Copper Plating Research Activities for Cryocooler Application

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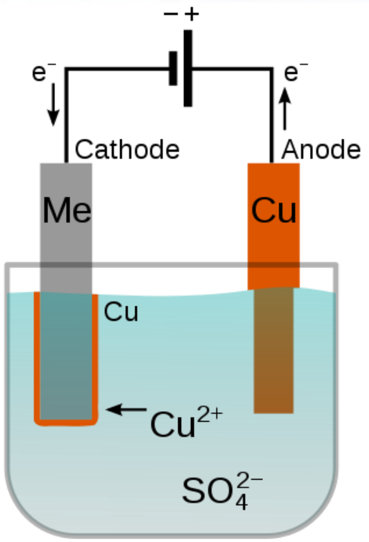
InnovEEA Project Meeting

Wednesday 30 March 2022, 14:00 - 17:00 Europe/Berlin

Copper Electroplating onto Niobium



For Cu-plating water-based acidic electrolytes are commonly used

Issues:

- Nb is an active metal: galvanic displacement reaction

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

Cu-film adhesion problem

Previously explored (reported in November):

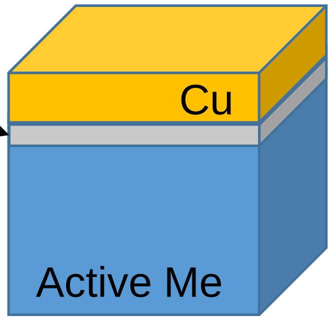
- commercial acidic electrolytes for steel (uChem)
- several alkaline electrolytes for steel

⇒ no good Cu-adhesion on Nb

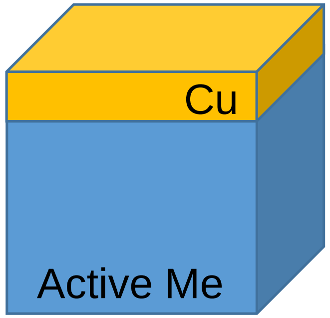
⇒ modification of electrolyte composition, plating parameters…

Cu-plating onto Active Metal

“less active” Me (Ni, Sn…)



Alkaline Electrolyte (worked for steel)



SEM

Cu film

Cu film

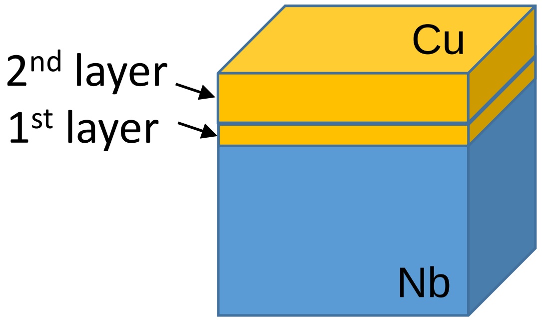
Cu/Nb Film: Liquid Nitrogen Test

Cu film passed
- liquid nitrogen test
- scotch-tape test

EDX

Cu/Nb Film: XRD

Cu/Nb Film



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-plaiting with Acidic Electrolyte

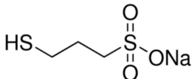
Electrolytes:

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

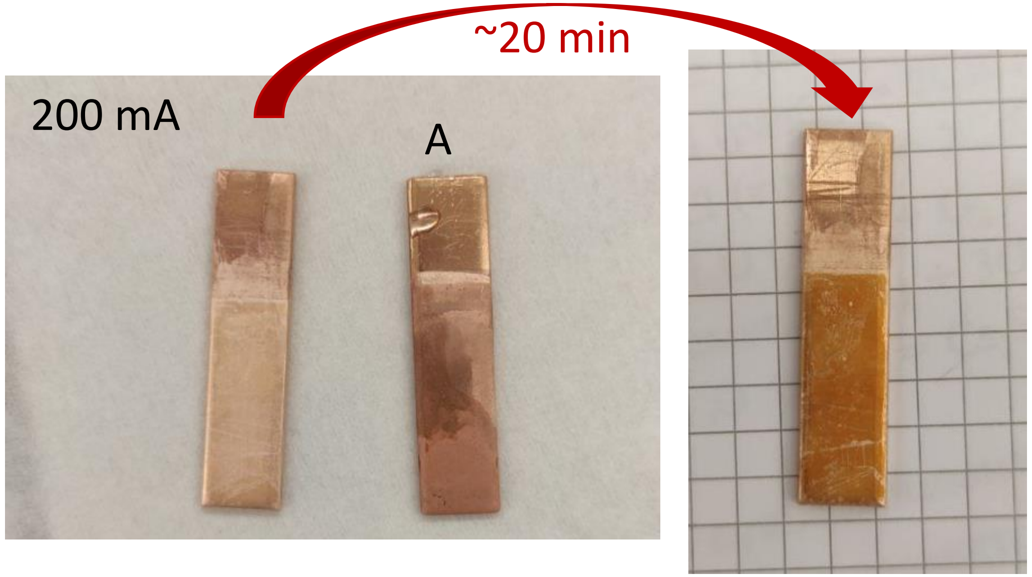
What was Studied:

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)

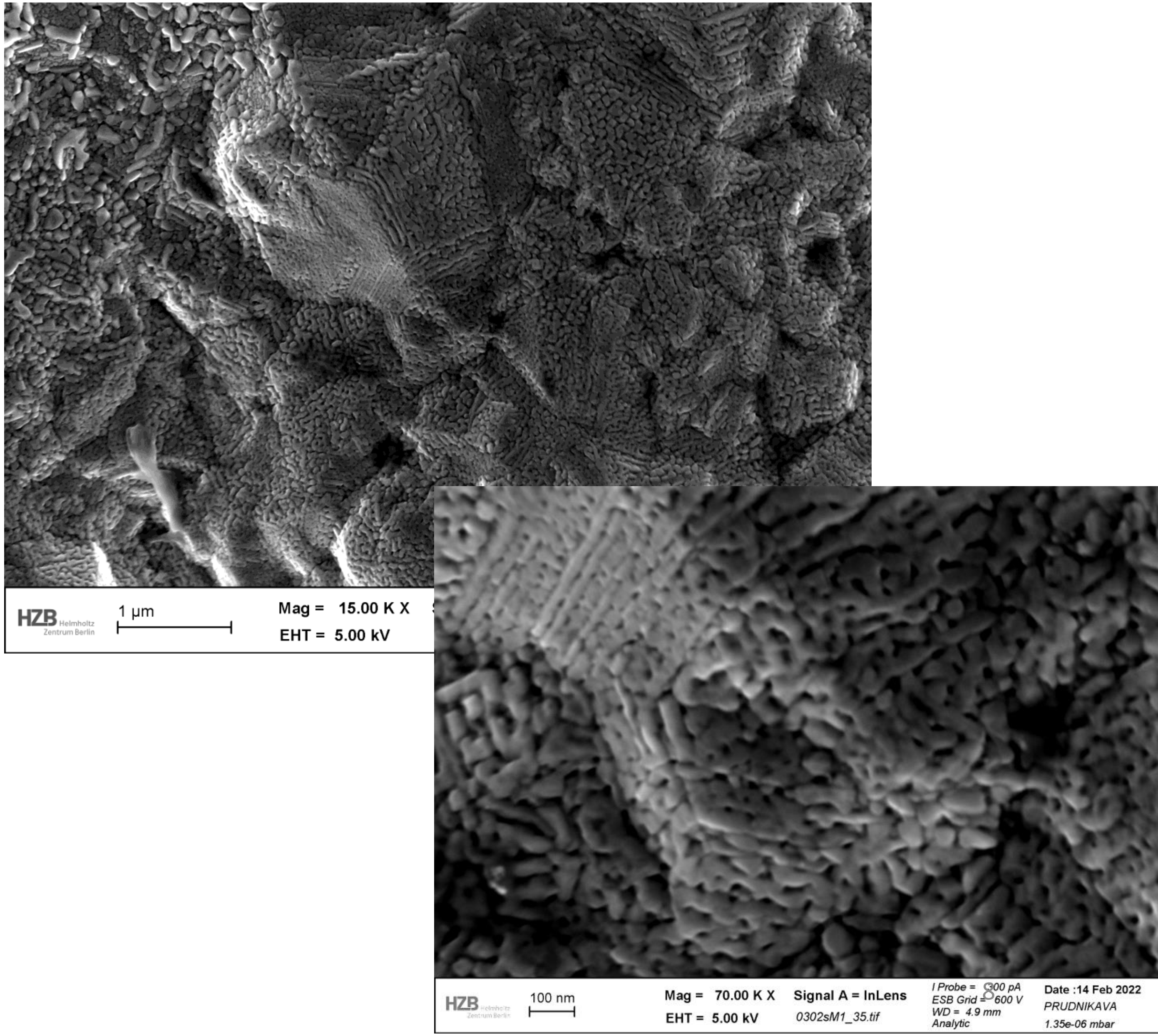
*MPS: Sodium 3-mercapto-1-propanesulfonate



Testing Acidic Electrolytes (1): Cu plating onto Copper



Visible film oxidation



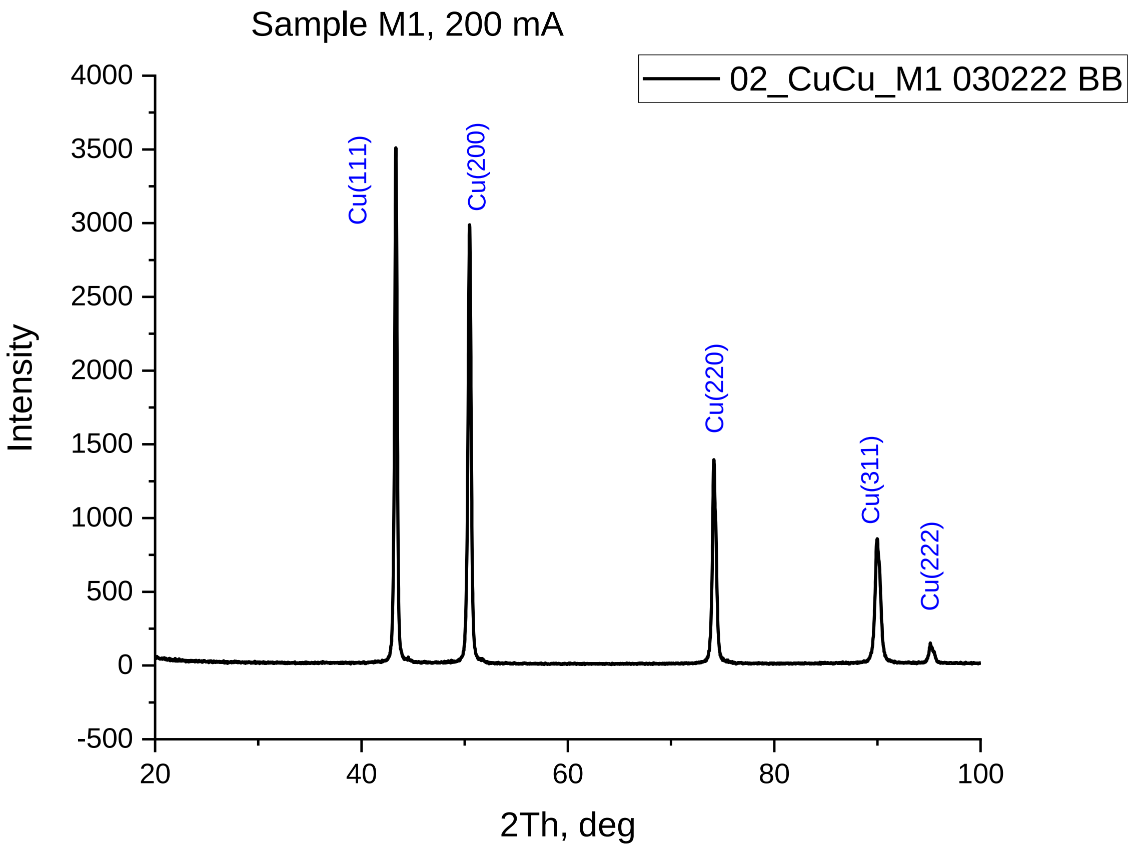
Electrolyte:

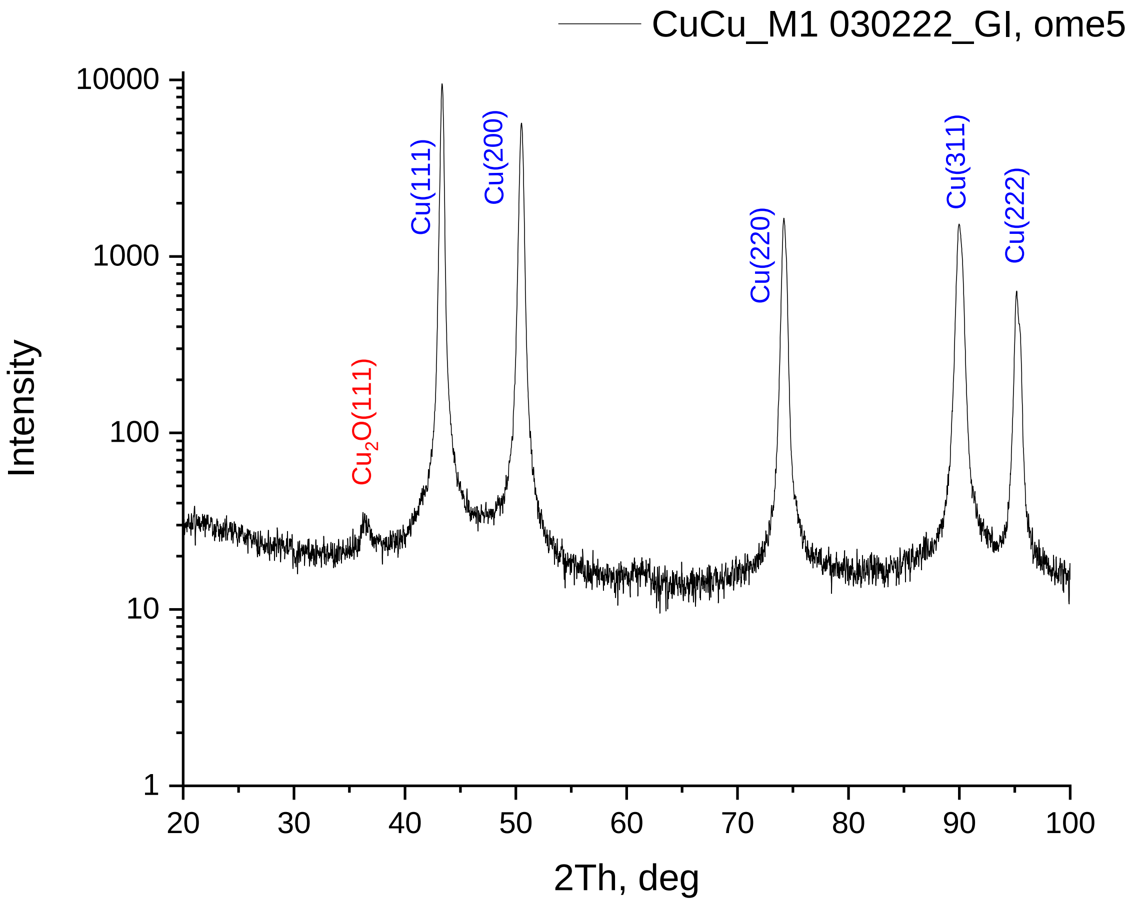
$CuSO_4 \cdot 5H_2O$
H_2SO_4
H_2O

Plating parameters:

j=2.7 A/dm^2
T=27°C
t=5 min

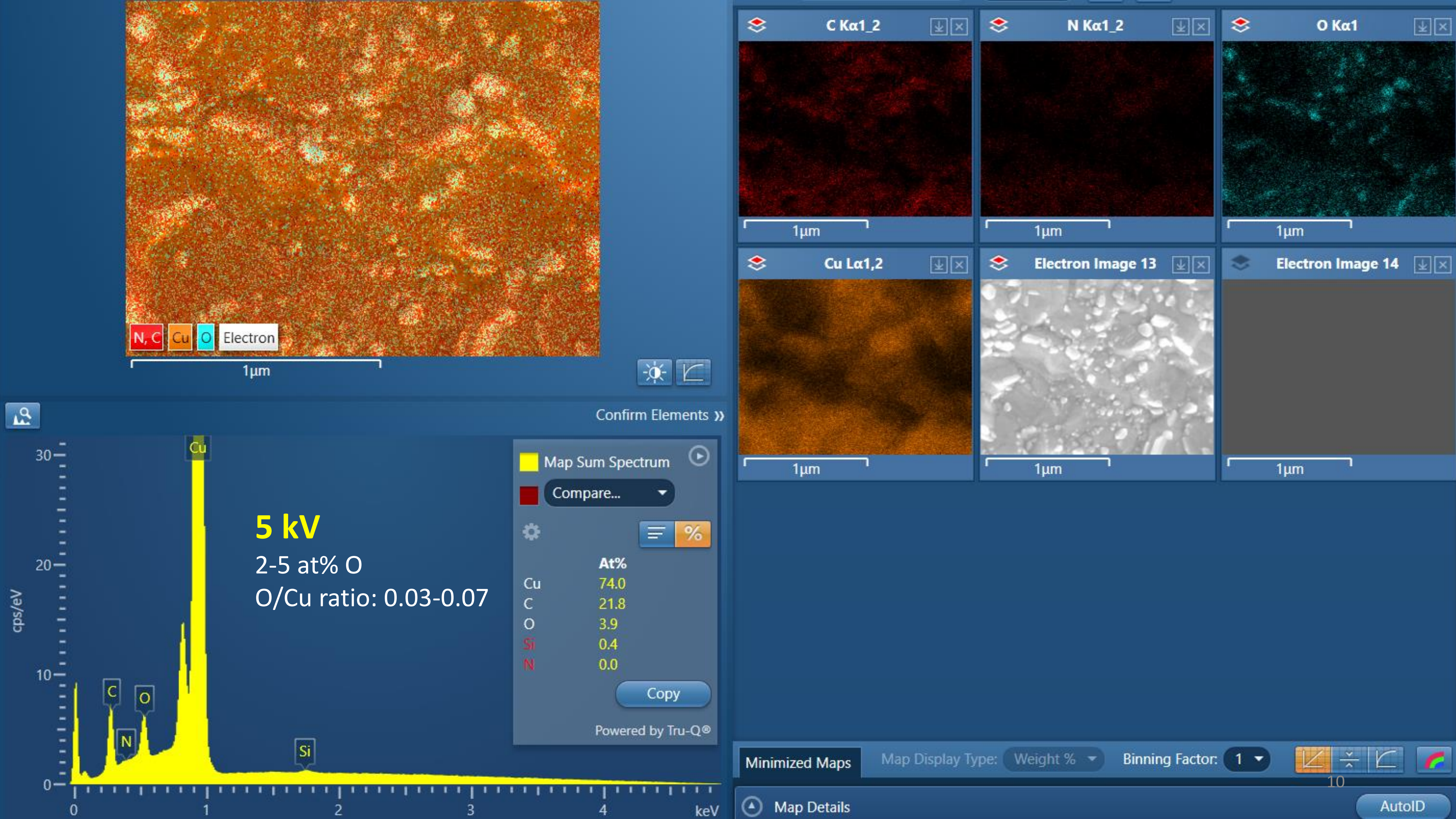
Testing Acidic Electrolytes (1): Cu plating onto Copper





Cu(111), Cu(200) are the preferential orientations

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


N, C
Cu
O
Electron
1µm
Confirm Elements »
C Kα1_2
N Kα1_2
O Kα1
Cu Lα1,2
Electron Image 13
Electron Image 14
1µm
Map Sum Spectrum
Compare...
At%
Cu 74.0
C 21.8
O 3.9
Si 0.4
N 0.0
Copy
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5 kV
2-5 at% O
O/Cu ratio: 0.03-0.07
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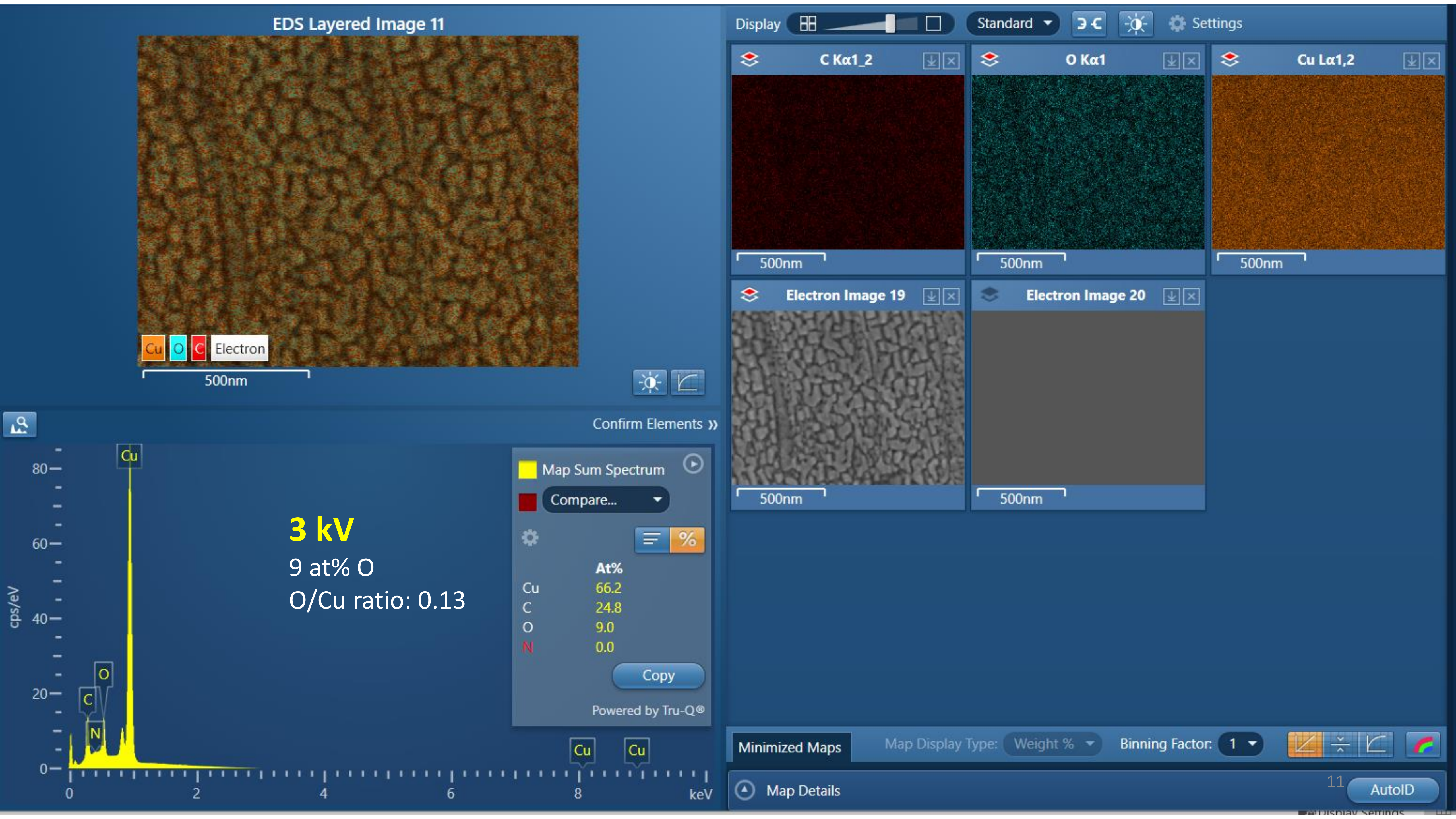
EDS Layered Image 11
Cu O C Electron
500nm
Display
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Settings
C Kα1_2
O Kα1
Cu Lα1,2
Electron Image 19
Electron Image 20
Confirm Elements »
Map Sum Spectrum
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At%
Cu 66.2
C 24.8
O 9.0
N 0.0
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Testing Acidic Electrolytes (1): Cu plating onto Copper

