



Fabrication and
Characterization of Oxidized
Tungsten-Based Thin Films for
Application in Cold Field
Emission Sources

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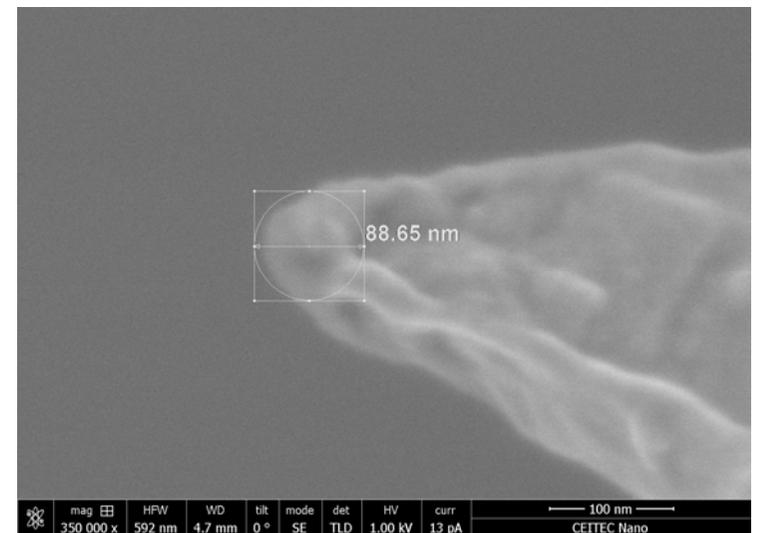
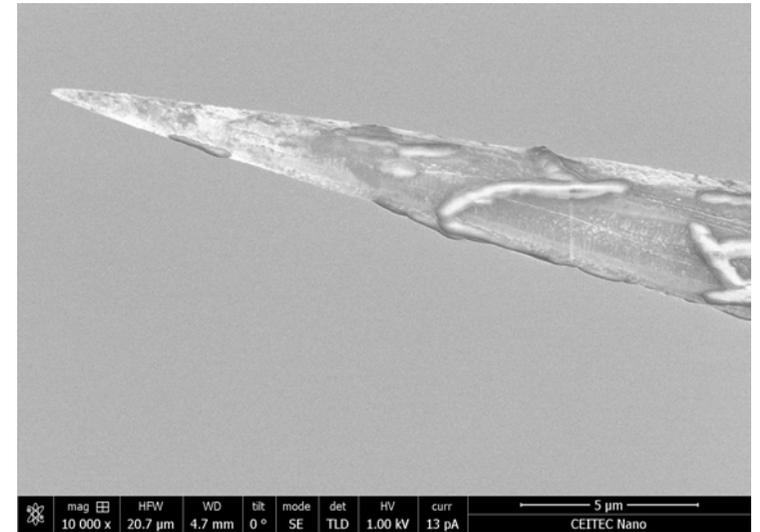
Institute of Scientific Instruments

