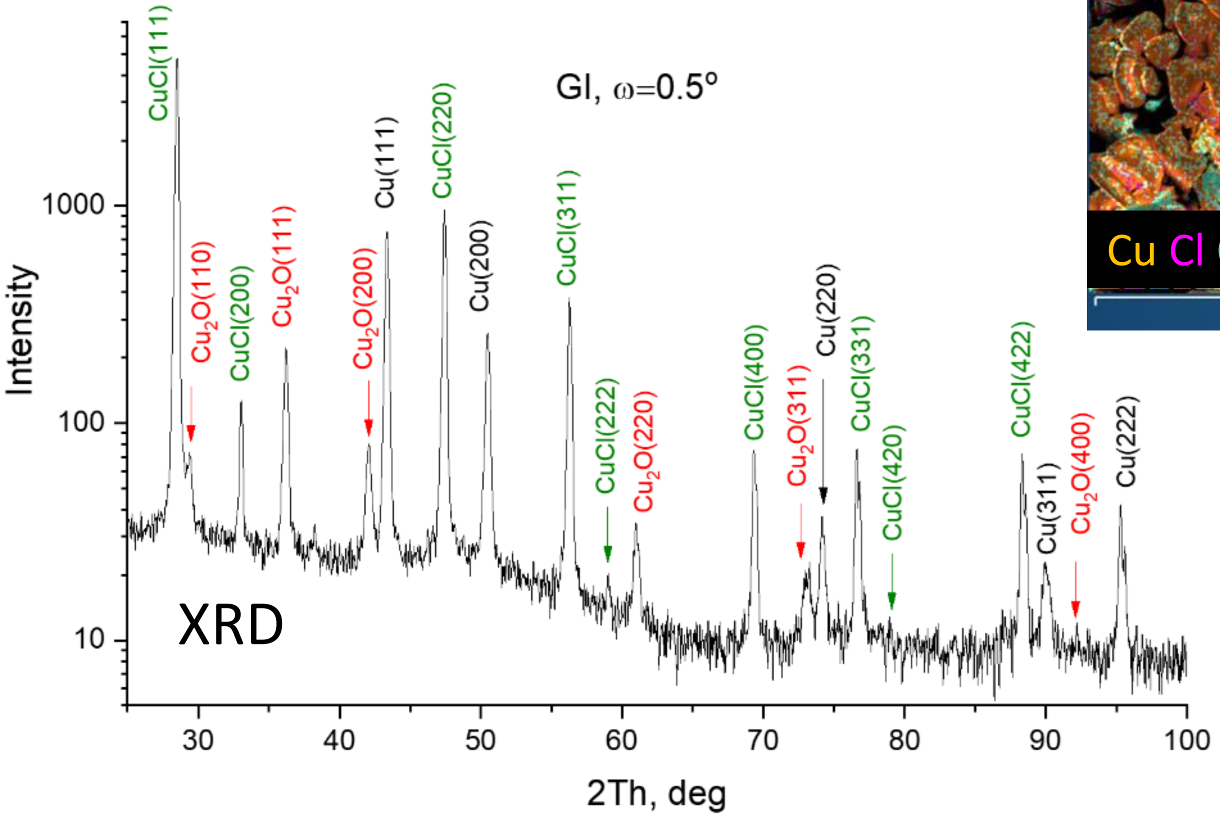


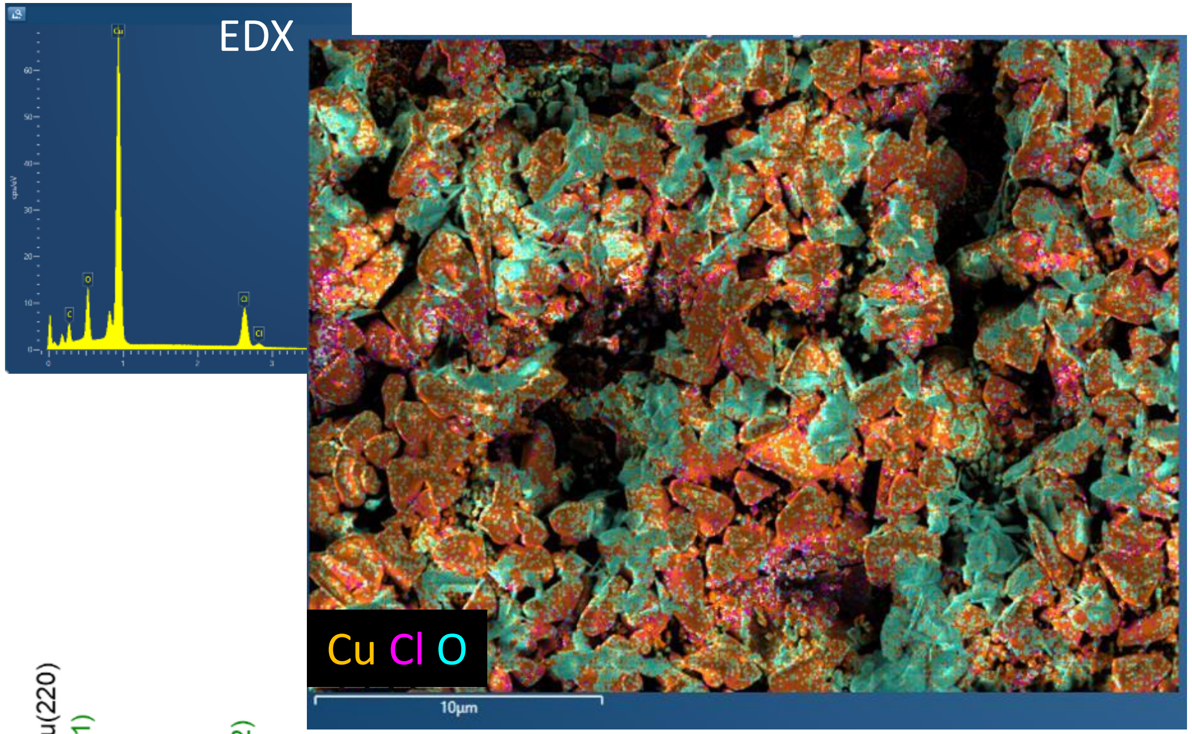
cubic Cu_2O and CuCl are present

⬄ related to Anode problem?

Testing Acidic Electrolytes (4): Cu plating onto Copper