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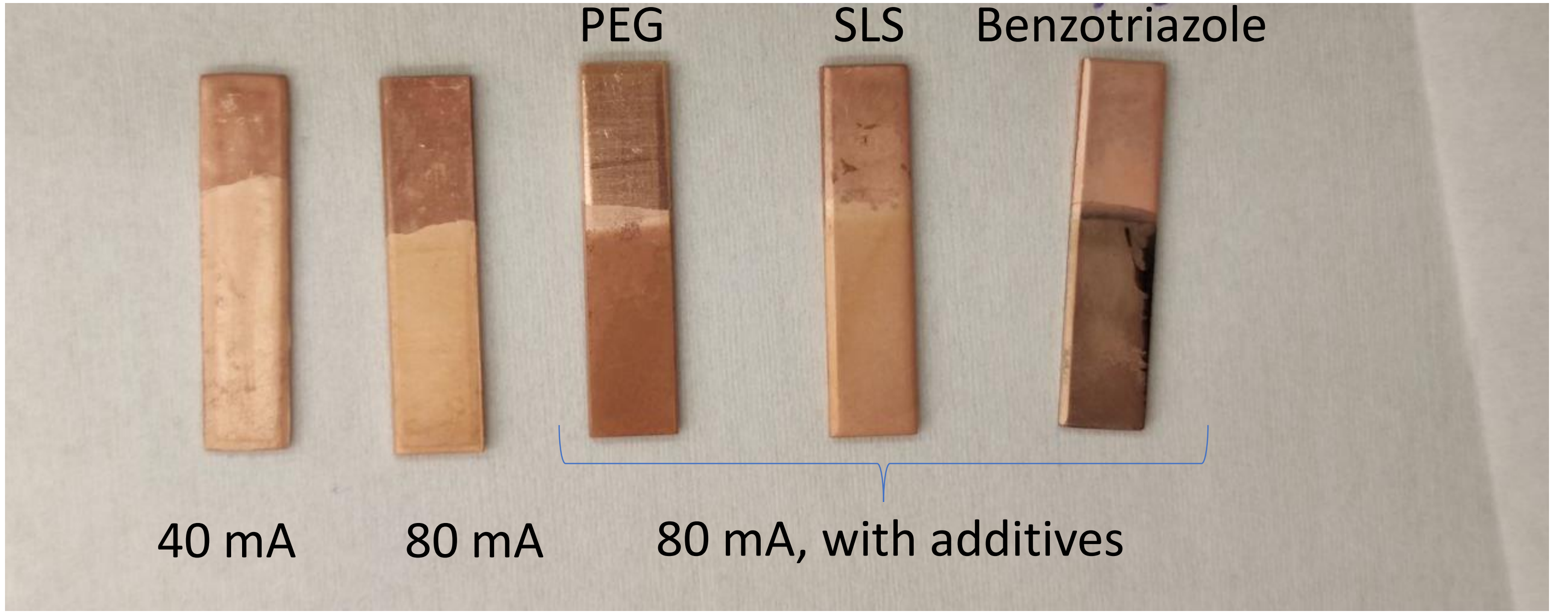

	I, mA	j, mA/cm^2	deposition rate, um/h	at% O at 5kV	O/Cu at 5kV	Cryst. Size Cu(111), nm
$CuSO_4$+H_2SO_4	200	27.8	-	3.9	0.05	30.18
$CuSO_4$+H_2SO_4	40	5.7	7.9	-	-	-
$CuSO_4$+H_2SO_4	80	13.2	17.4	4.5	0.06	32.76
$CuSO_4$+H_2SO_4+PEG	80	13.2	17.5	5.5-5.9	0.07-0.08	29.86
$CuSO_4$+H_2SO_4+SLS	80	13.2	17.4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

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
- sodium lauryl sulphate
- benzotriazole

Testing Acidic Electrolytes (1): Cu plating onto Copper

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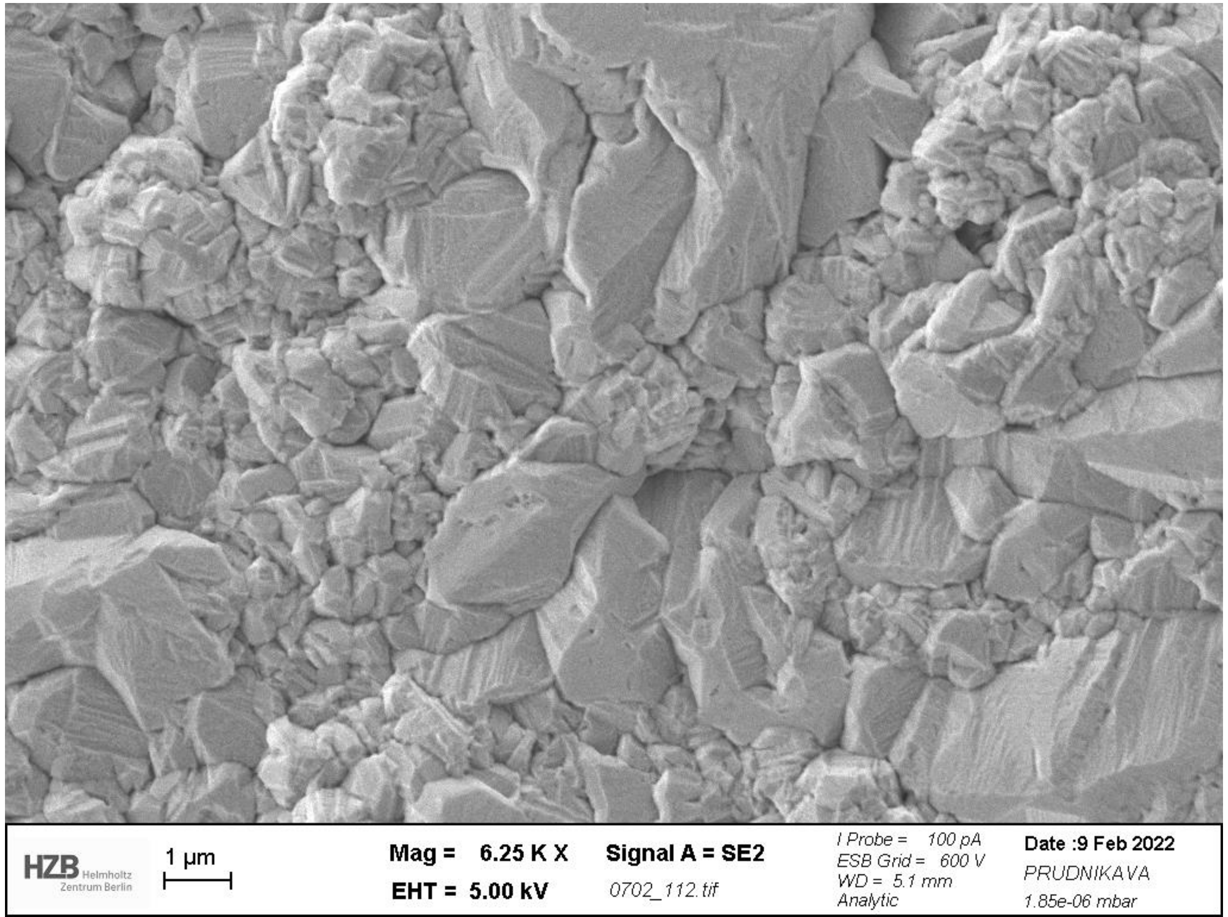
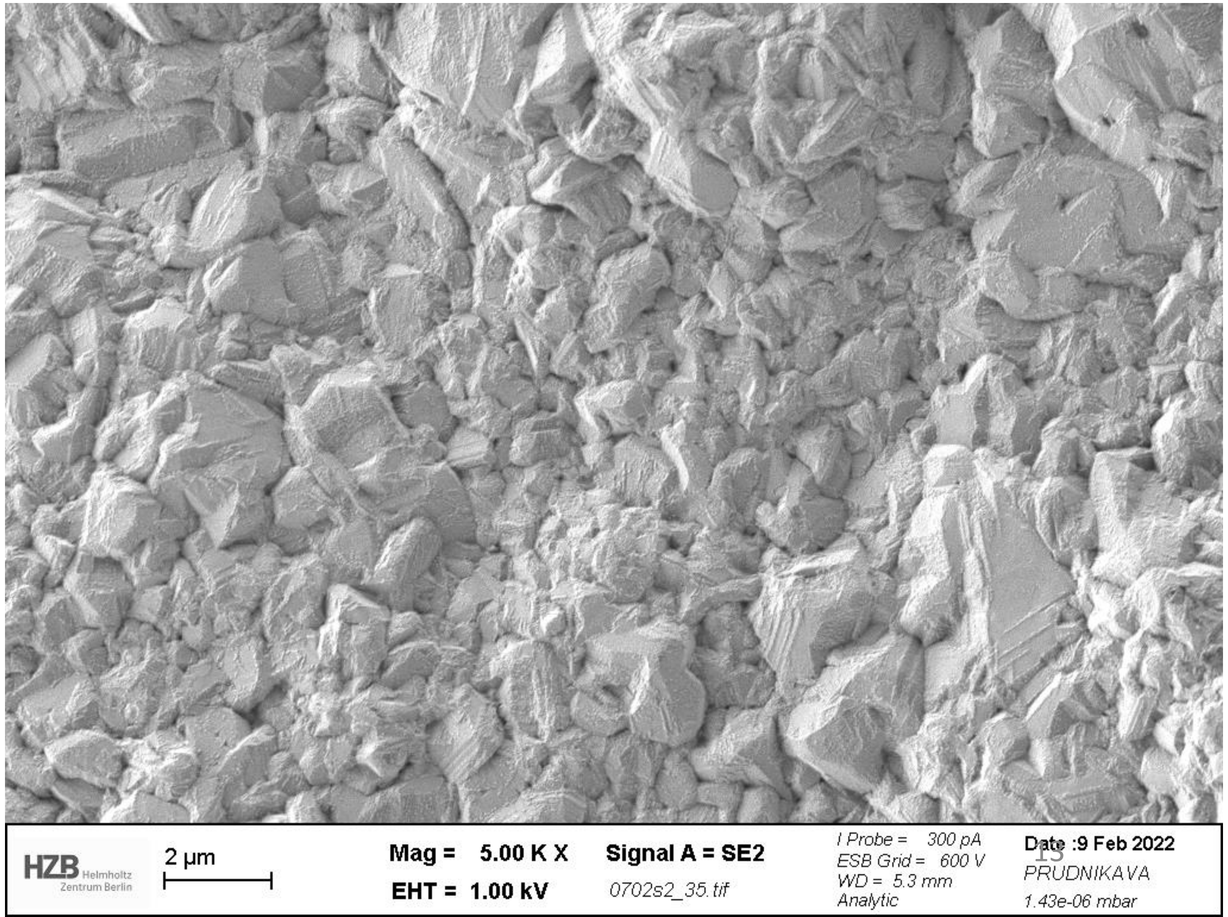
Cu-film morphology: General view (SEM)

Current density effect

40 mA

80 mA





Testing Acidic Electrolytes (1): Cu plating onto Copper

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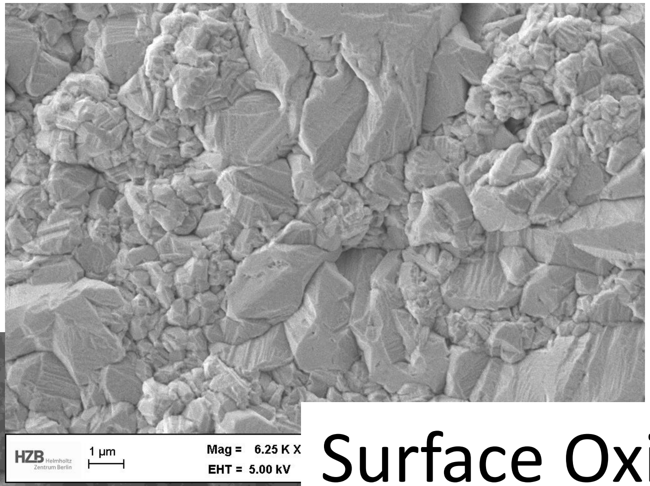
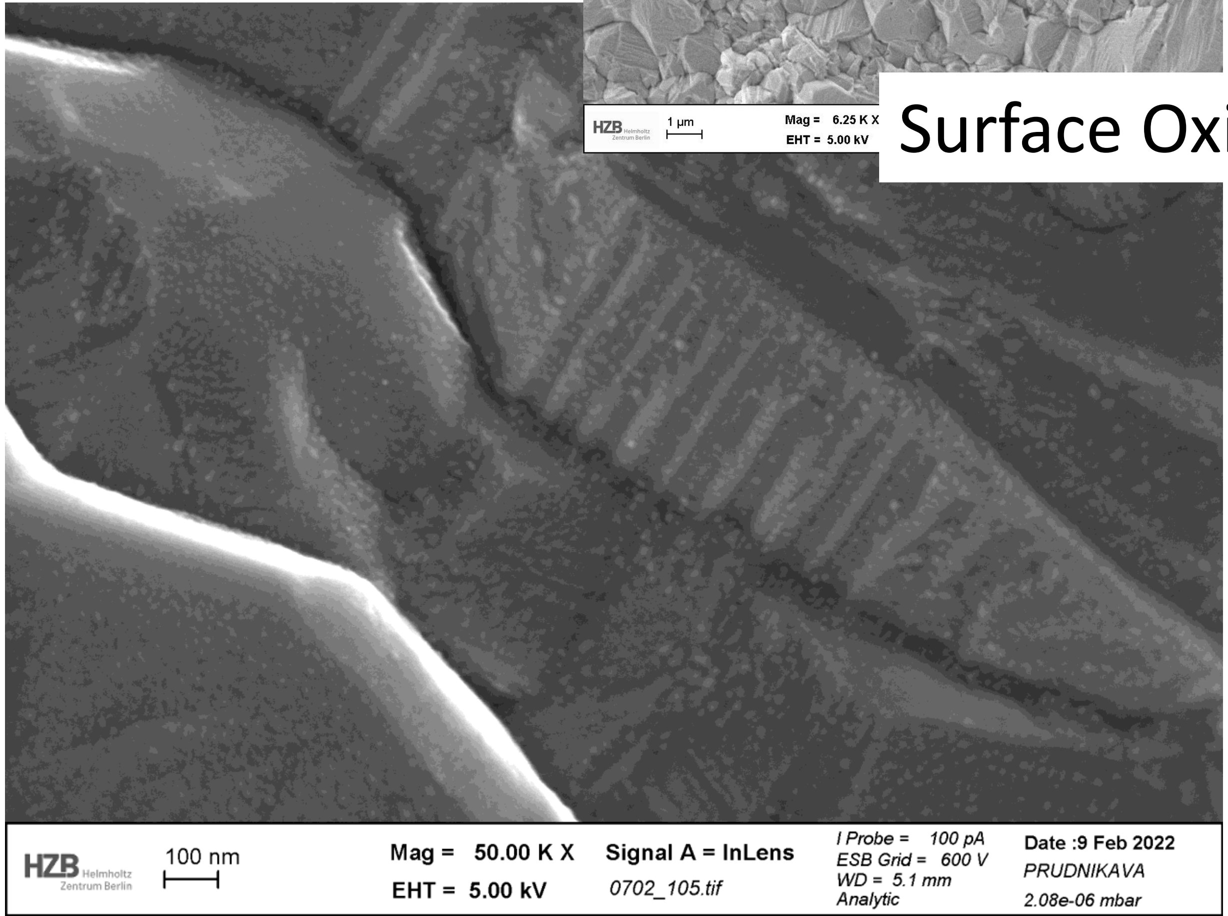
Higher current => larger Cu_2O precipitates

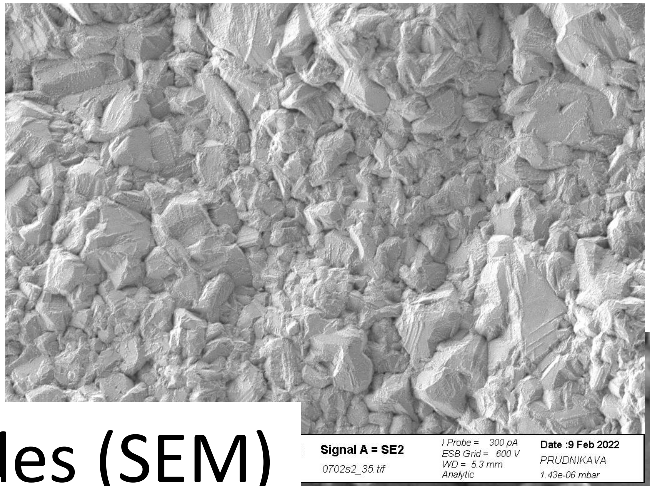
Surface Oxides (SEM)

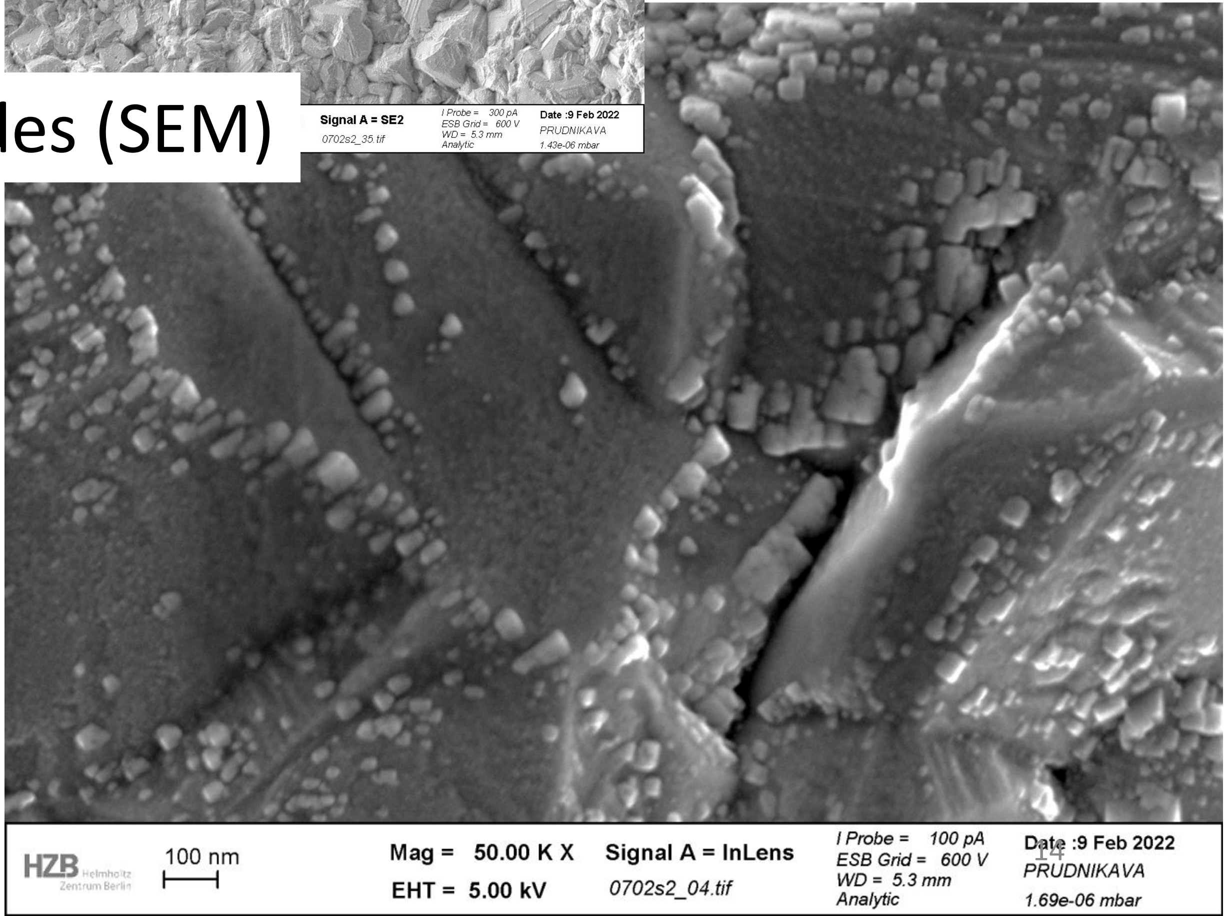
40 mA





80 mA



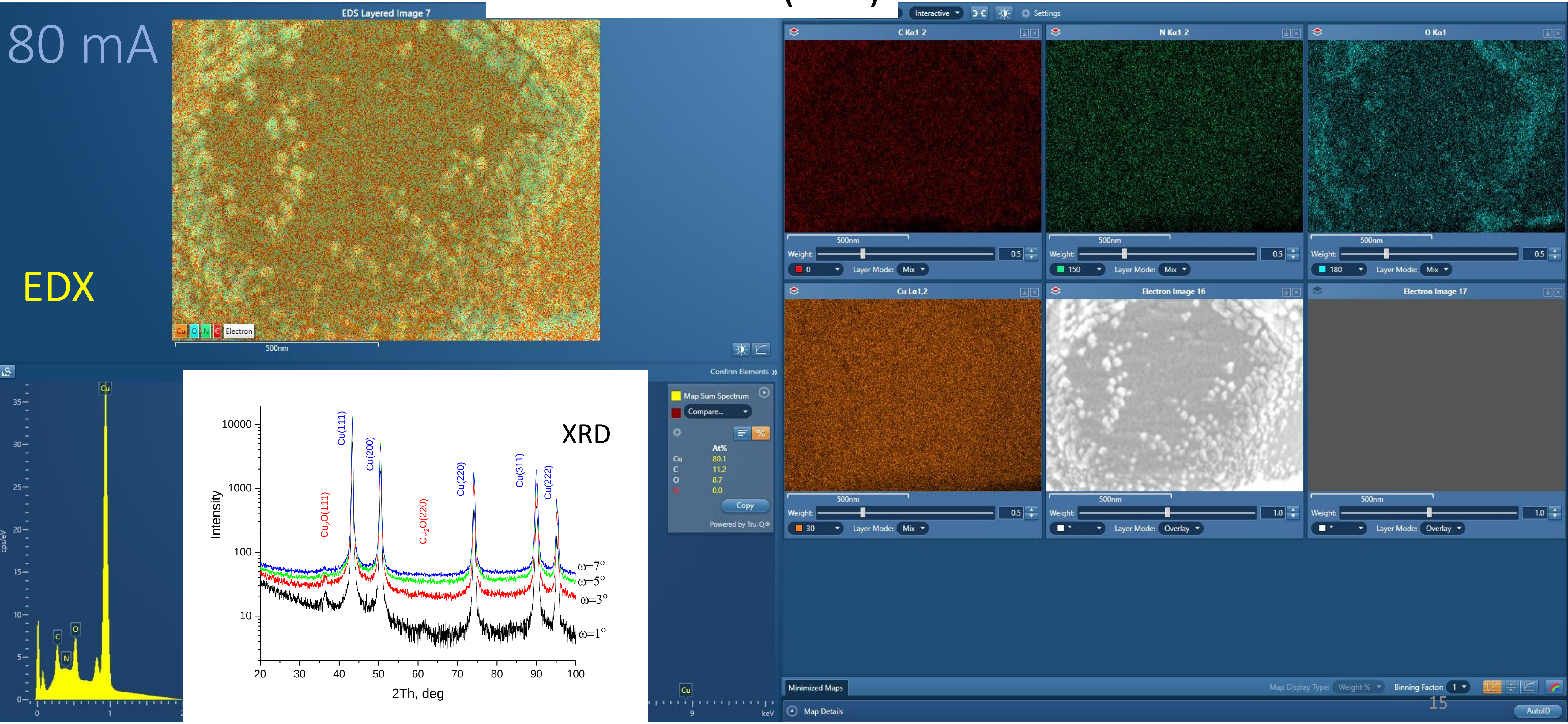


Testing Acidic Electrolytes (2): Cu plating onto Copper

Surface Oxides (EDX)