The 9th ITG International Vacuum
Electronics Workshop (IVEW)
2024



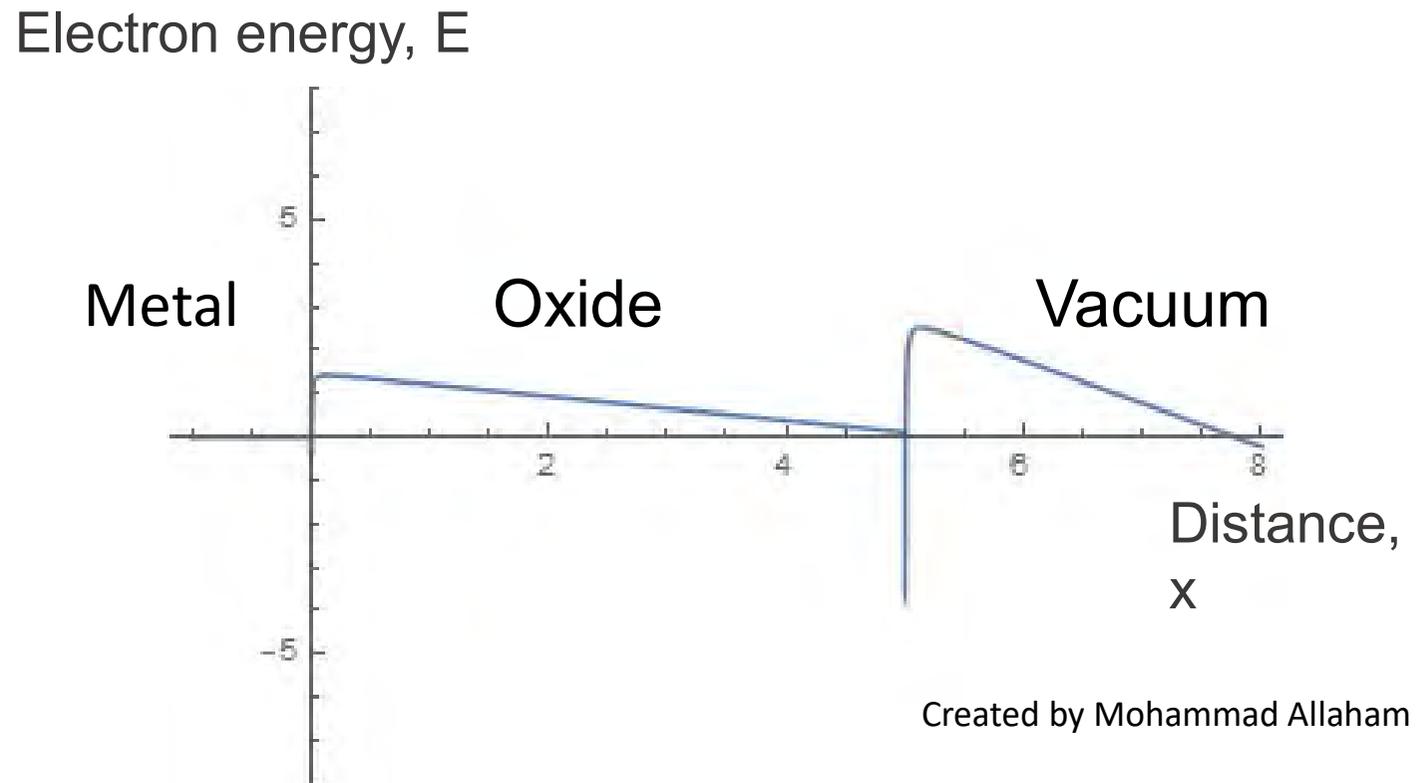
Introduction

- Main criteria:
 - high melting point
 - a low work function
 - large mechanical strength
 - low chemical affinity
- Tungsten remains widespread material for cathodes, but lowering work function (some kind of chemical activation needed)
- Can withstand stresses during operation (high field, temperature ...)
- When trying to create an electron beam with a small diameter and significant current density, it is preferable to choose the smallest feasible cathode,
- Although causing instability -- individual atoms can affect beam current