Cu Anode





- cubic Cu_2O and CuCl are present

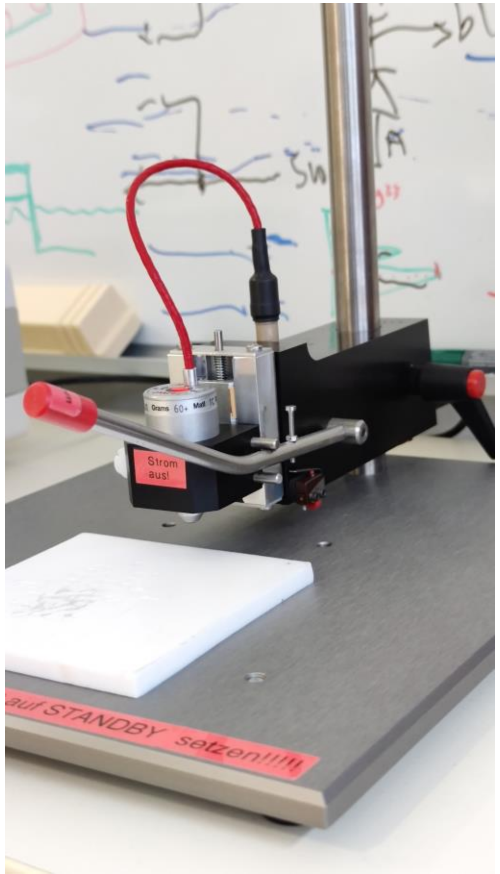
⇔ Anode degradation (even if smaller current densities are applied to Anode)