80 mA

EDX



Testing Acidic Electrolytes (1): Cu plating onto Copper

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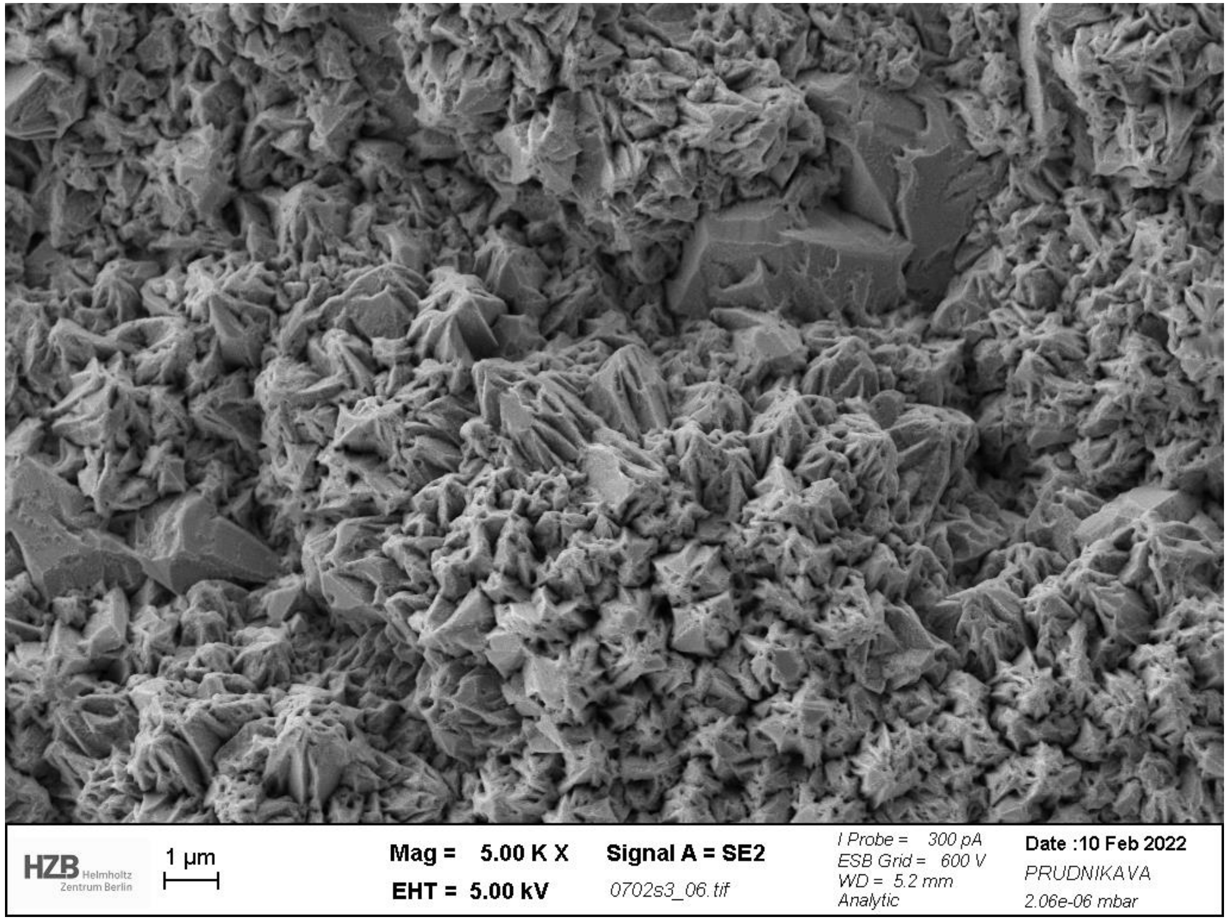
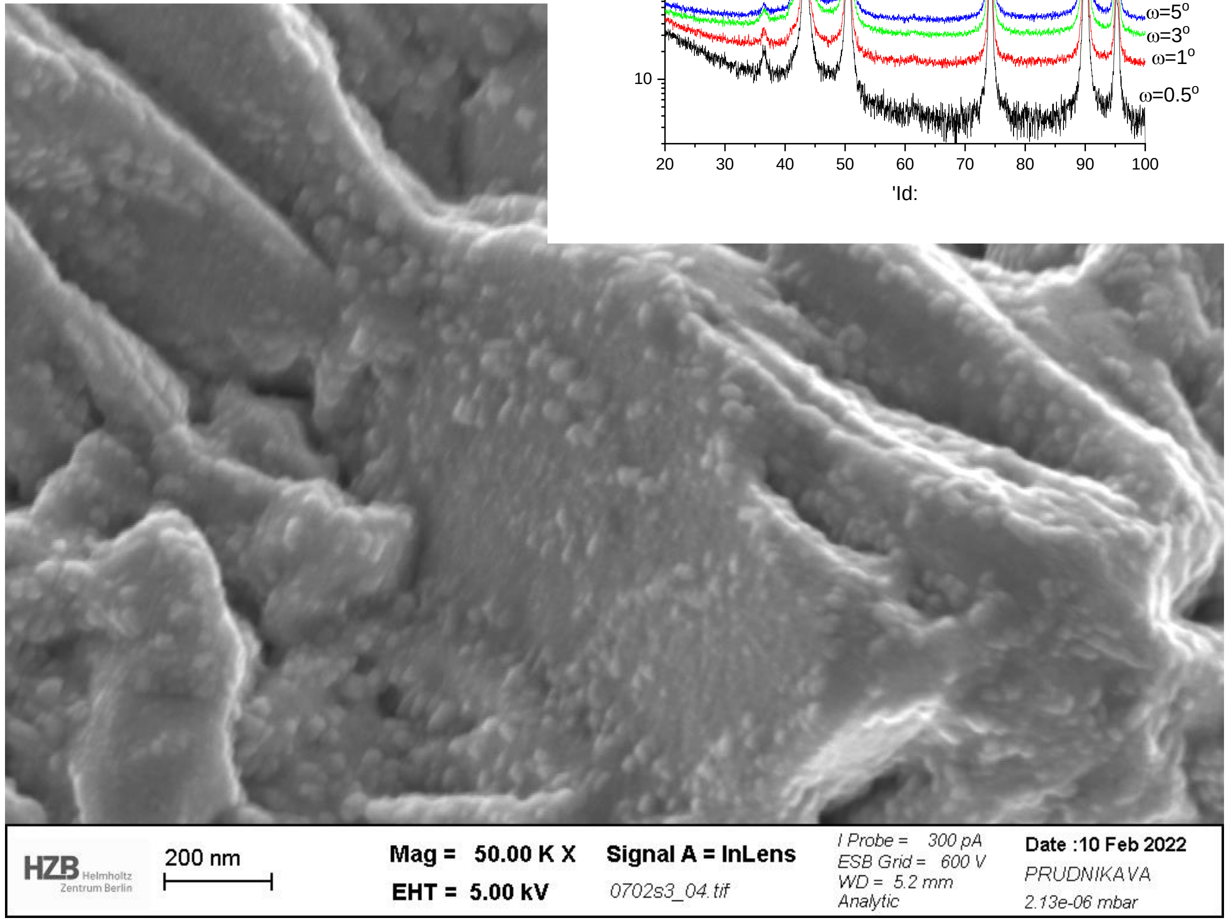
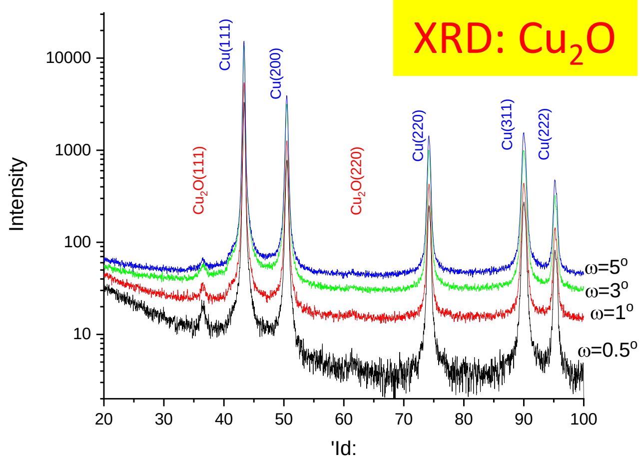
$C_{2n}H_{4n+2}O_{n+1}$

with Polyethylene glycol

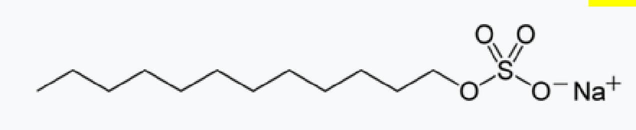




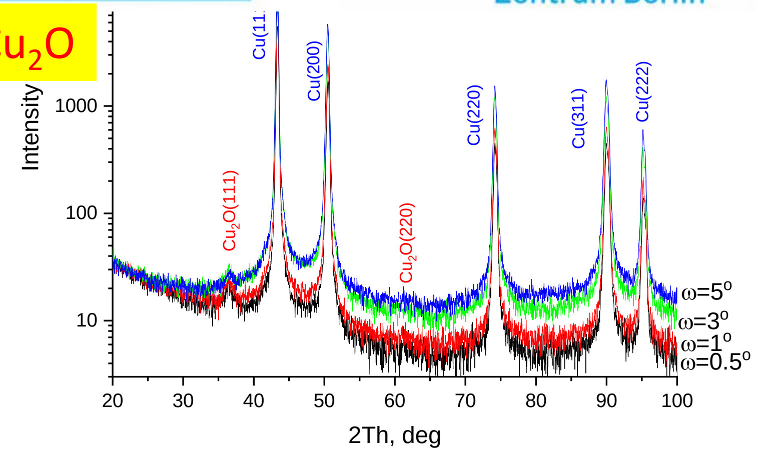


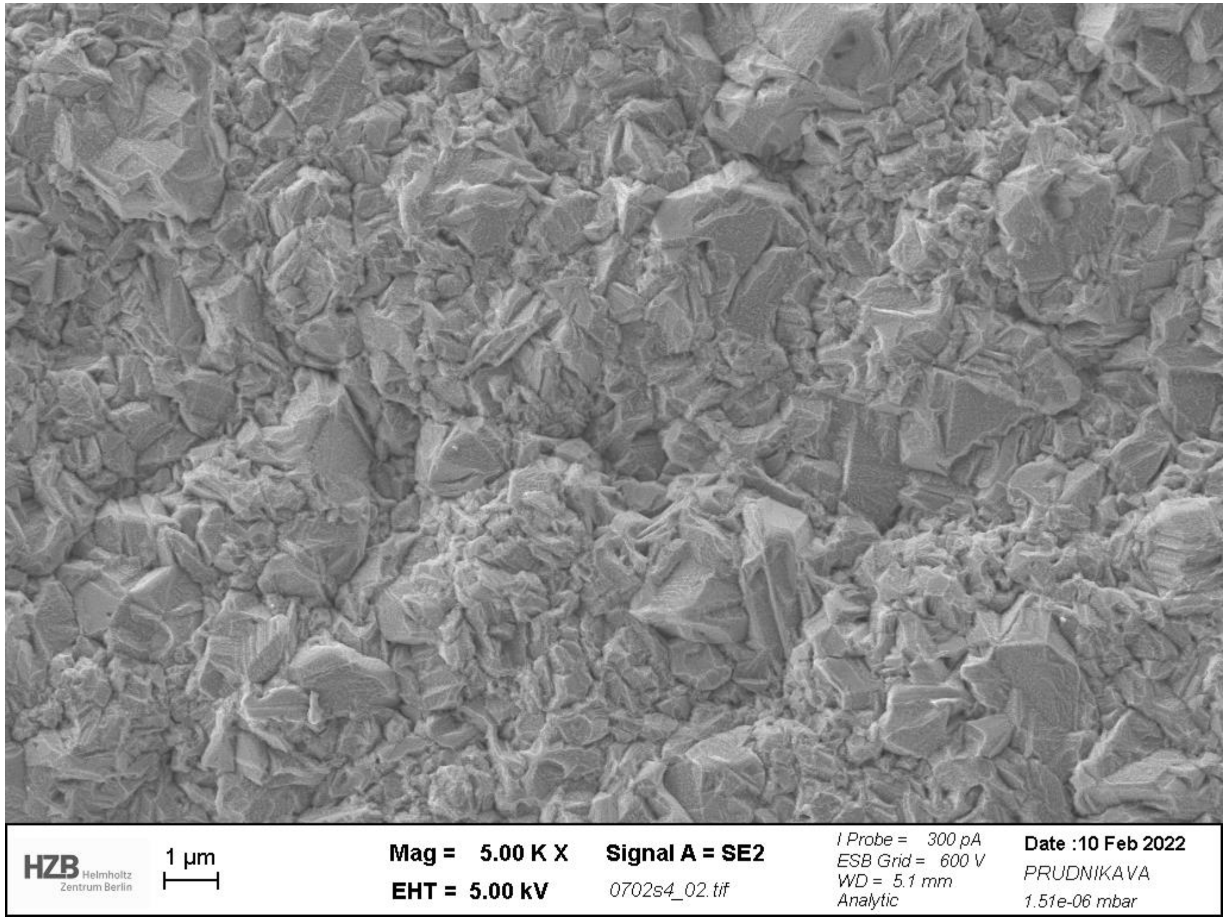
Testing Acidic Electrolytes (1): Cu plating onto Copper