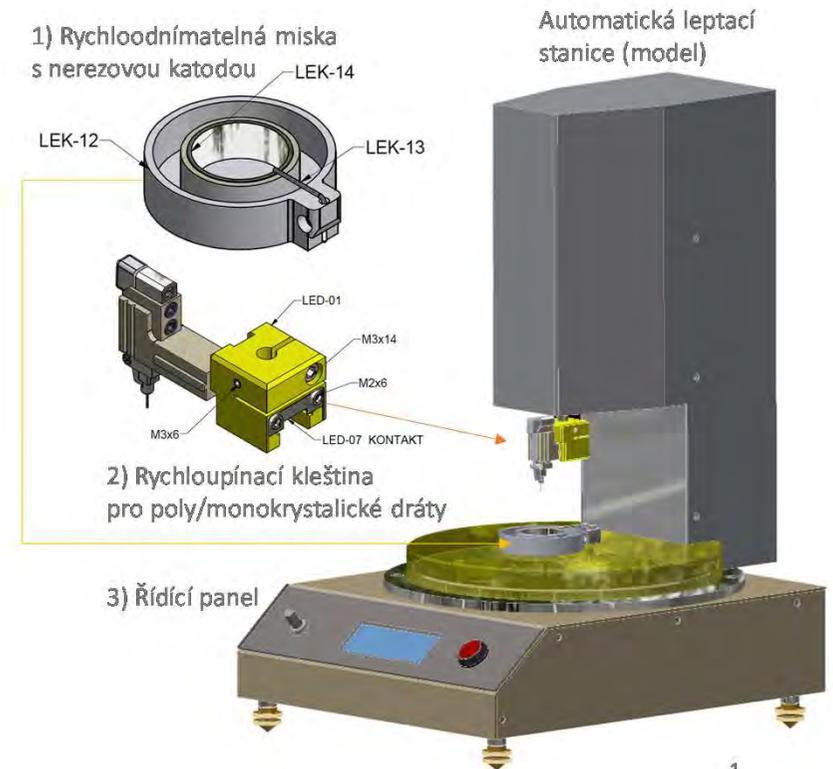
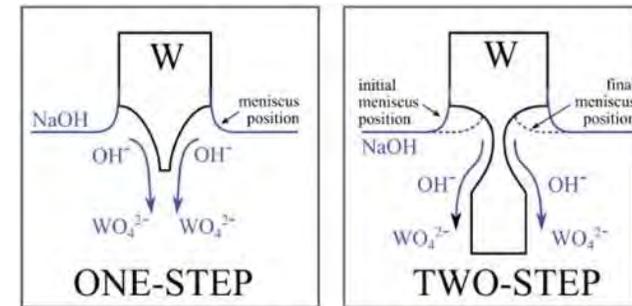
Advantages of the oxide layer

- Particle energy filter
- Protection against positive ions
- Oxide layers significantly change the band structure