⇒ Glassy Carbon Anode

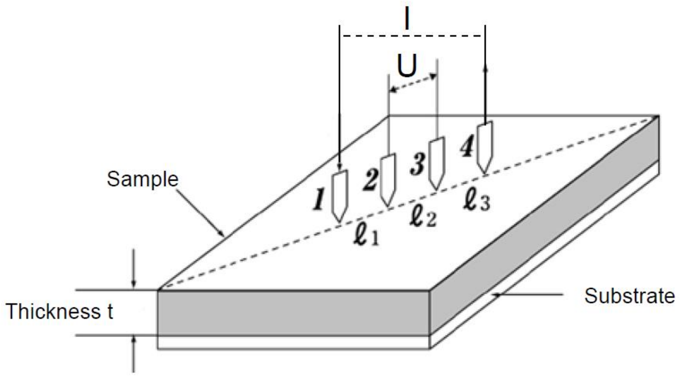
to be tested

Anode area was increased x2

4-probe resistivity measurement



Current: up to 100 mA
Voltage:
0 – 150 mV High-resolution mode
150 mV-1.2 V Low-resolution mode



Pressure: m = 60 g
Probe radius 300 μm
probe spacing 1 mm

Nb (0°C)	Cu
15.2*10^{-6} Ohm*cm	1.67*10^{-6} Ohm*cm

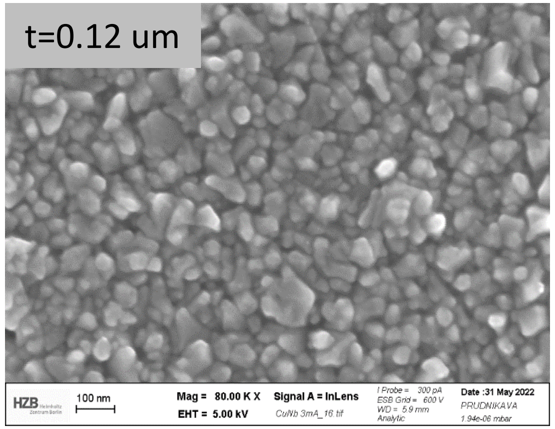
For films (t < *l*/2):

Volume Resistivity ρ_v [Ω·cm] = R [Ω] · RCF · t [cm]

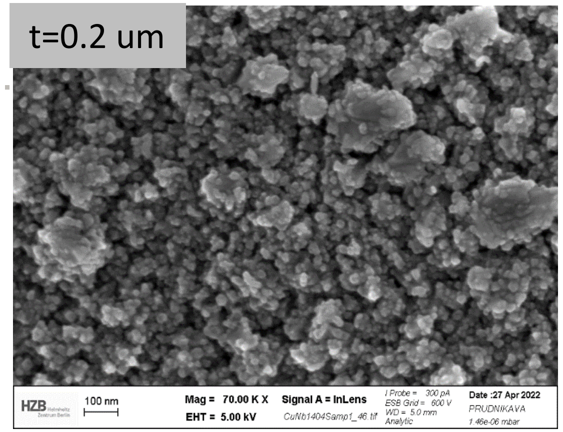
t is the film thickness

Cu/Nb

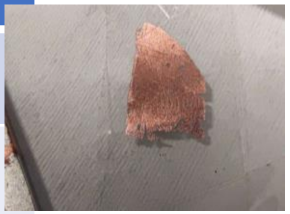
t=0.12 um



t=0.2 um



	I, mA	t, um	U, mV	Resistivity, Ohm*cm
Cu/Nb films, …	10^{-5} -100		0	
Cu and Nb - bulk	10^{-5} -100		0	
Cu/Nb (16.03.22)	100	0.12	0.8 – 2.8	(0.47 – 1.5)*10^{-6}
Cu/Nb (14.04.22)	100	0.2	0.5-2.9	(0.53 – 2.8)*10^{-6}



Cu-film on a tape

Summary and Ongoing Activities

- Procedure for direct plating of Cu onto Nb elaborated (“Cu/Nb-plating”). A thin Cu-film with good adhesion was possible to produce (~200 nm). Patent application was submitted.
- The results of our research were presented at the TTC meeting in Japan.
- Several types of hi-speed Cu-plating baths have been investigated on Cu electrodes (commercial and from the literature) with various additives (“Cu/Cu-plating”). Plating parameters providing the Cu-films at deposition rates up to 40 um/h have been demonstrated (with the decreased amount of CuO_x, 20-25 um/h).

Ongoing:

- experiments on the increasing of the Cu-film thickness.

The thickness of Cu-film on Nb is planned to be used as “a buffer layer”, it’s thickness is to be increased to ~3-5 um. Currently, it reached ~2.1 um but with poor adhesion.

- The exploration of the HF-free etching of niobium will be started in parallel.

Thank you very much
for your attention!