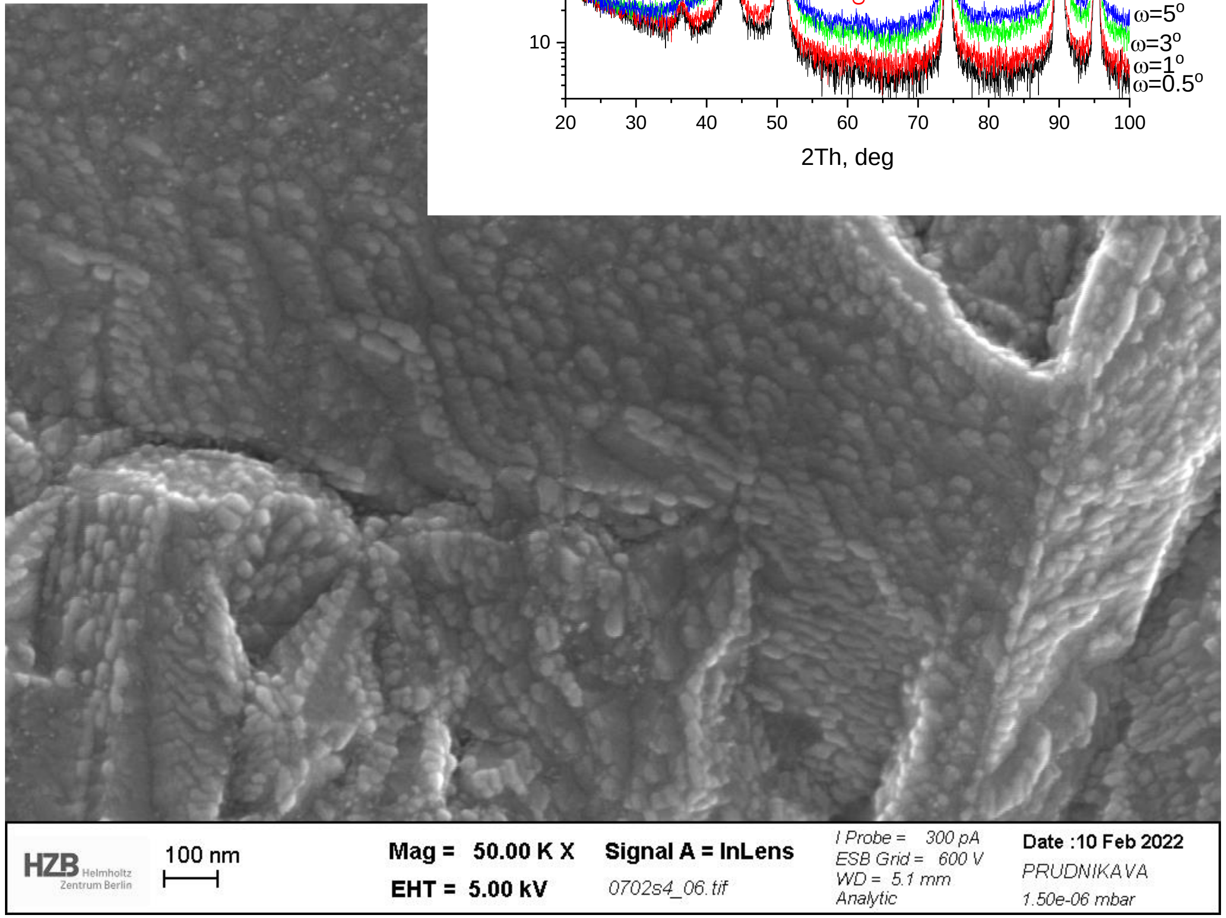
with Sodium Lauryl Sulphate



XRD: Cu_2O

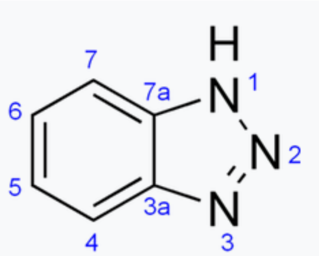


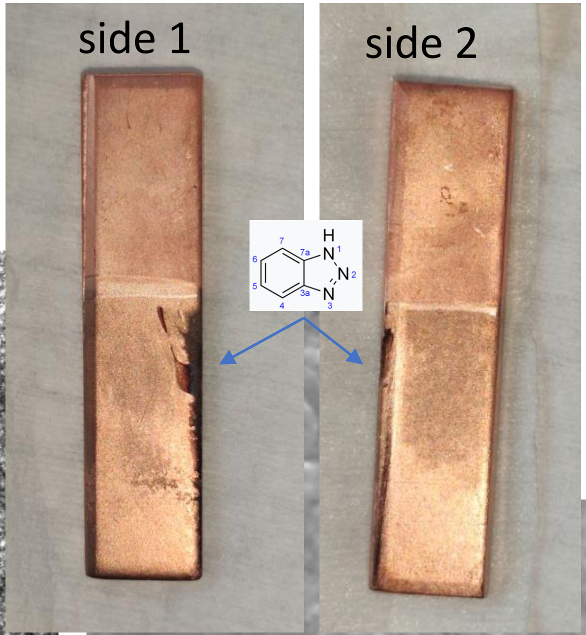


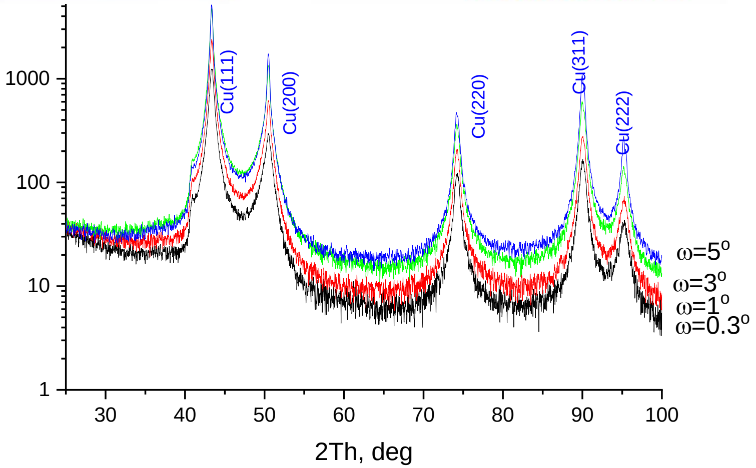


Testing Acidic Electrolytes (1): Cu plating onto Copper

with benzotriazole

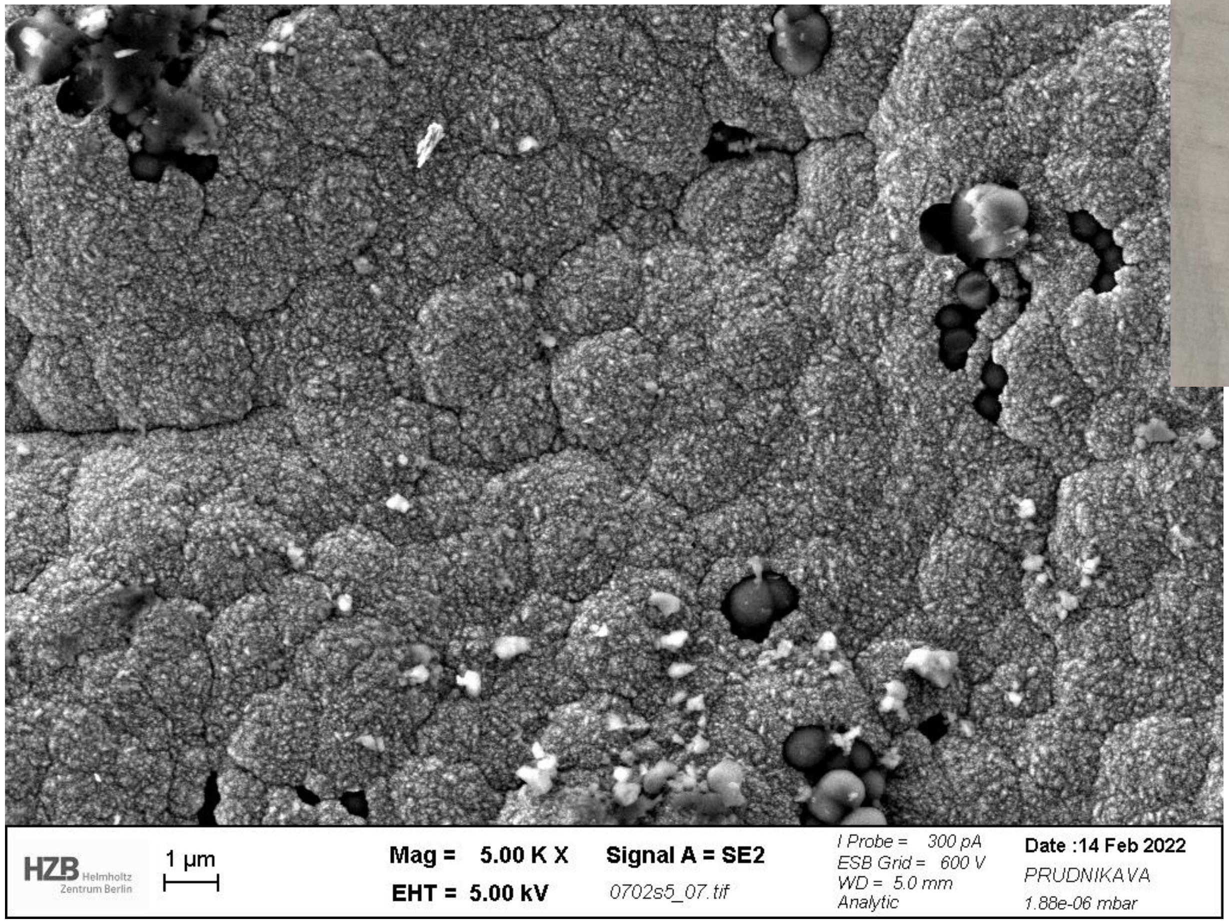


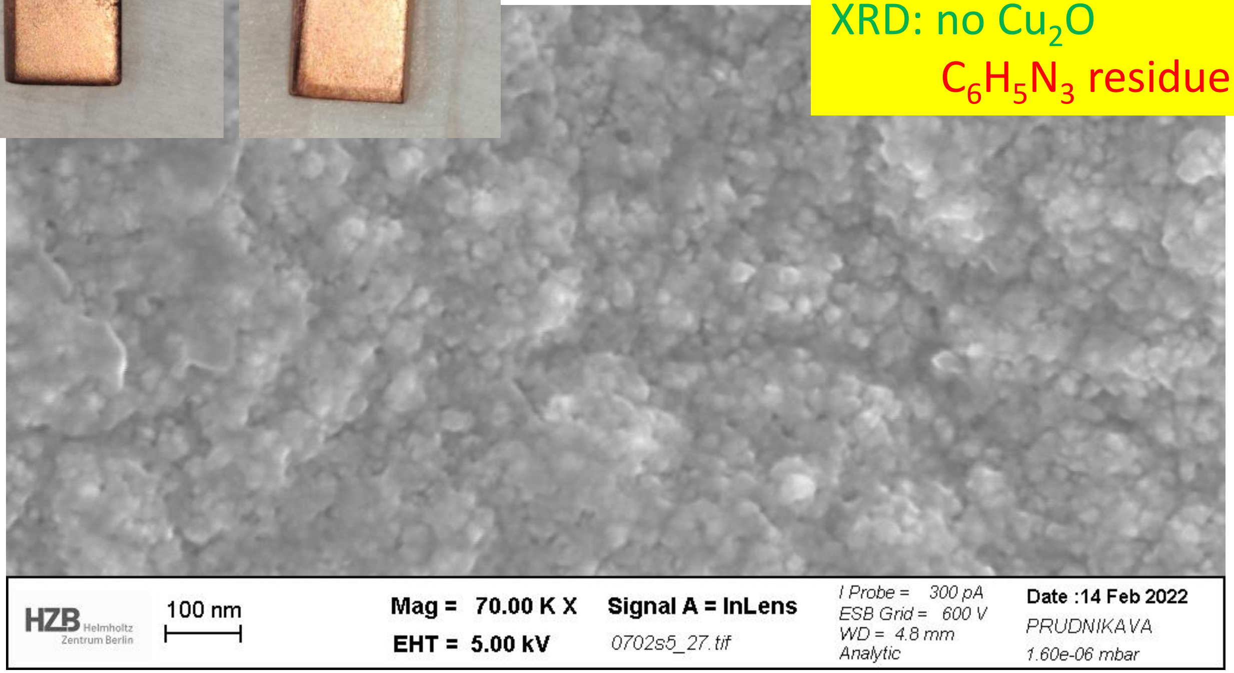




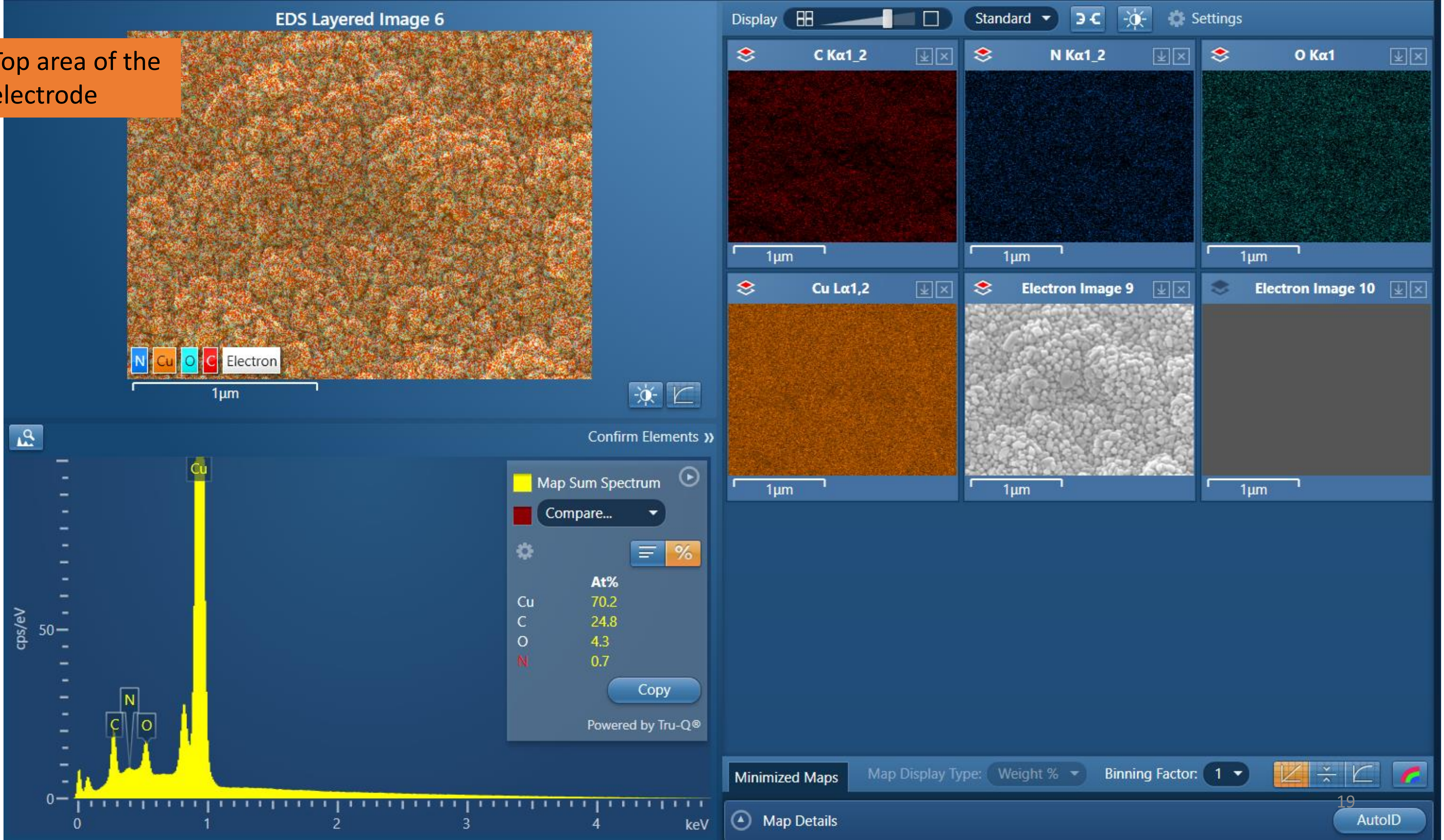
XRD: no Cu_2O

$C_6H_5N_3$ residue

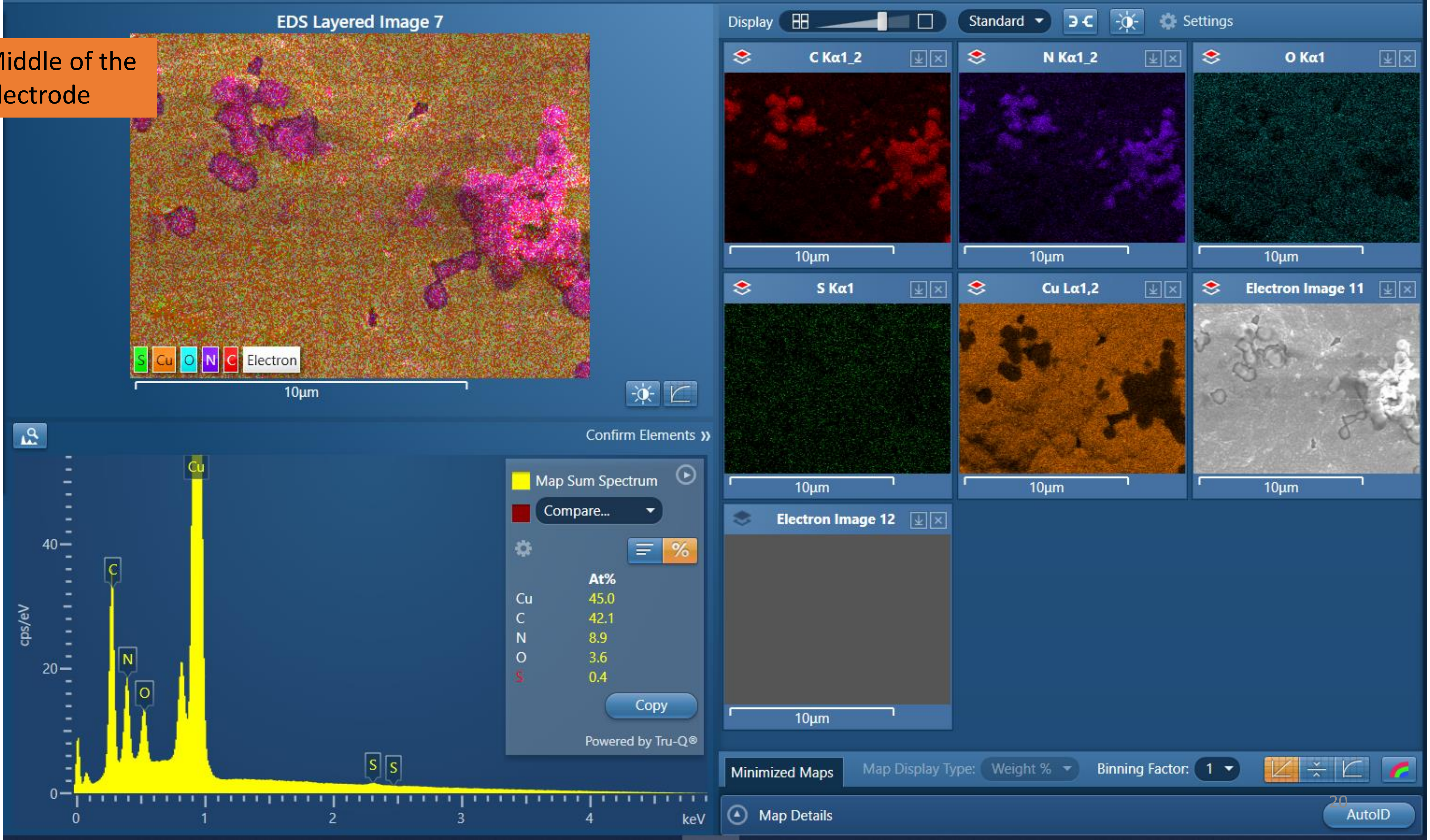




Top area of the electrode



Middle of the electrode



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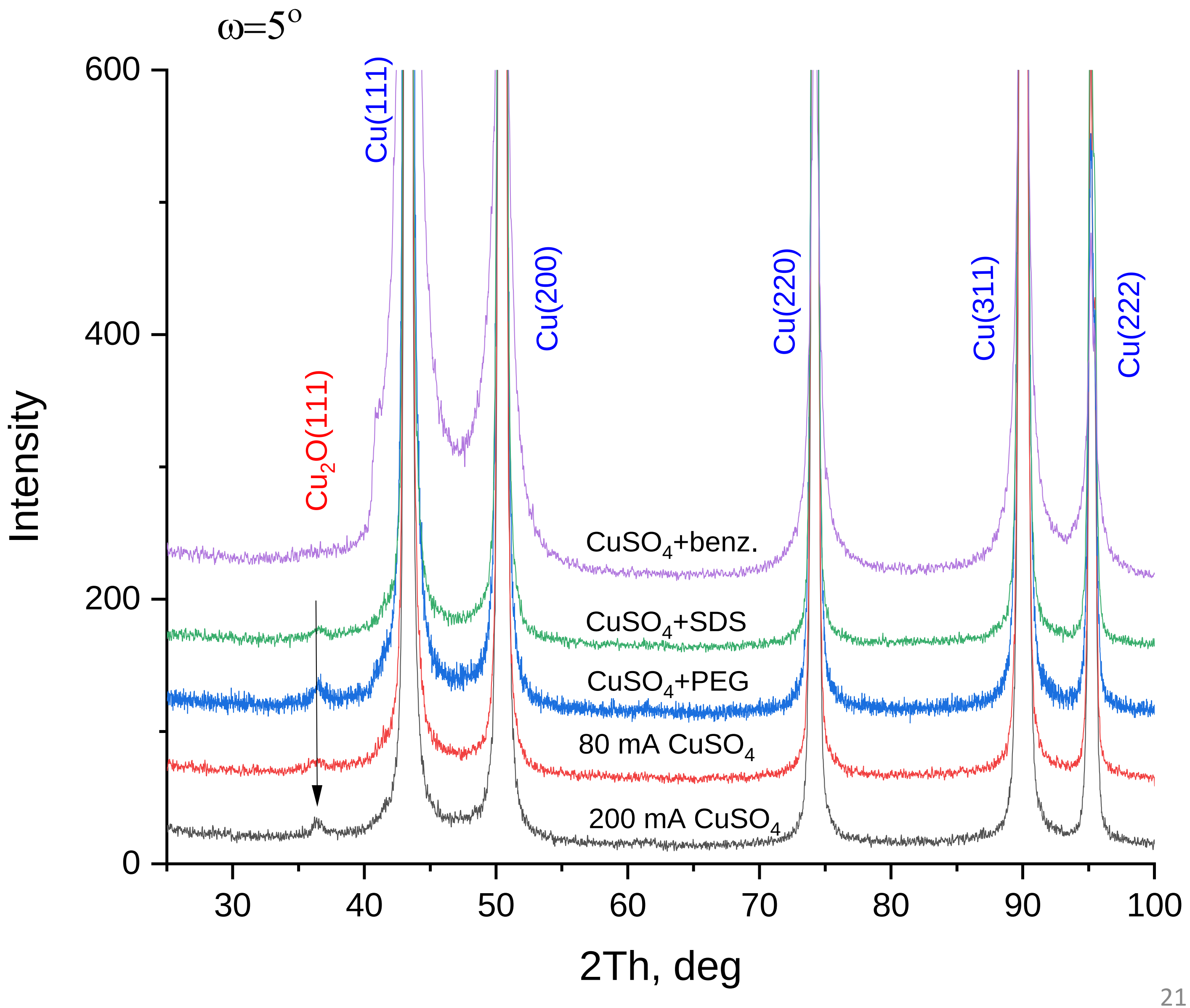
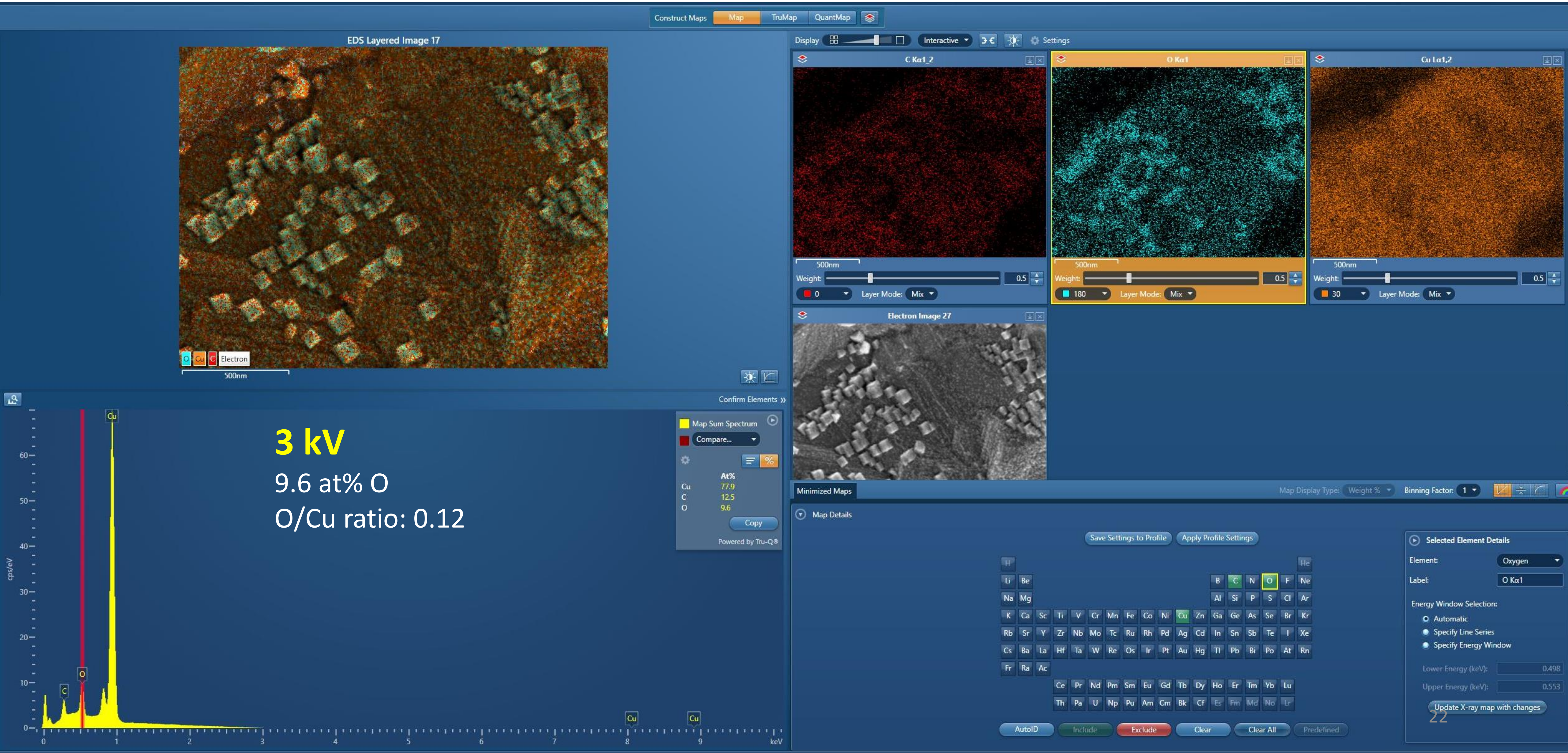
XRD

comparison at ω=5°

only benzotriazole additive affects the Cu_2O formation



Cu electrode surface after chemical etching

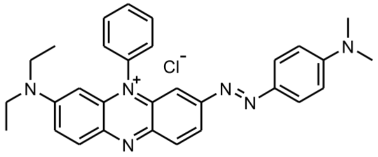


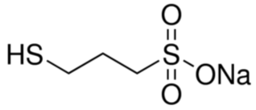
Testing Acidic Electrolytes (2): Cu plating onto Copper

Electrolyte:

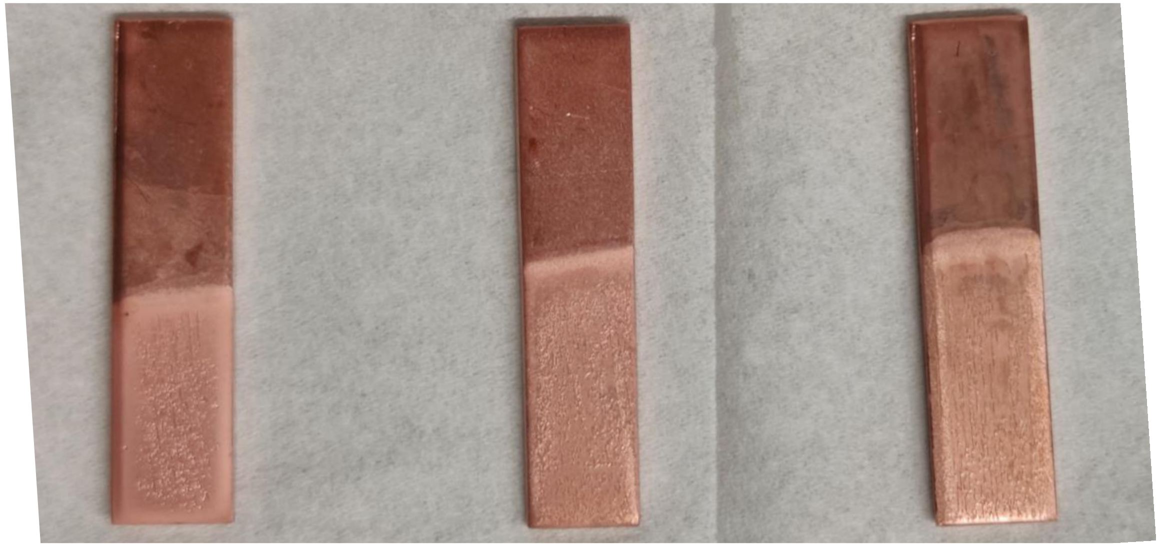
$CuSO_4 \cdot 5H_2O$
H_2SO_4
H_2O
additives:

- NaCl
- Janus Green B
- MPS





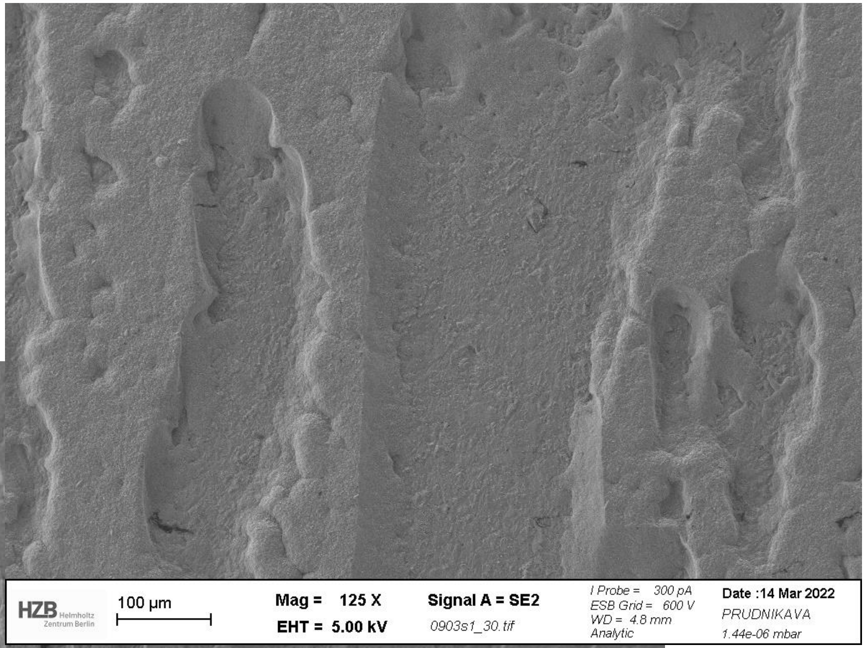
Sample 1 Sample 2 Sample 3

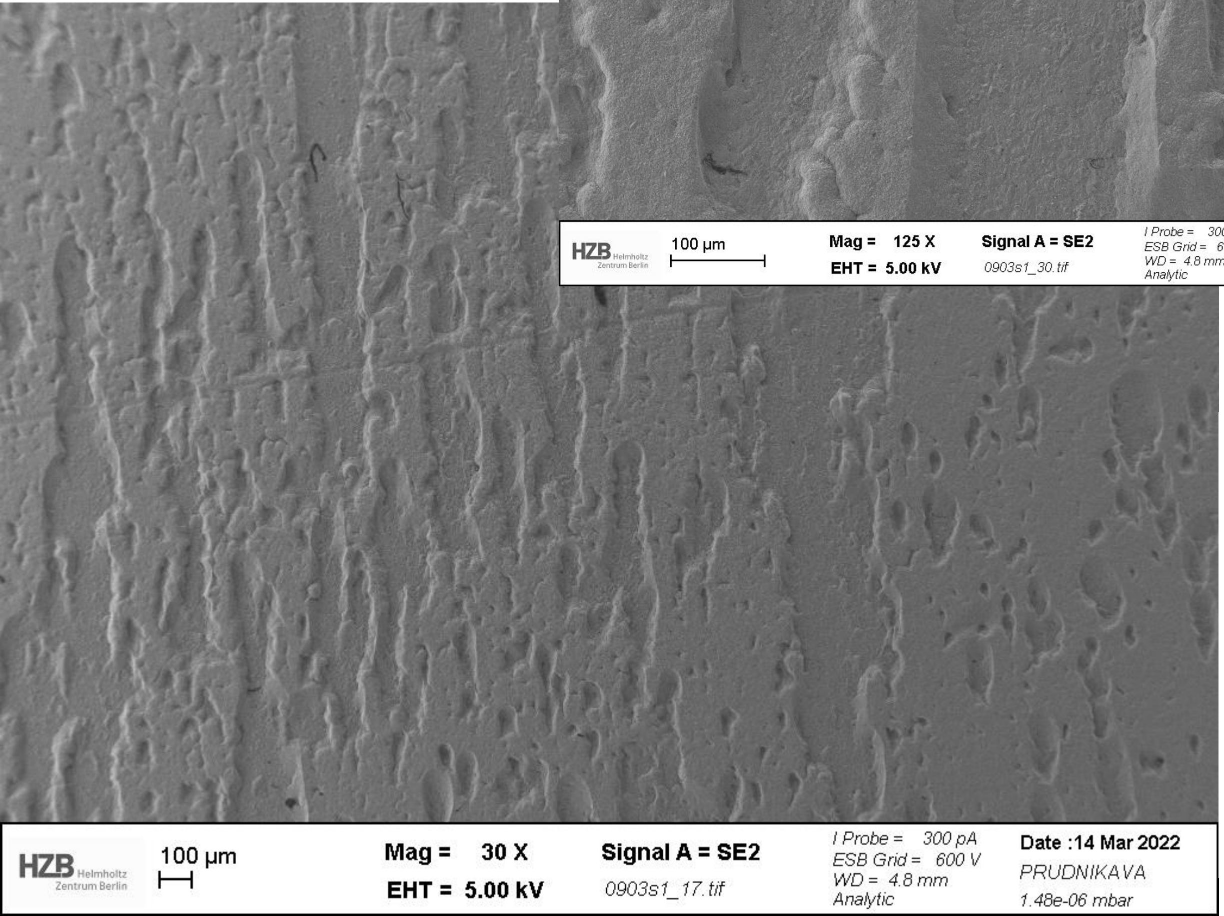


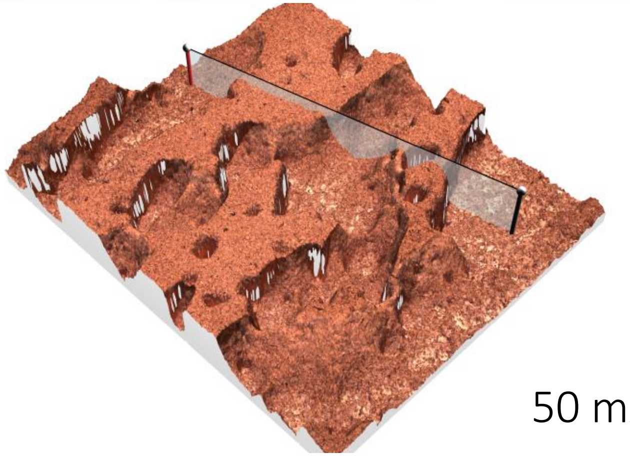
	I, mA	j, mA/cm²	deposition rate, um/h	at% O at 5kV	O/Cu at 5kV	Cryst. Size Cu(111), nm
$CuSO_4$+H_2SO_4+NaCl +Janus Green B	80	17.6	24.5	2.1-3.6	0.02-0.04	29.64
$CuSO_4$+H_2SO_4+NaCl +Janus Green B	50	13.2	13.5	2.7	0.03	33.28
$CuSO_4$+H_2SO_4+NaCl +Janus Green B+MPS	50	13.2	12.9	3.5-4	0.04-0.05	33.40

Testing Acidic Electrolytes (2): Cu plating onto Copper

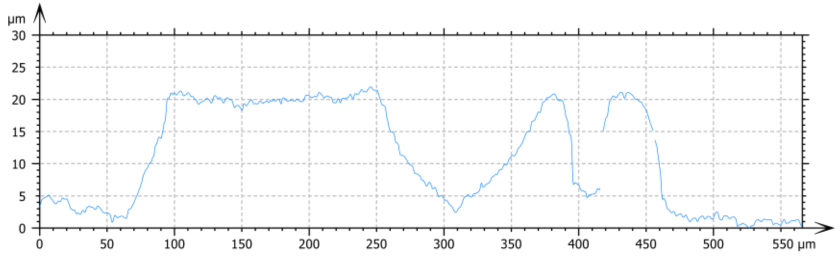
80 mA





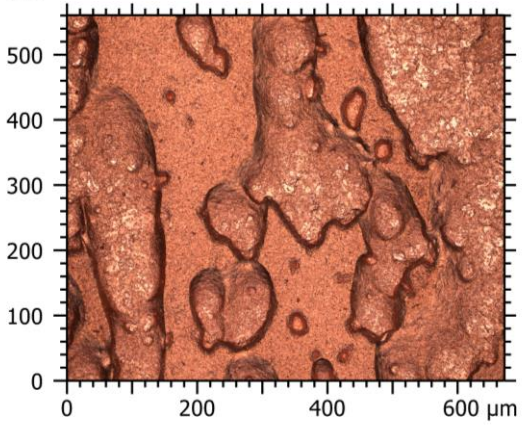


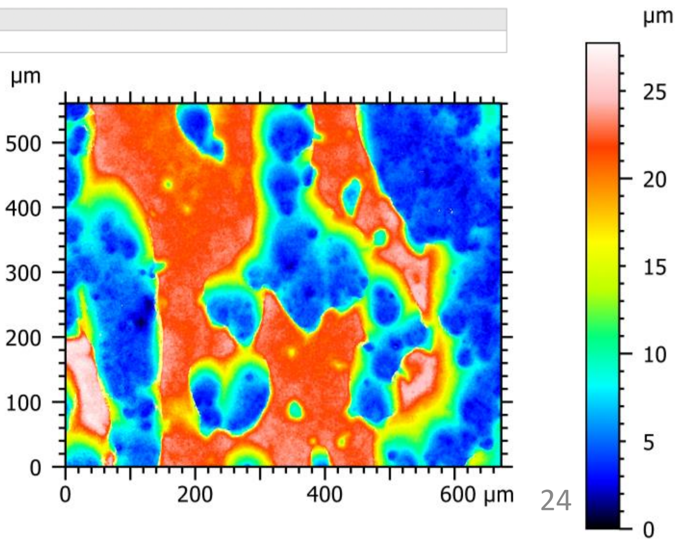
50 mA



Parameters	Value	Unit
Length	566.0	µm

x 20





Testing Acidic Electrolytes (2): Cu plating onto Copper

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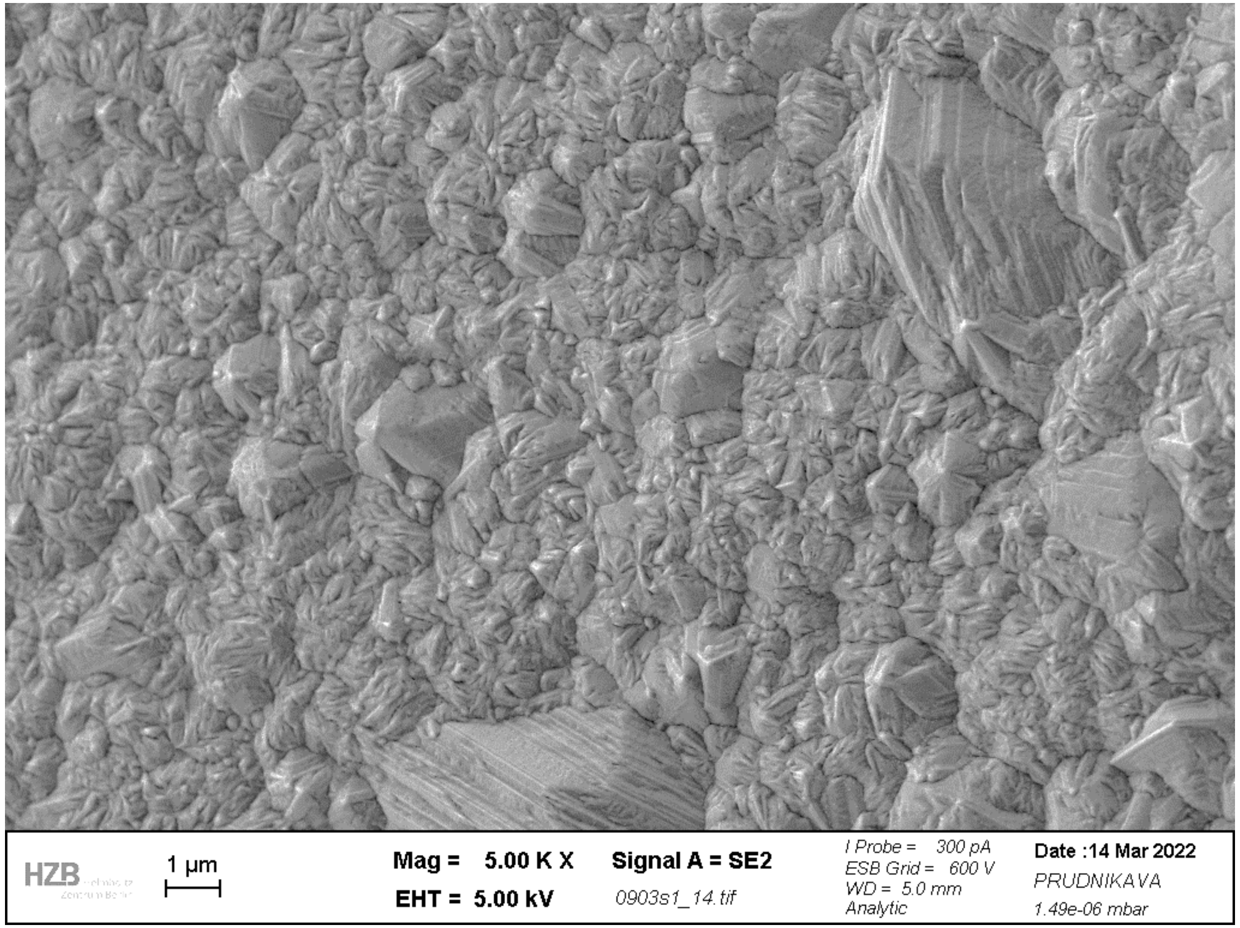
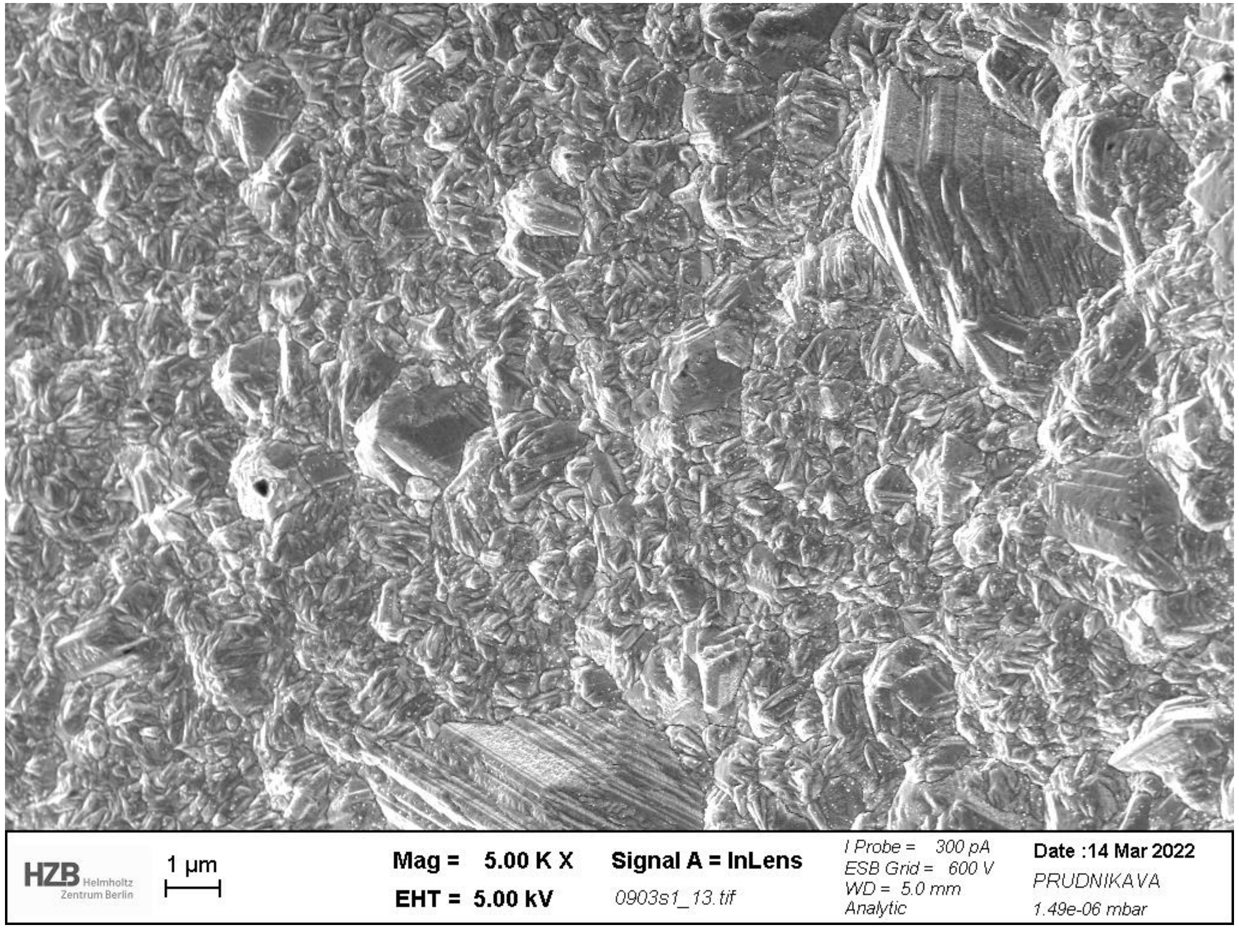
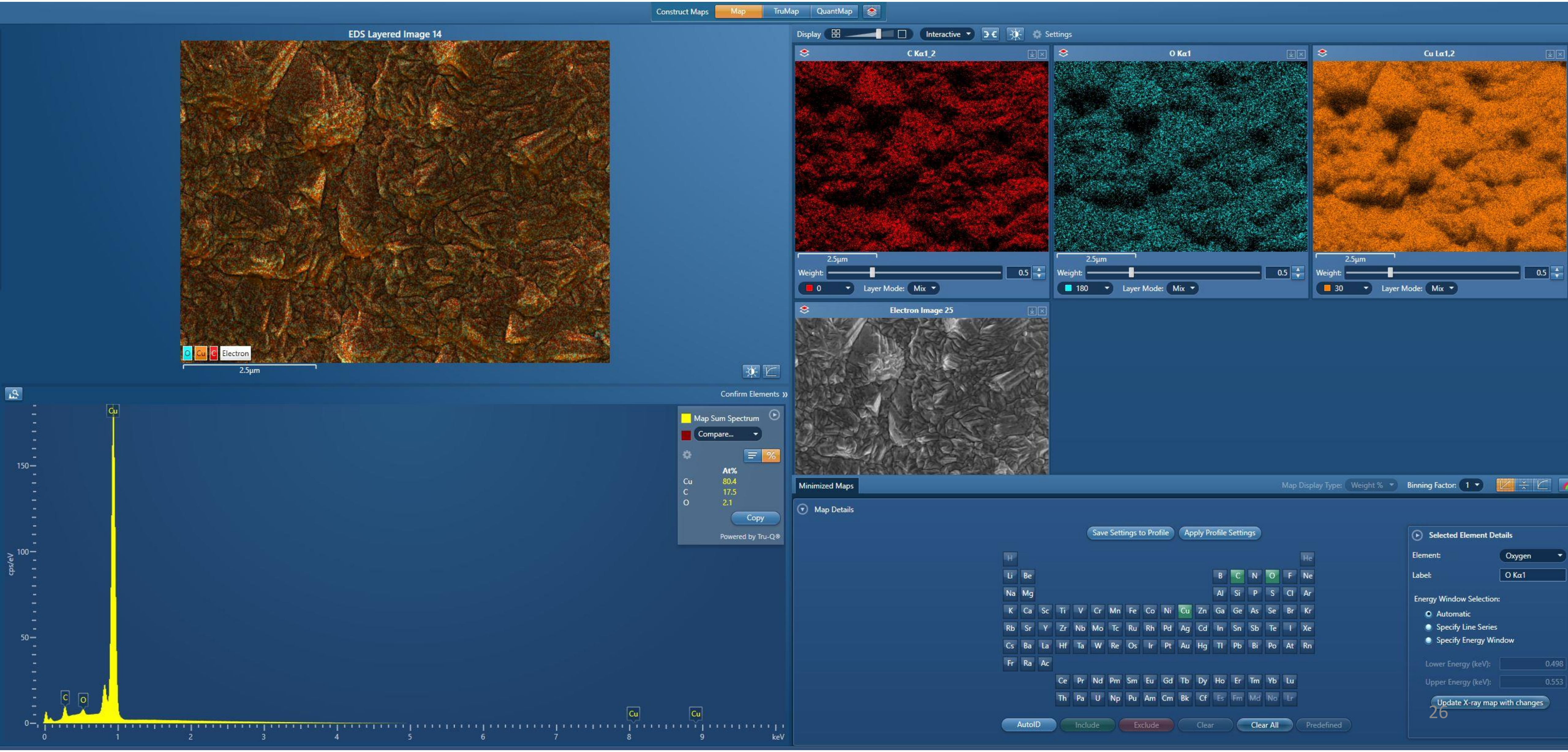
Morphology of the Cu-films (SEM)

80 mA

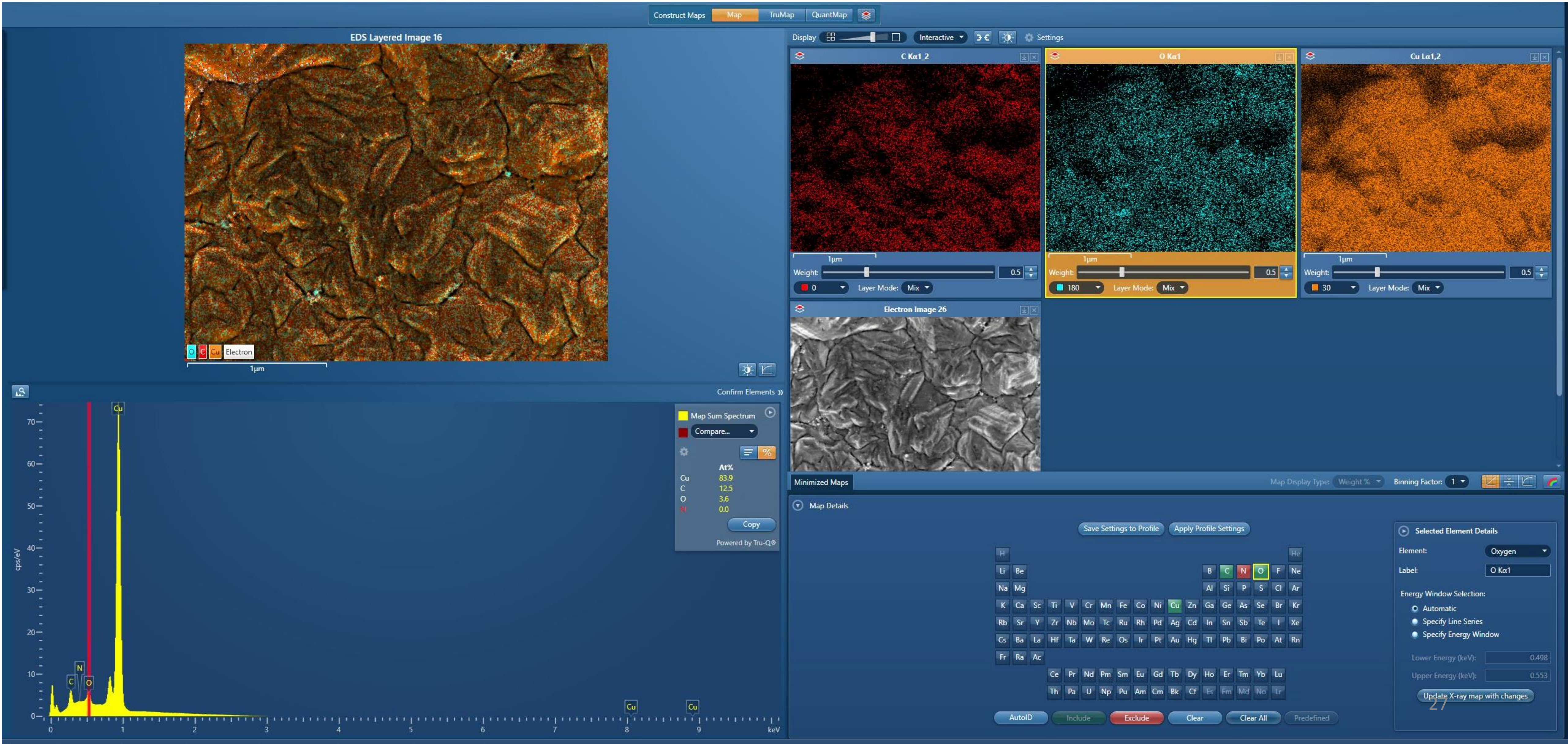




Sample 1, 80 mA



Sample 1, 80 mA



Testing Acidic Electrolytes (2): Cu plating onto Copper

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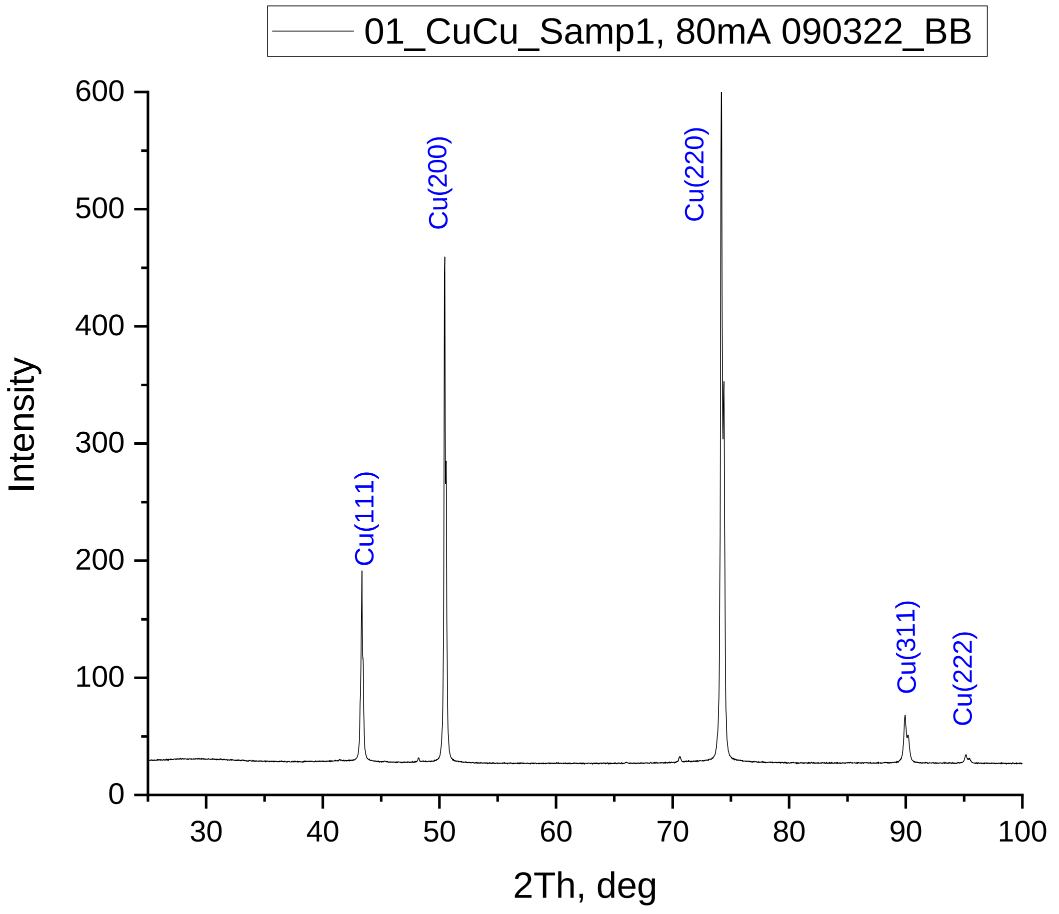
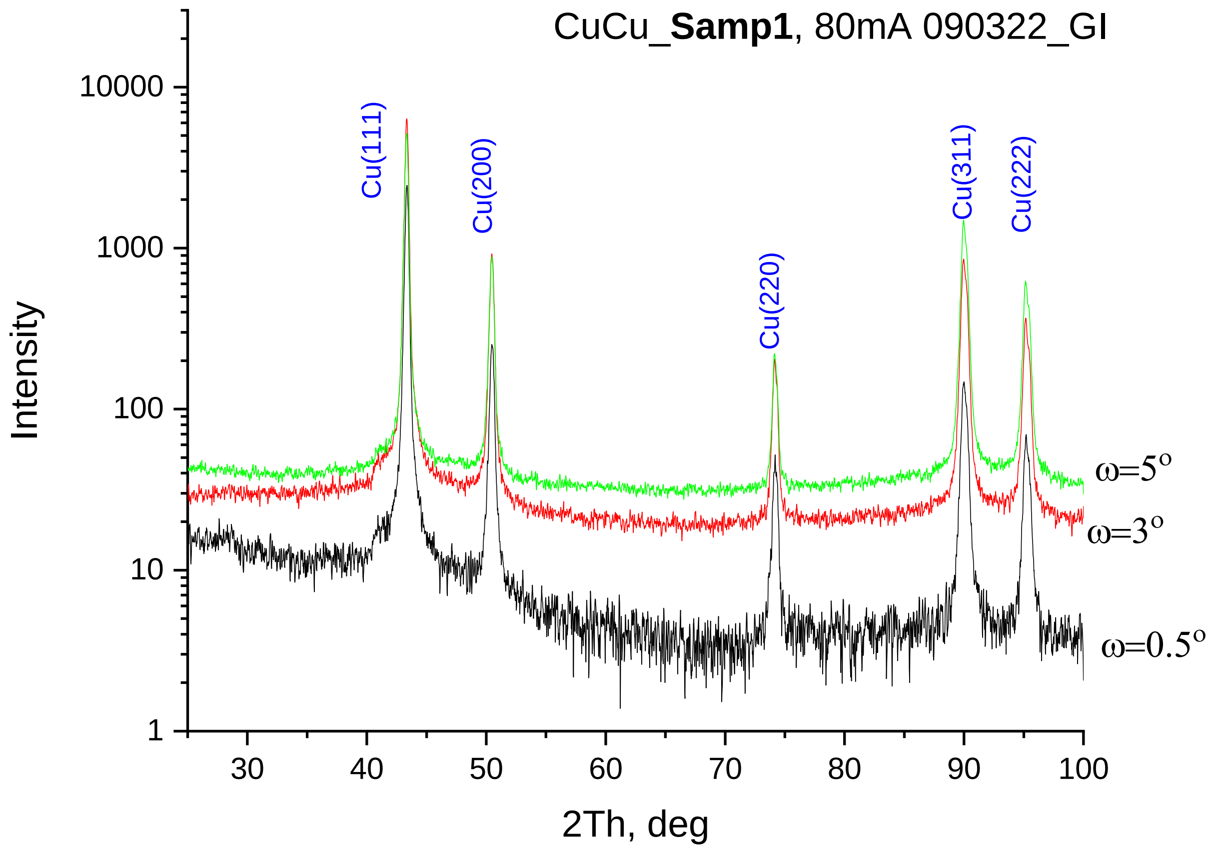
80 mA (without MPS)



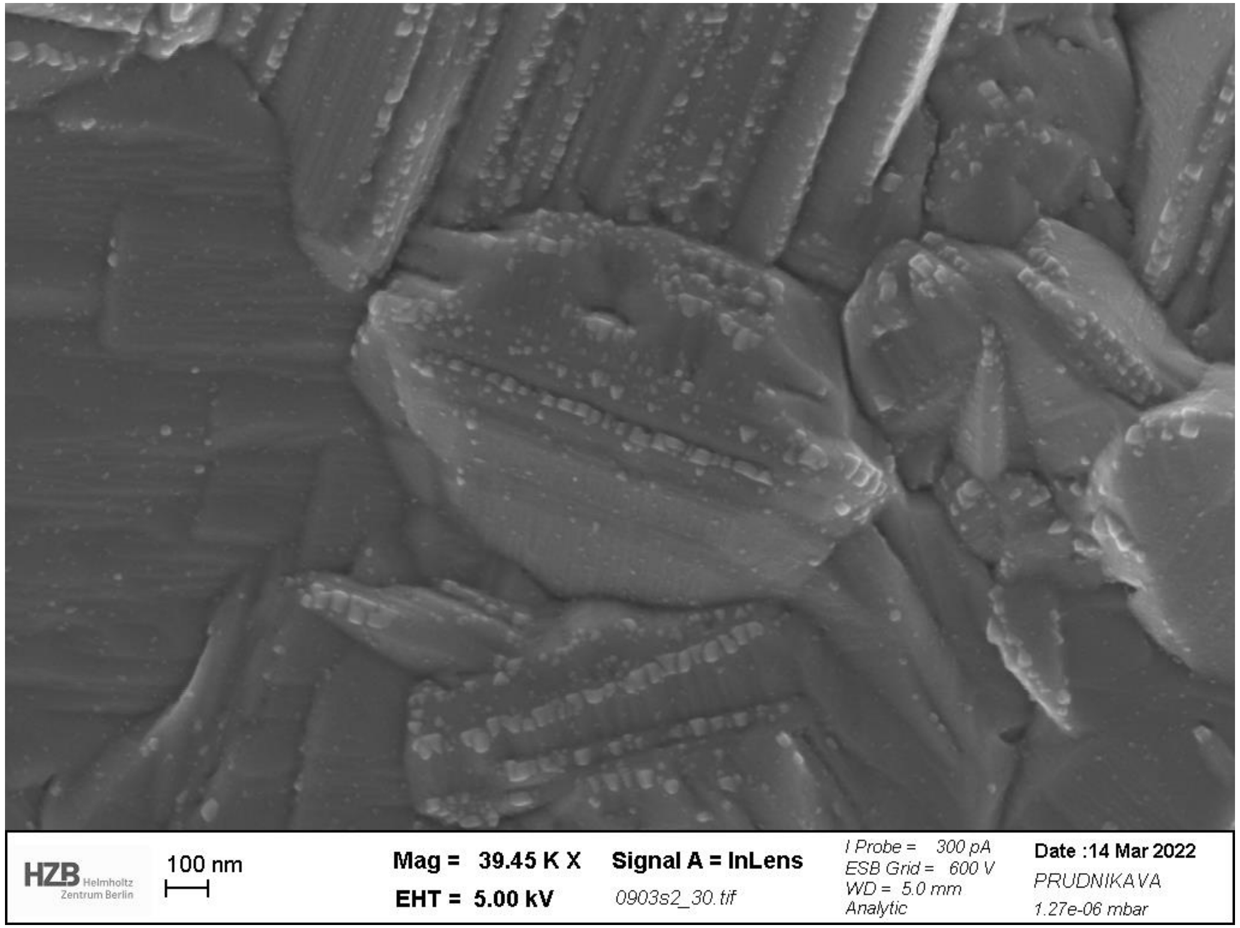
Cryst. Size 29.64 nm

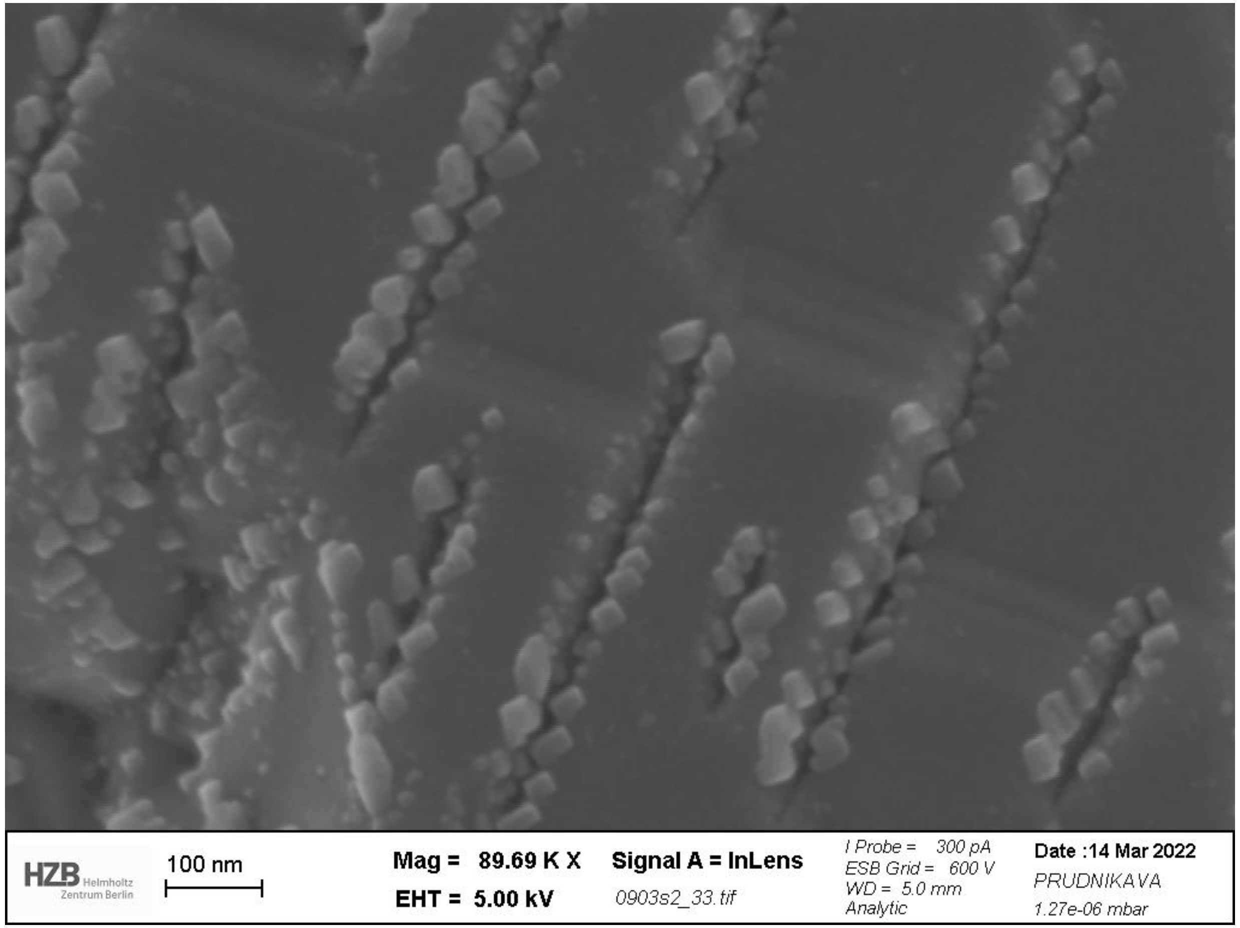


no visible oxidation

Testing Acidic Electrolytes: Cu plating onto Copper

some crystal planes reveal oxide particles

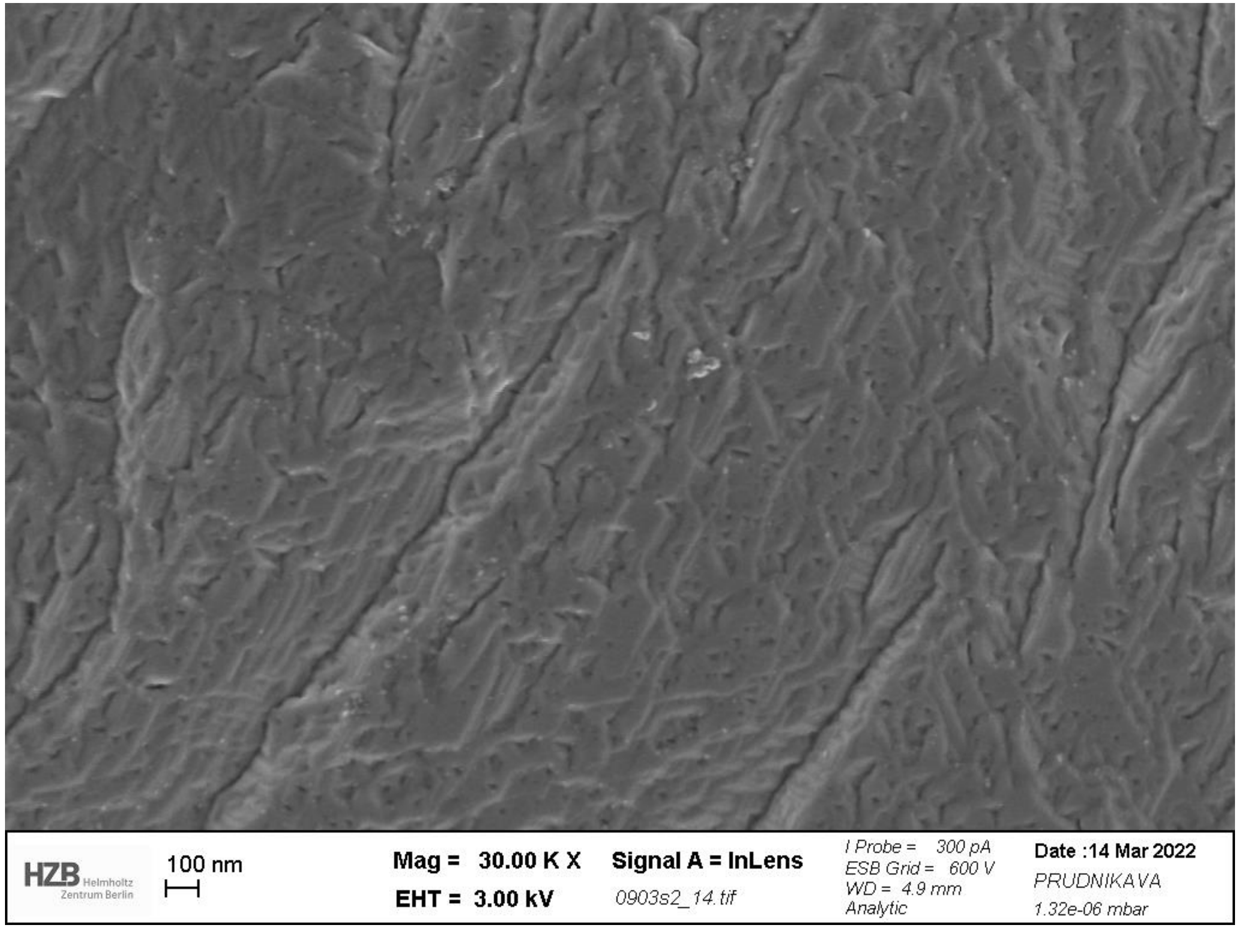


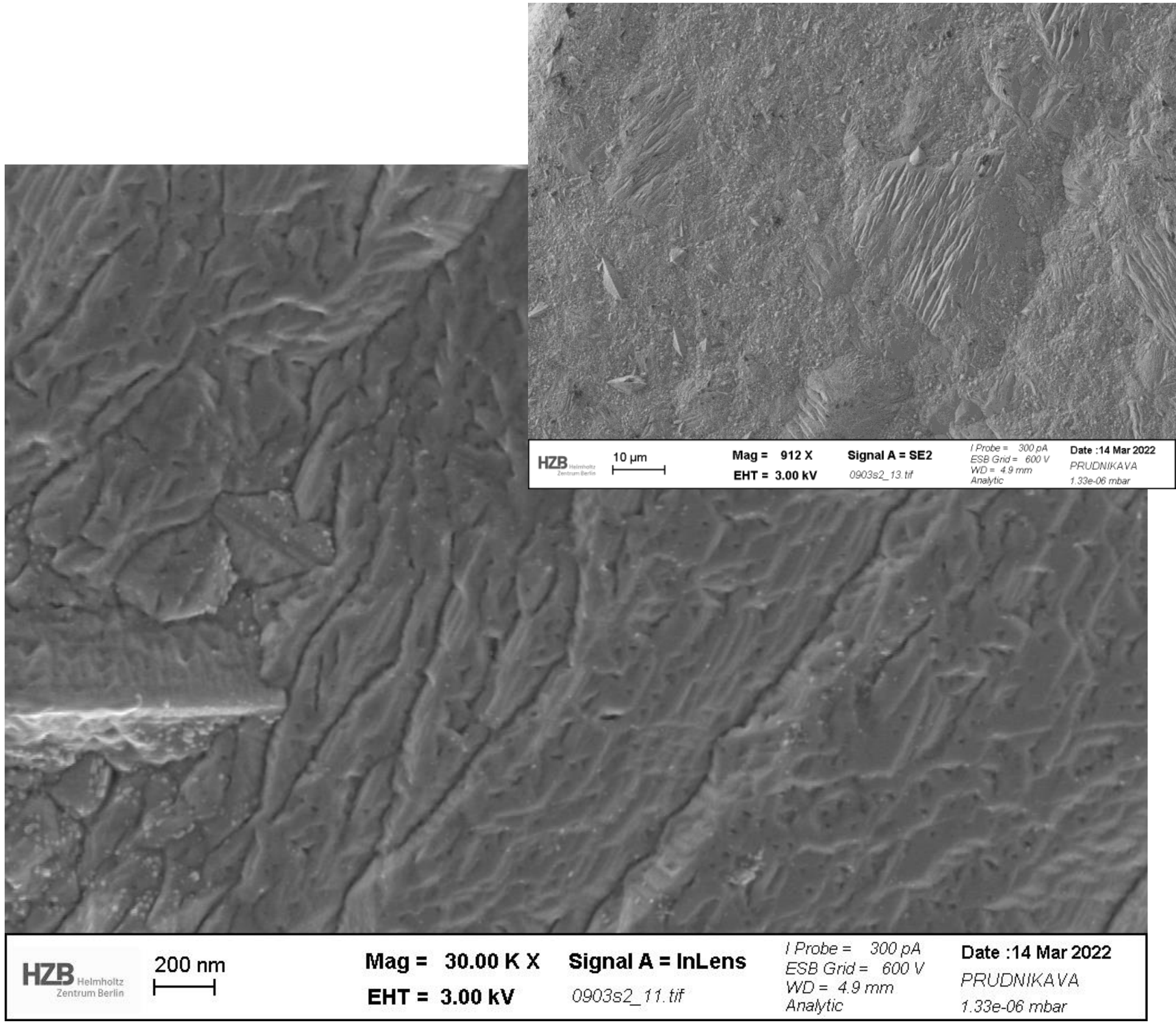


Sample 2 (50 mA, no MPS)

Testing Acidic Electrolytes (2): Cu plating onto Copper

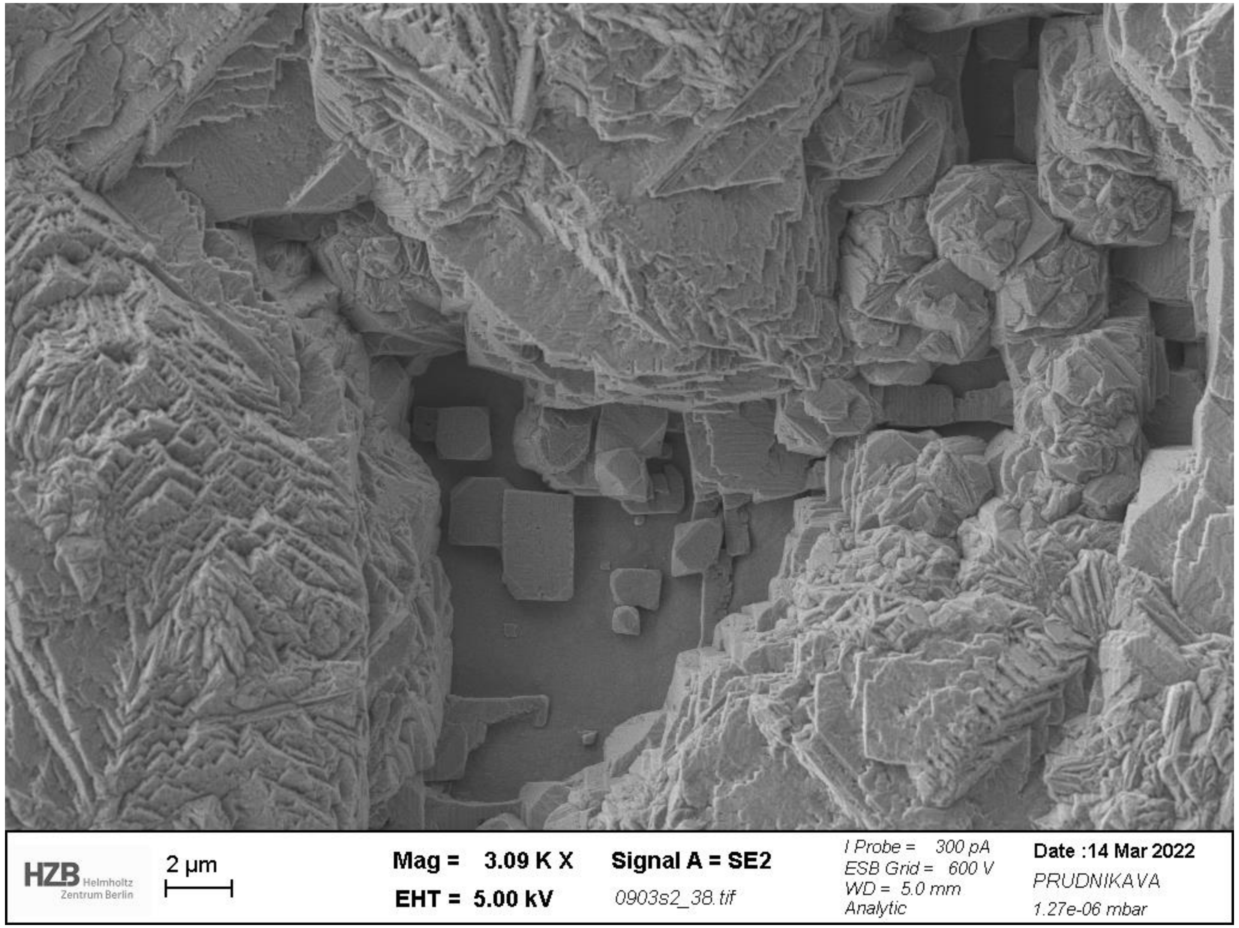
some - do not..

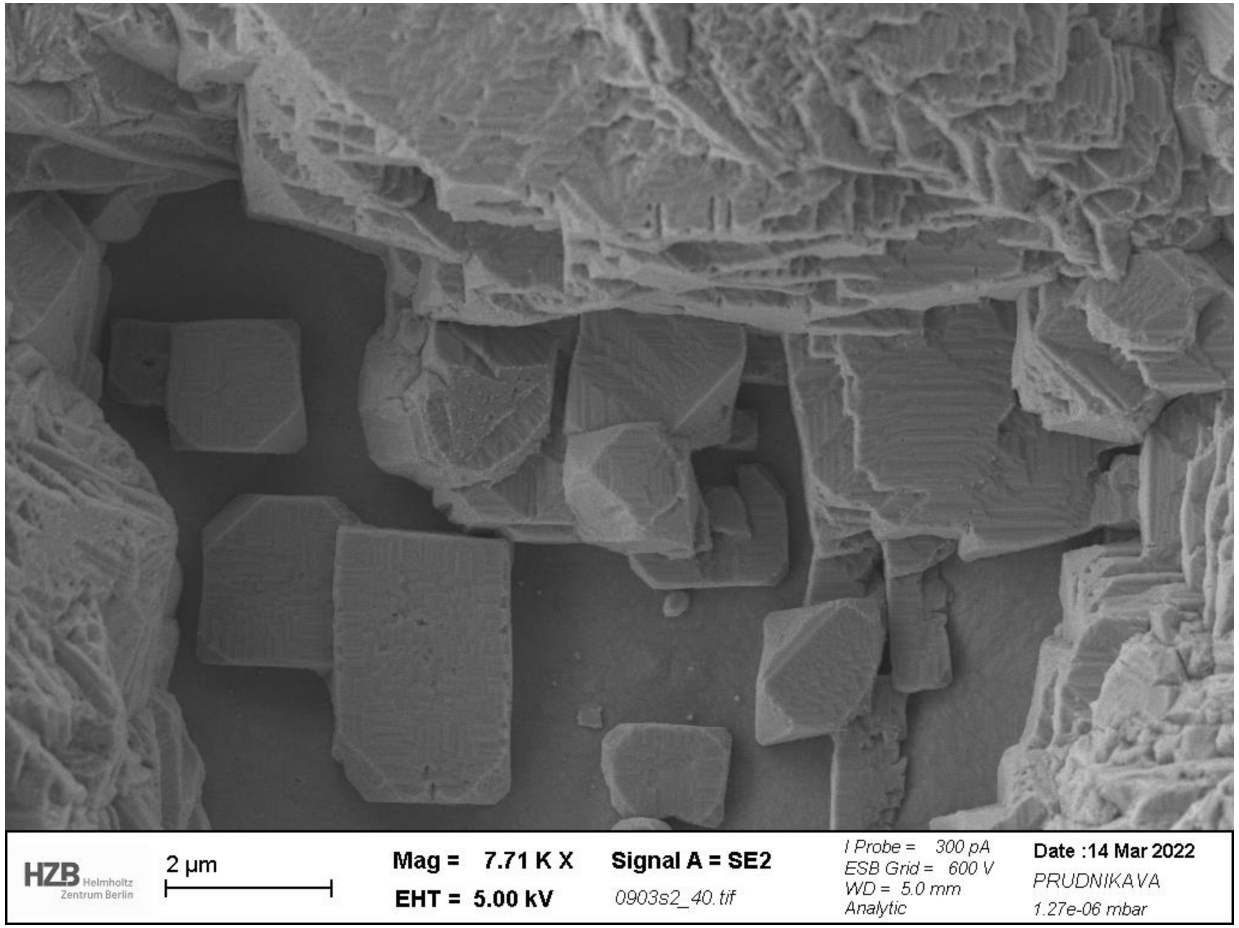




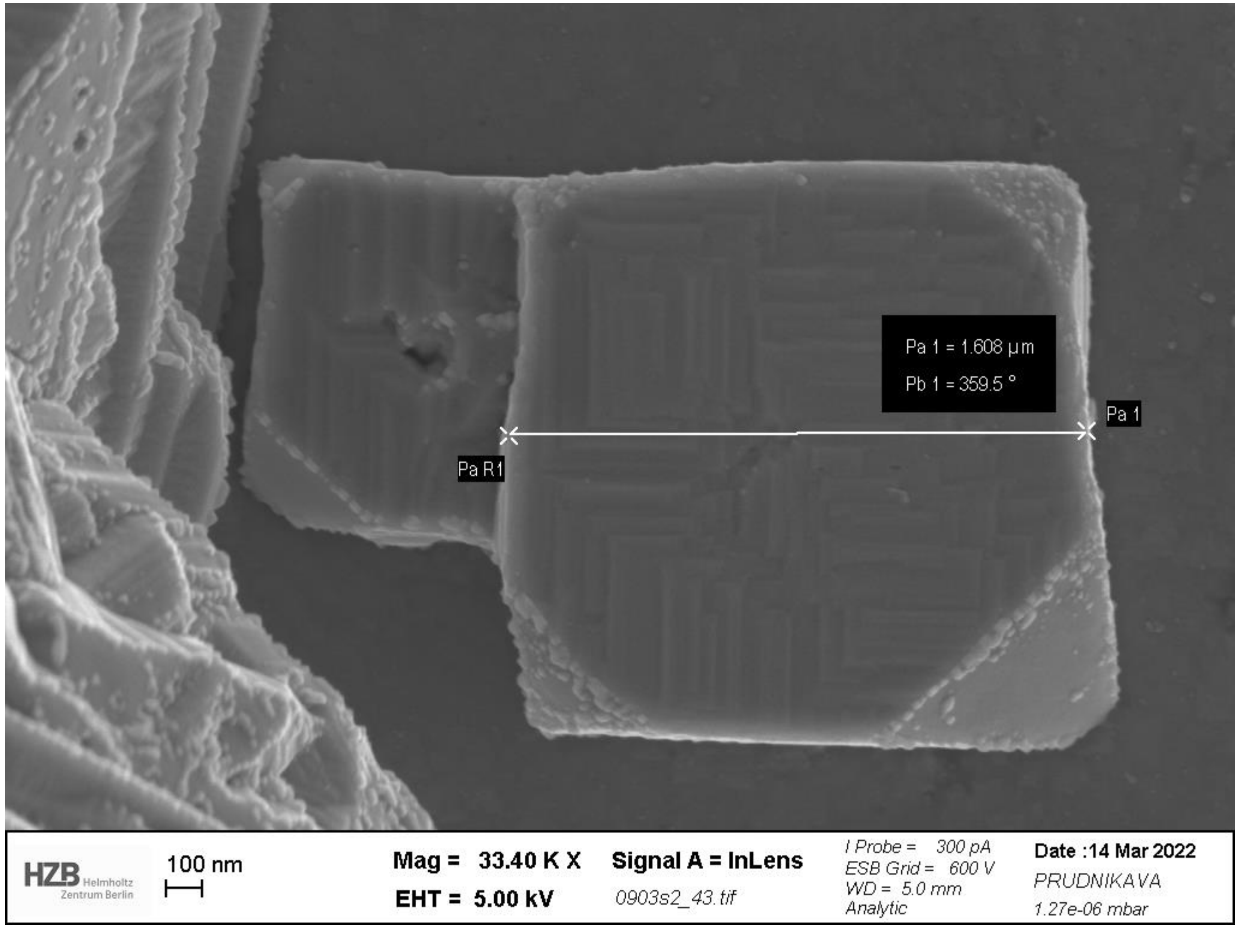
Sample 2 (50 mA, no MPS)

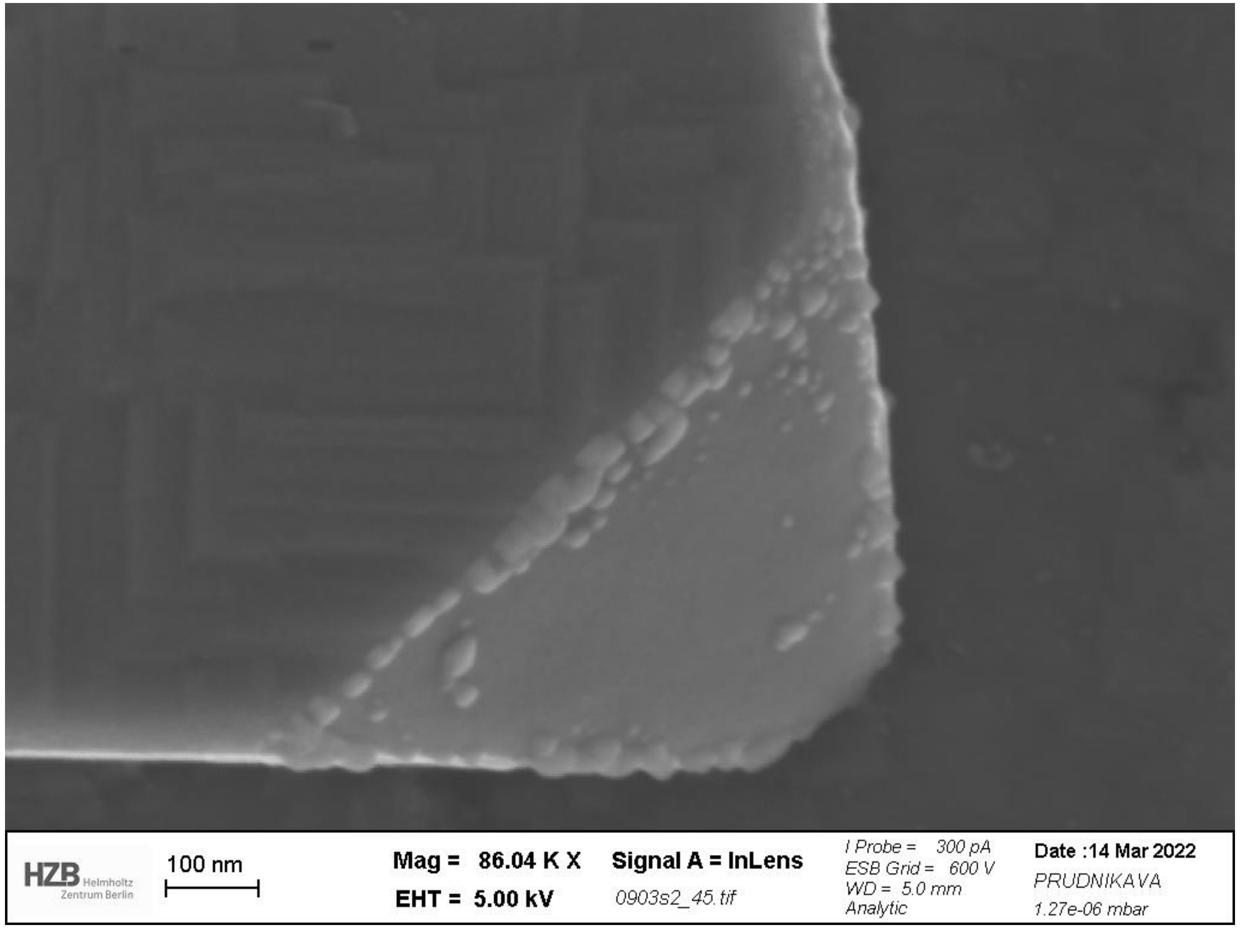
Testing Acidic Electrolytes (2): Cu plating onto Copper





Testing Acidic Electrolytes (2): Cu plating onto Copper





Testing Acidic Electrolytes (2): Cu plating onto Copper

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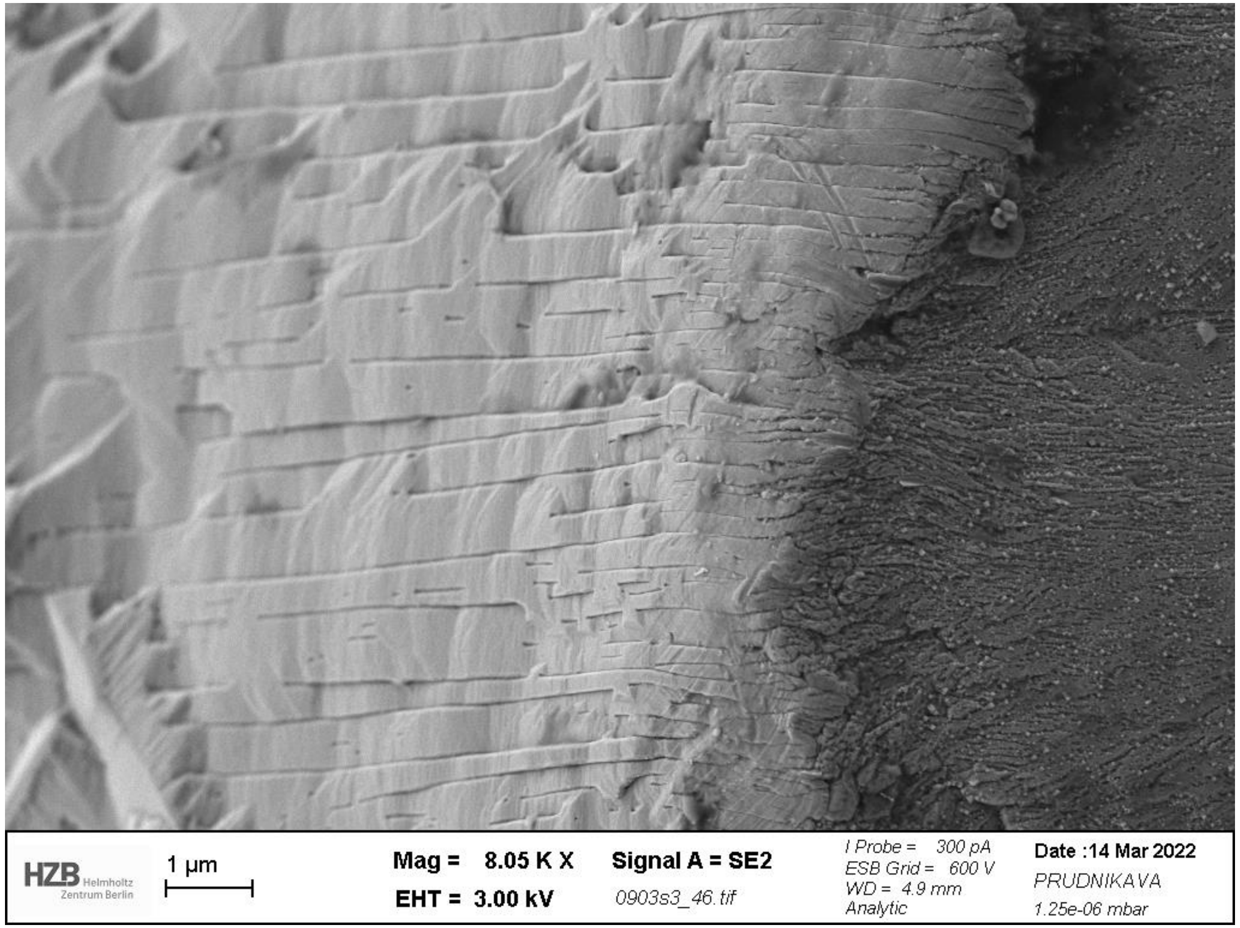
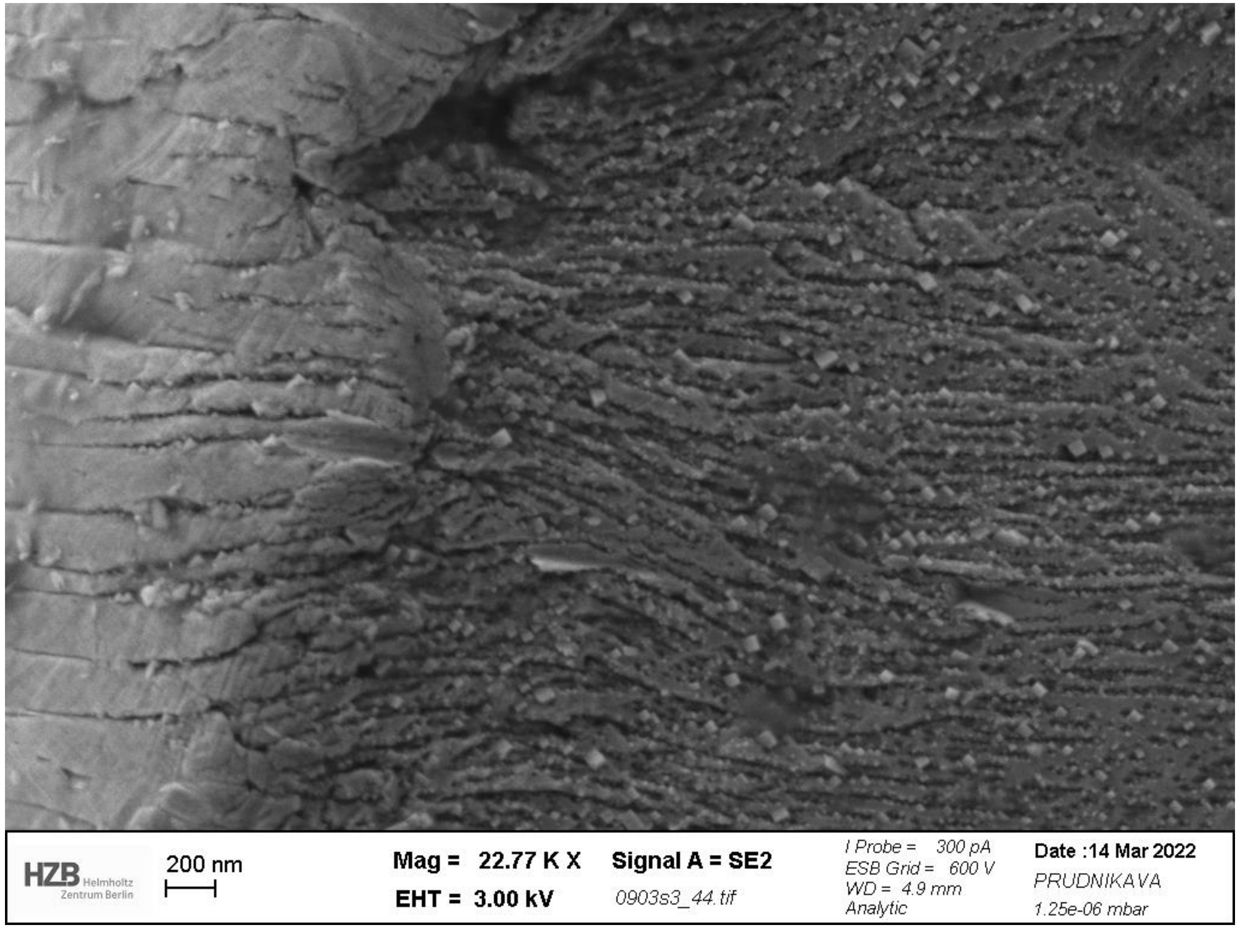
continuous growth of the Cu grain along one crystallographic direction

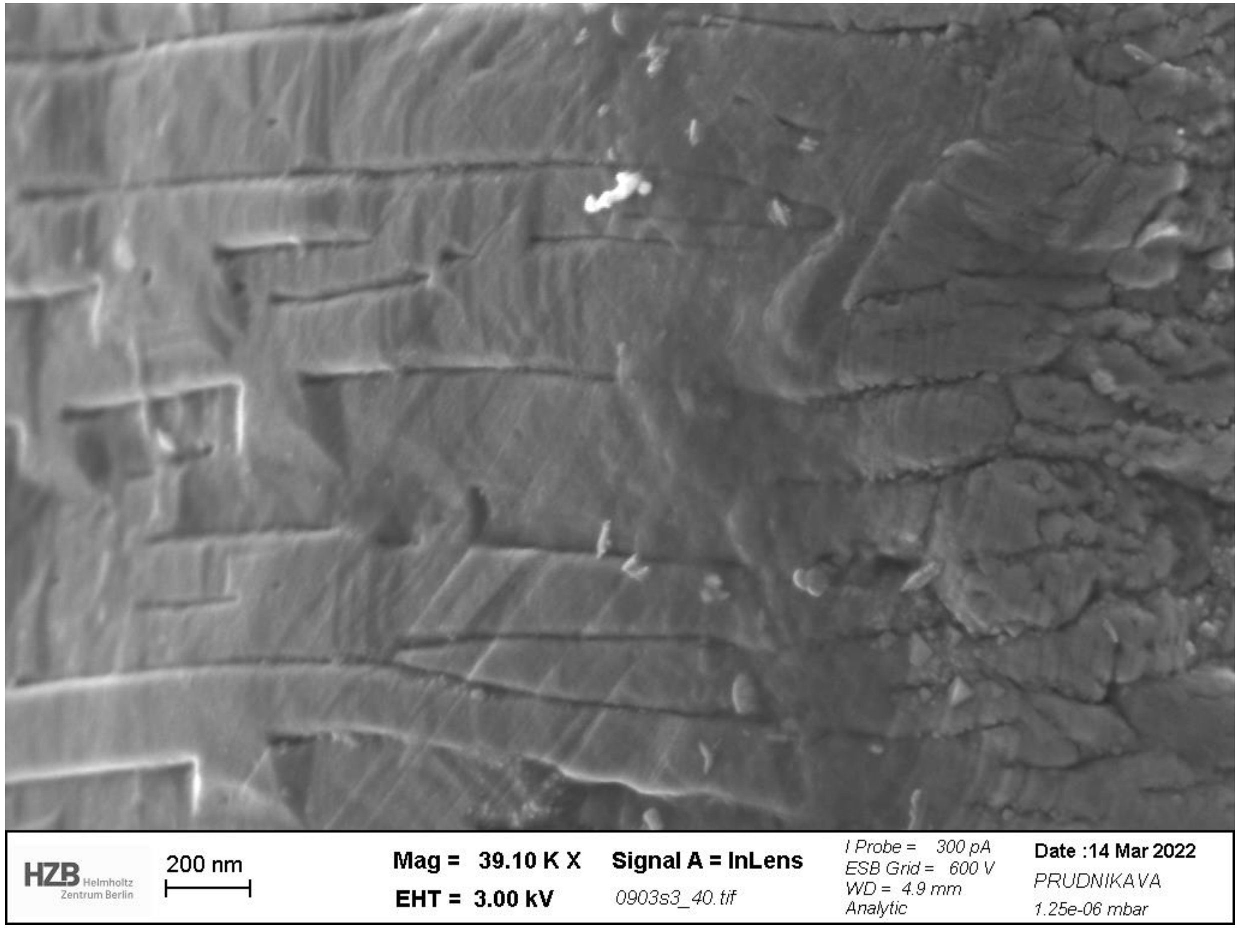


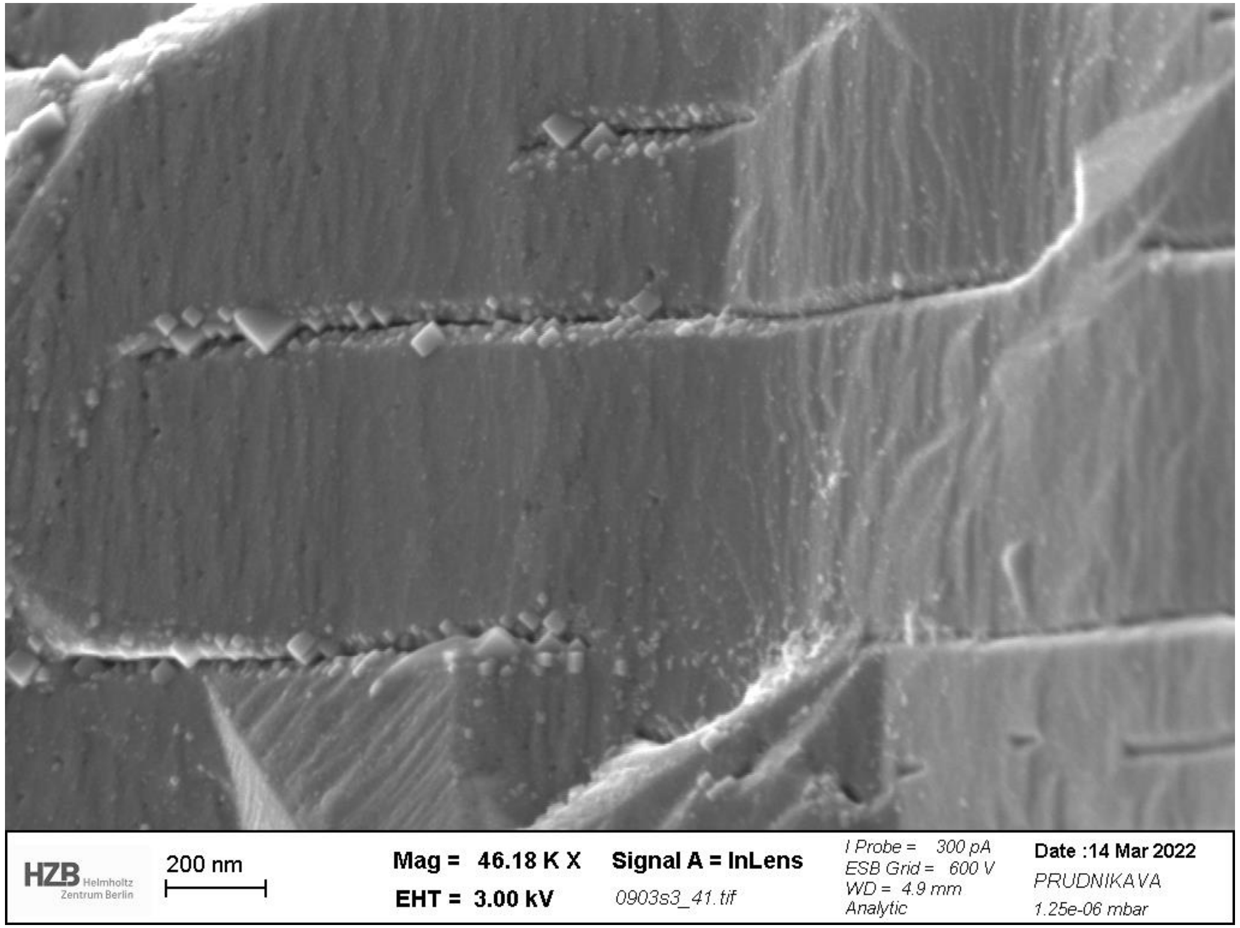


Sample 3 (50 mA, MPS)

Testing Acidic Electrolytes (2): Cu plating onto Copper

continuous growth of the Cu grain along one crystallographic direction



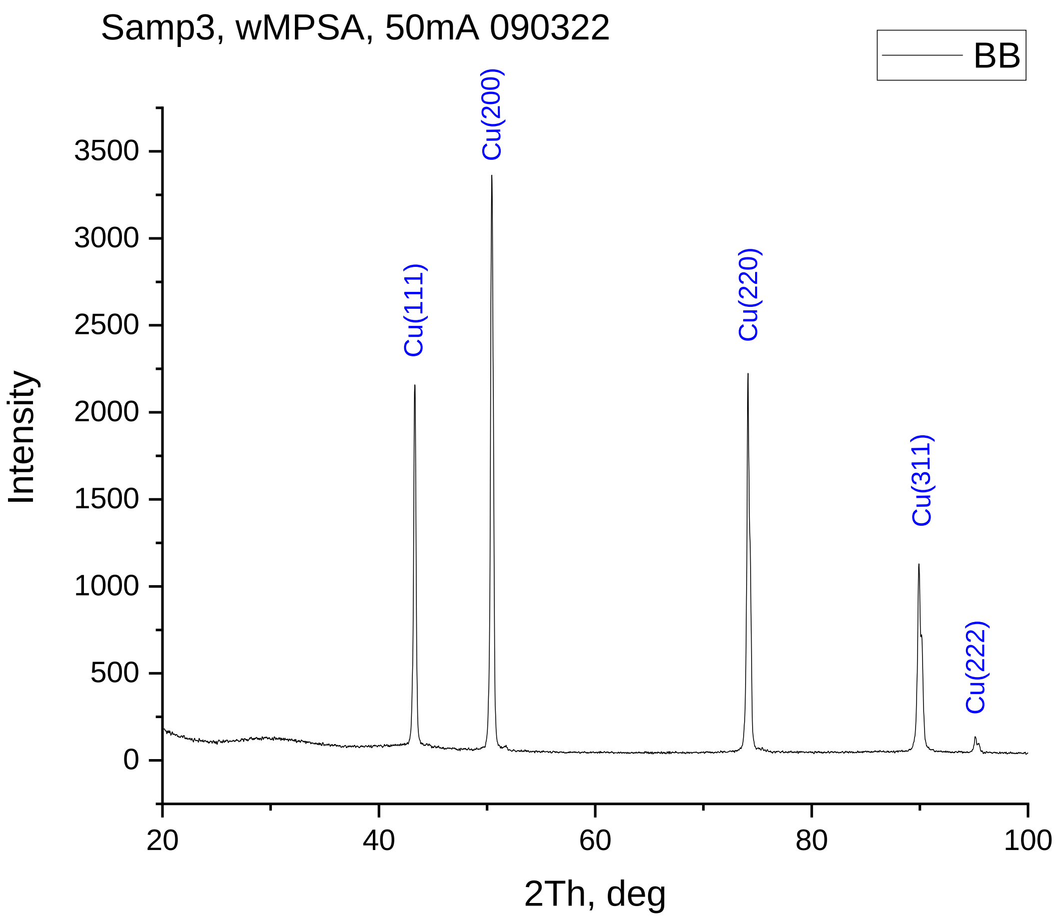


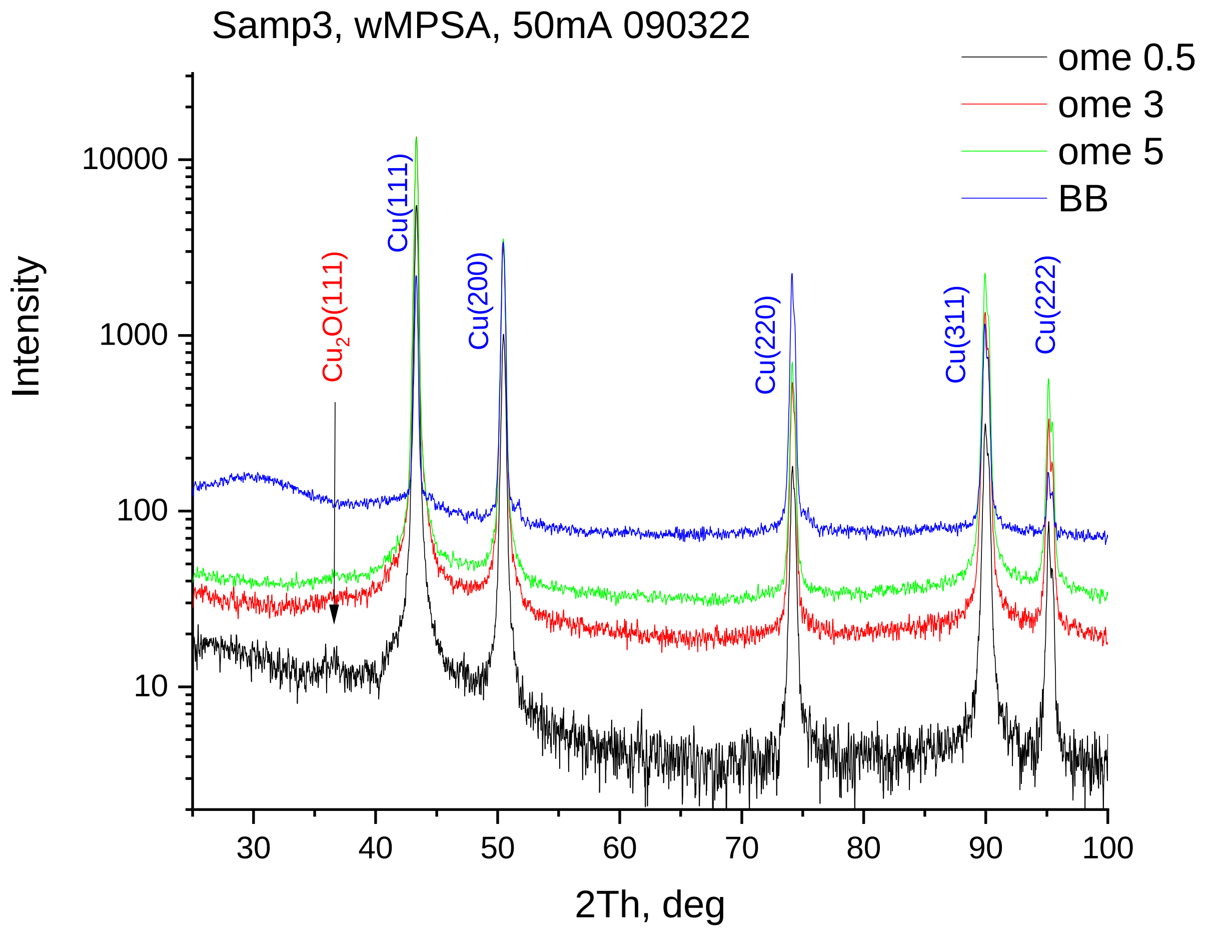
Sample 3 (50 mA, MPS)

Testing Acidic Electrolytes (2): Cu plating onto Copper

80 mA (with MPS)

Cryst. Size 33.40 nm





Cu(200) is the preferential crystal growth plane

Possible origins of the topographic pattern of Cu-film:

1. Rough Cu-electrode surface after chemical etching => changed Cu-seed layer precipitation behavior
2. Relatively low electrolyte bath temperature (17-8C as compared to the best results at 30-35°C)

Testing Acidic Electrolytes (2): Cu plating onto Copper

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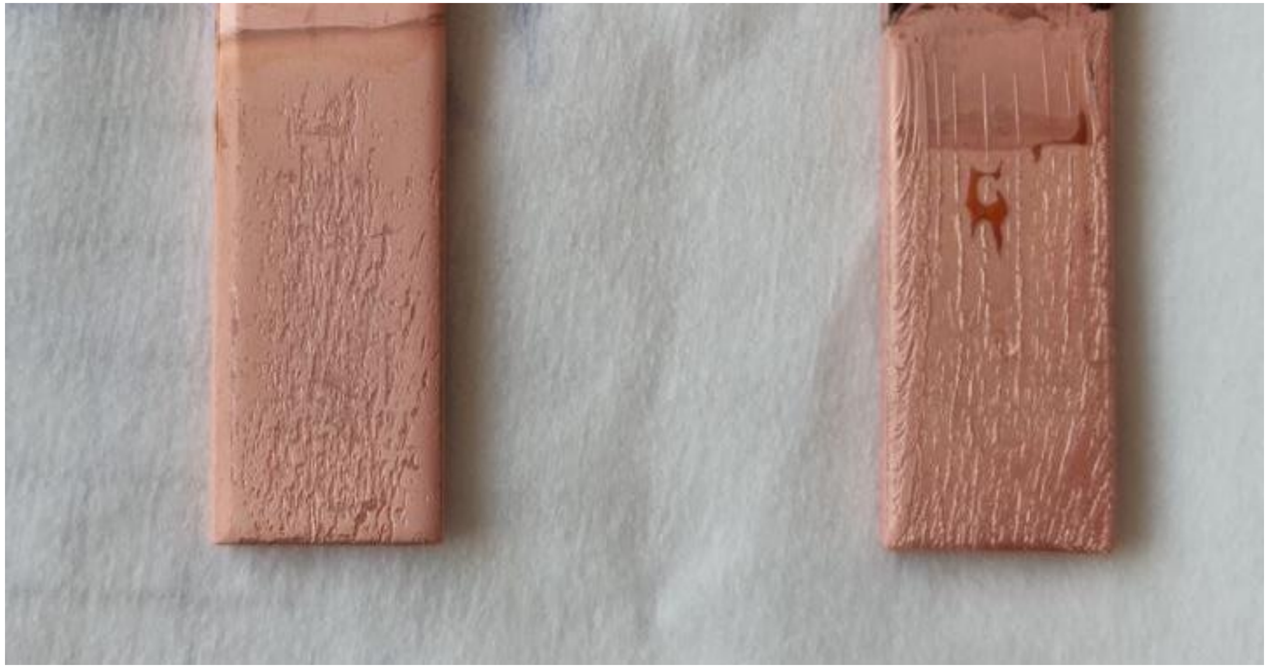
Possible origins of the topographic pattern of Cu-film:

1. no
2. no

1.	2.
Cu-plating onto smooth Cu	Cu-plating at 30°C onto smooth Cu
Sample 1 80 mA, 17-18 ° C	Sample 2 80 mA, 30-32°C

$CuSO_4 \cdot 5H_2O$
H_2SO_4
H_2O
additives:
- NaCl
- Janus Green B
- MPS



deposition rate: *v*=20.2 um/h *v*=18.6 um/h

Testing Acidic Electrolytes (3): Cu plating onto Copper

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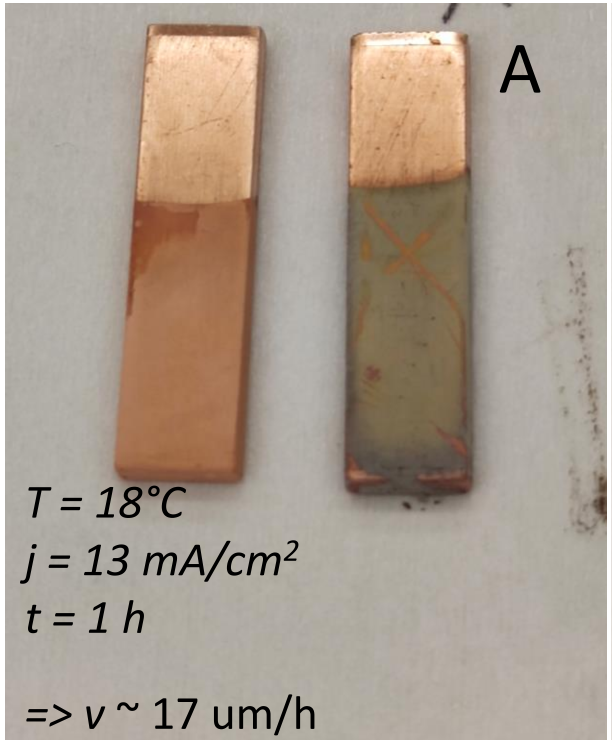
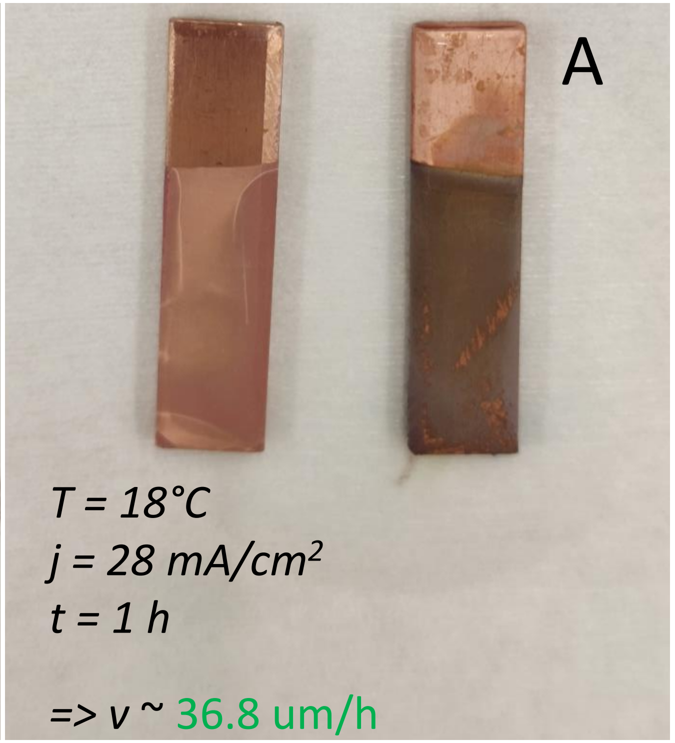
Electrolyte: High speed bright copper electroplating solution by Sigma Aldrich (up to 5 µm/min)

80 mA



200 mA

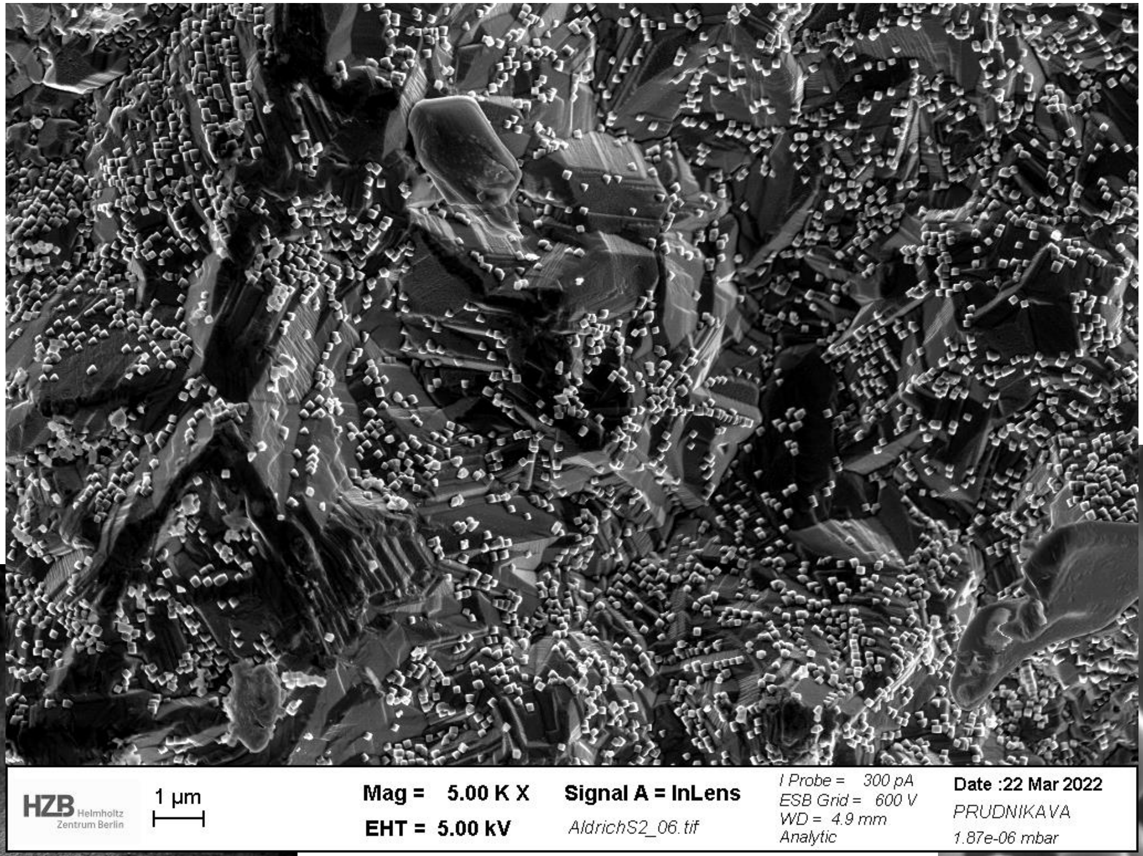


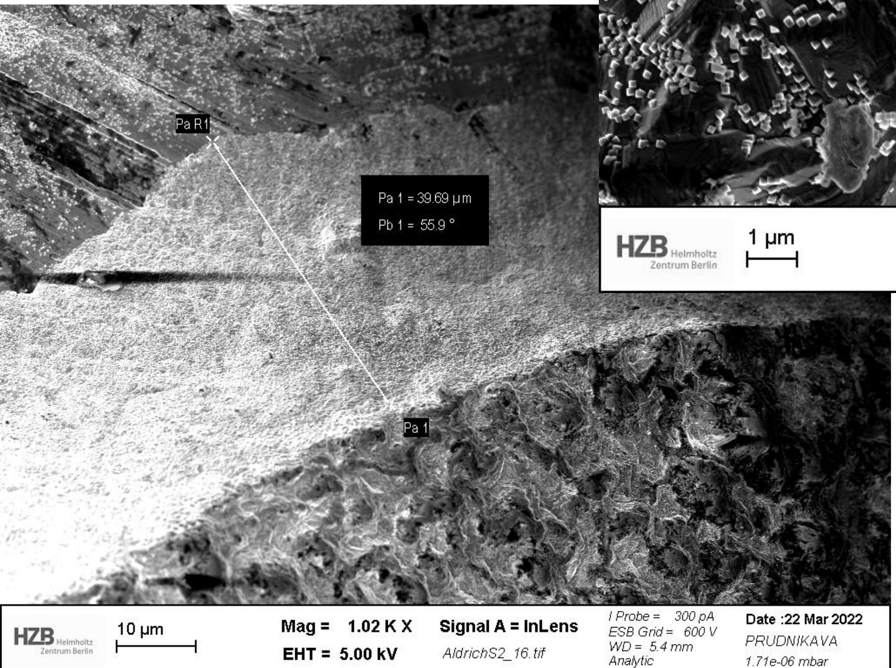
- Anode degradation (even if a decreased current densities are applied to Anode)

Testing Acidic Electrolytes (3): Cu plating onto Copper

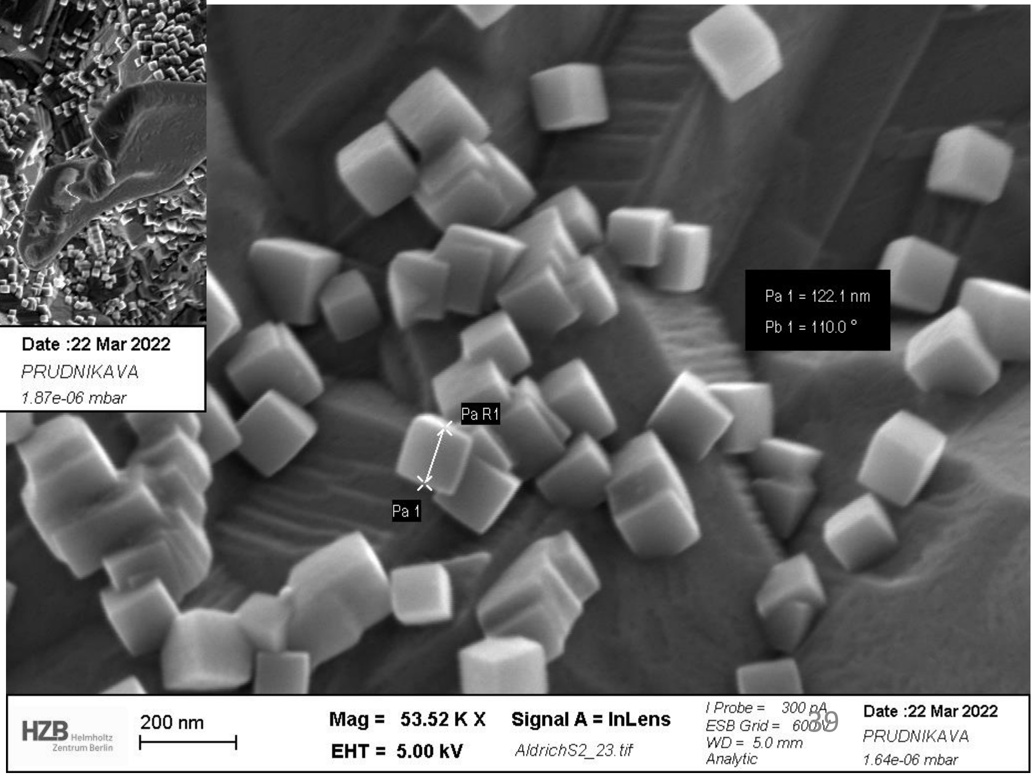
Cu-film

Sigma Aldrich, 200 mA





Cu-film oxidation (larger particles as compared to other samples)



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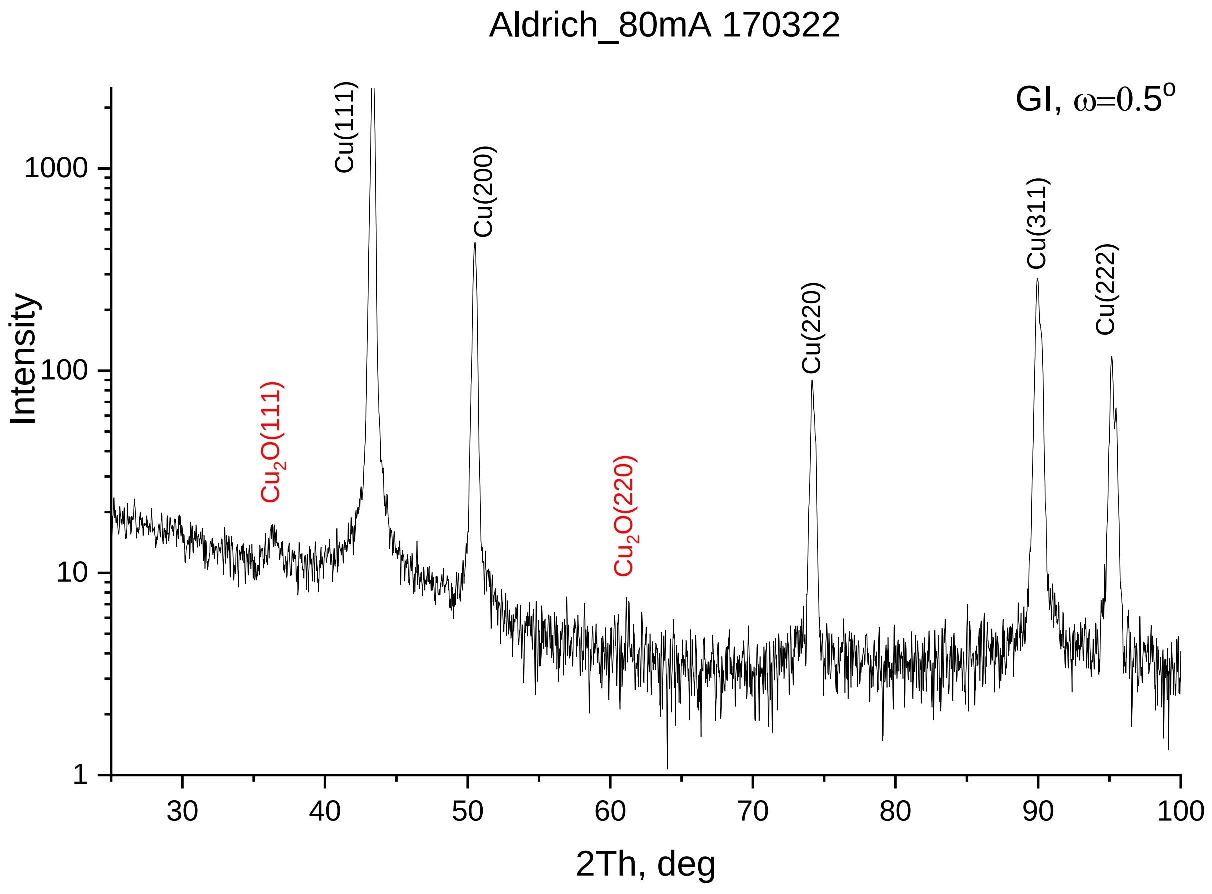
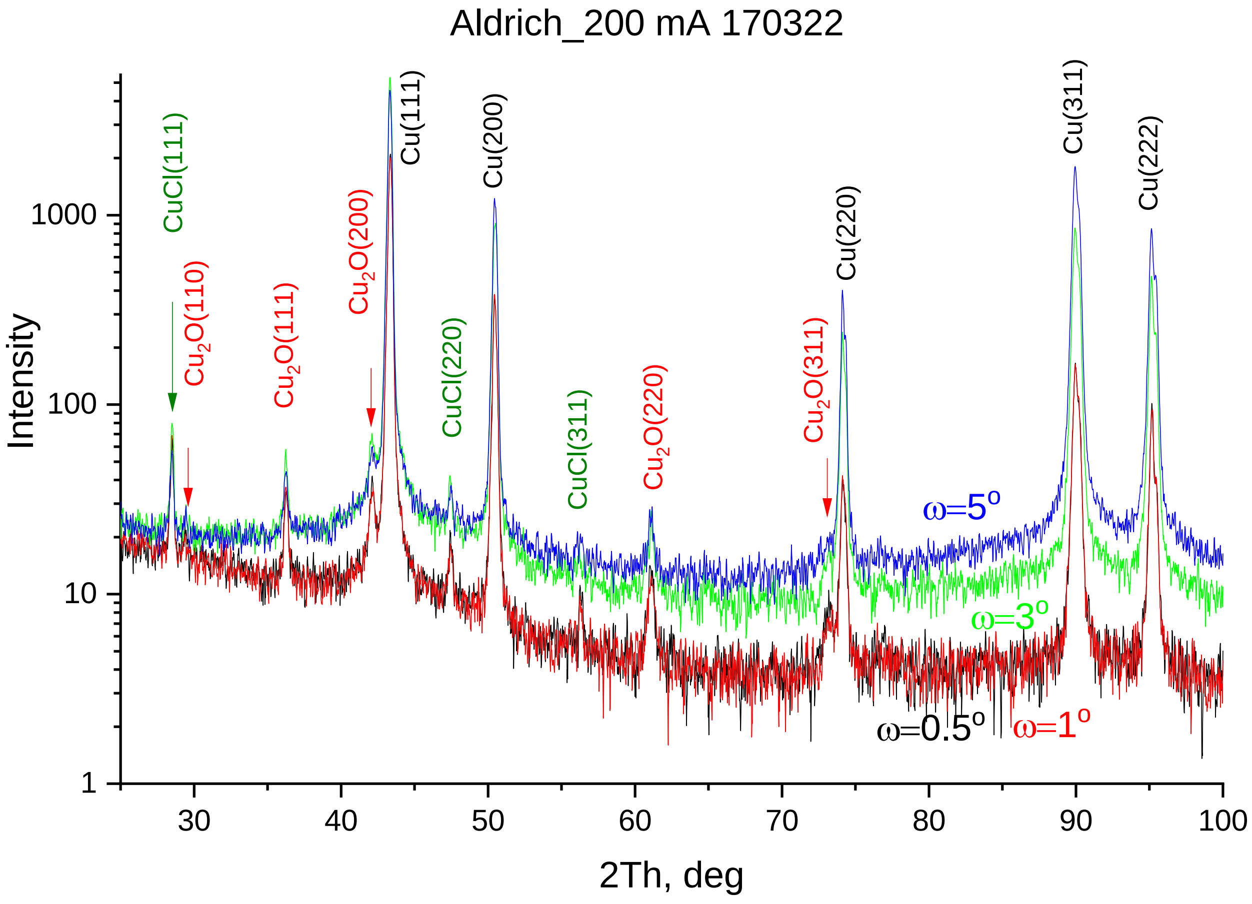
XRD: Cu films



cubic Cu_2O is present



cubic Cu_2O and CuCl are present

⇔ related to Anode problem?

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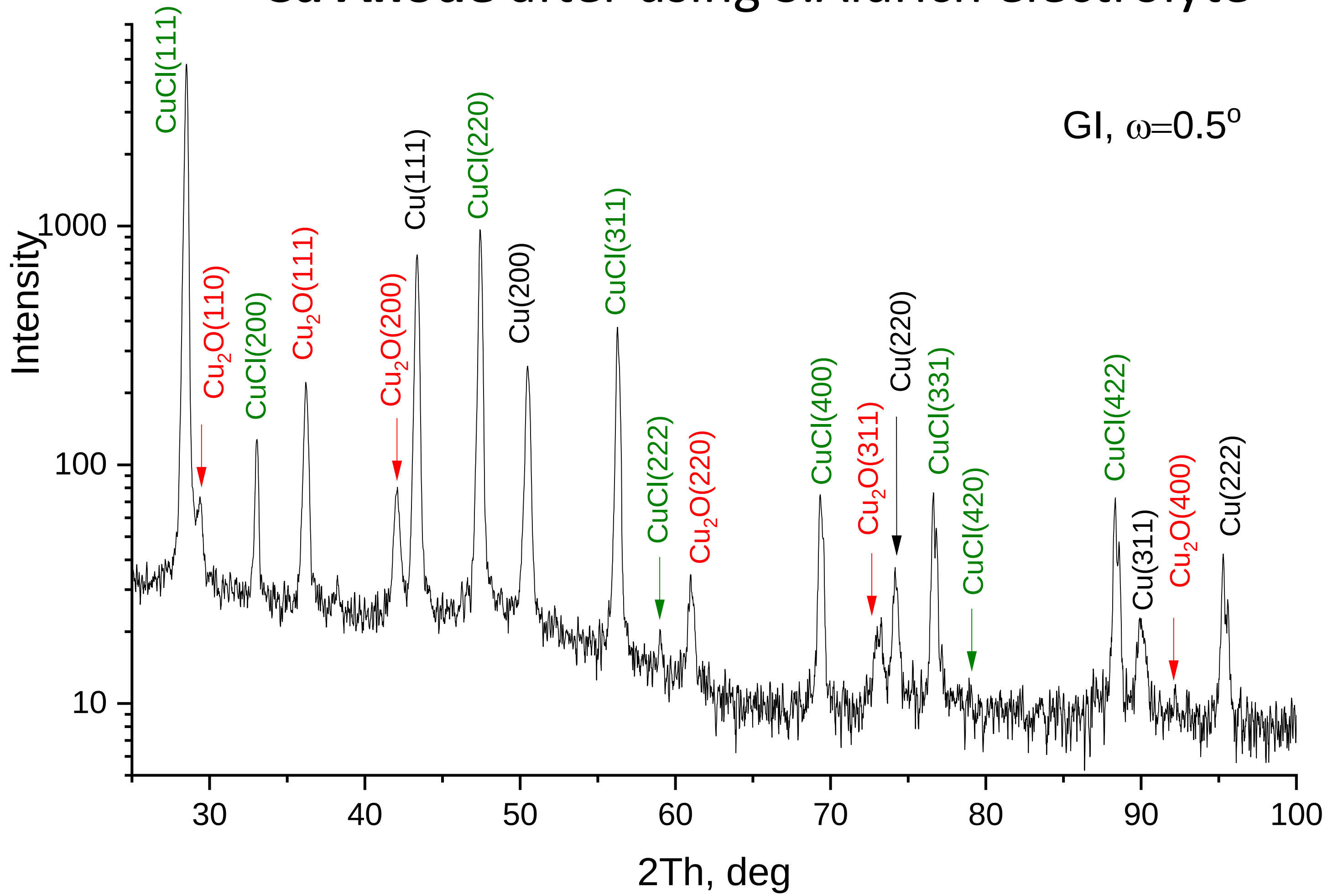
XRD: Cu Anode

Cu Anode after using S.Aldrich electrolyte



⇒ Glassy Carbon Anode to be tested

Testing Acidic Electrolytes (3): Cu Anode

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Summary and Ongoing Activities

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- Procedure for direct plating of Cu onto Nb developed (“buffer layer”). Thin Cu-film was possible to produce (~170 nm). Scotch-tape and liquid nitrogen tested. To be used as a buffer layer, it’s thickness to be increased to 3-5 um.

- Several types of hi-speed Cu-plating baths have been investigated. The plating parameters providing deposition rates up to 37 um/h and surface-oxide-free Cu-films have been demonstrated (yet 25 um/h).

- **Ongoing:**

- Patent preparation for the Cu/Nb thin film recipe;
- building up the thickness of “the buffer Cu layer”;
- the commercial conductivity meters for Cu (at RT) to be tested
- preparing the four-probe conductivity test setup for cryo-T (Y. Tamashevich)
- creating Cu/Cu/Nb structure

Cu film

Electrolyte after 2.5 months storage reproduced the results on Cu-plating of Niobium
=> Stable solution!

Newly prepared electrolyte worked as well for Niobium
=> reproducible results