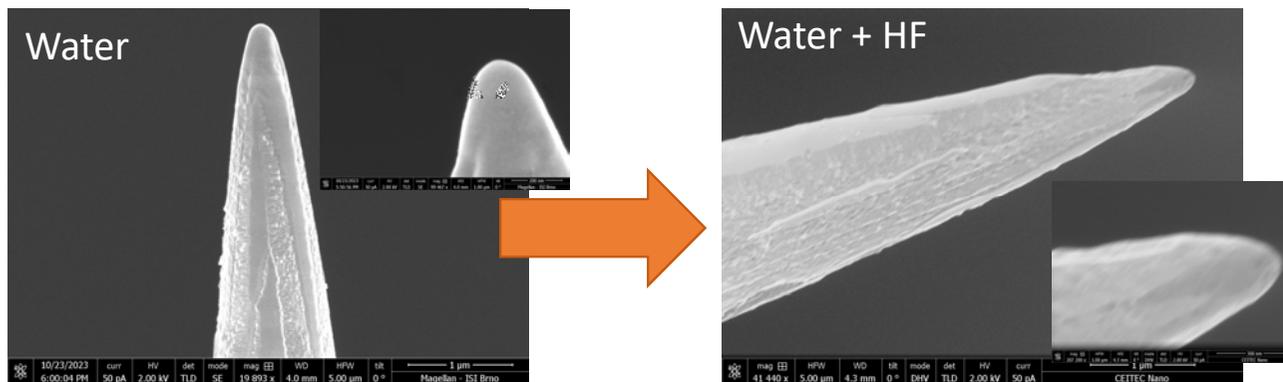
Production of W emitters

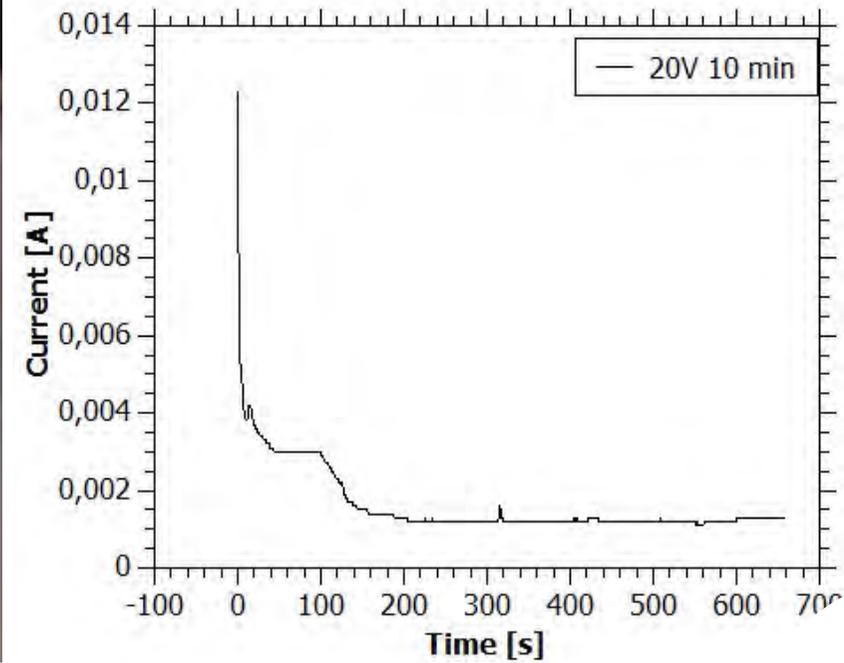
- 2-step etching using automated etching equipment (Armin) based on anodic dissolution with a Pt cathode.
- The electrolyte used was 2 M NaOH at 6.9 V of direct current voltage.
- The immersion depth and the current for terminating the first etching phase are also crucial parameters.
- Material used: Polycrystalline sintered tungsten wire.
- Gradient detector.



Cleaning and Characterization

- Electrochemical cleaning -- polished using an AC current of defined frequency and amplitude
- Hydrofluoric acid + ethanol + water cleaning (Tungsten does not react with HF, but all of its oxides are soluble in a concentrated HF solution; NaOH soluble in water)
- However irregular oxide shapes develops very quickly





Anodic oxidation

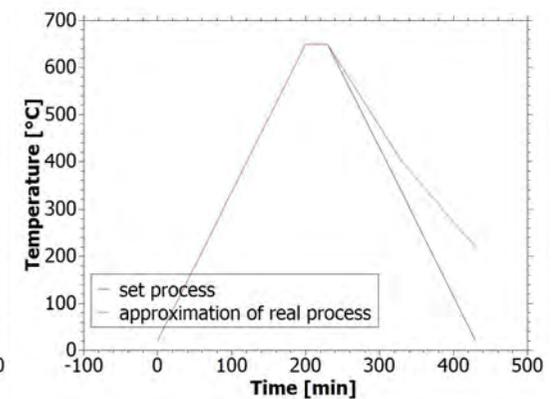
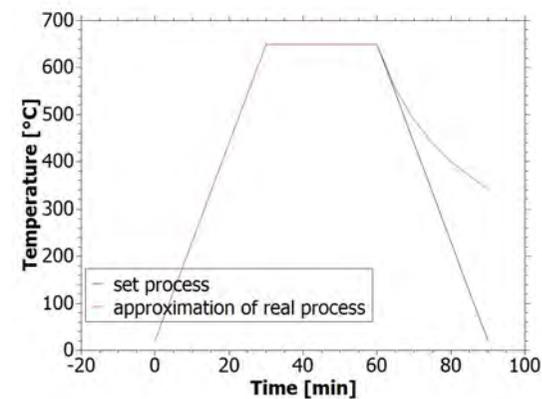
Device for anodization and its current characteristics

- Extension of the existing etching equipment for anodic oxidation
- Designed and manufactured in ISI for this purpose
- 0.3 M Phosphoric acid (H_3PO_4)

Procedure of creating thin layer with thermooxidation



- Glass tube, cooling liquid, controlled gas supply, divided into three heaters
- 10^4 Pa or lower pressure of 10^3 Pa
- Slower or faster procedure



Requirements of the oxide layer

- There are many methods that can provide thin films (ALD, sputtering, thermoxidation, anodization...)
- Anodization, Thermoxidation: available, suitable for tip shape, control of parameters available (time, temperature, pressure)
- Colorization – due to different thickness (and also little different chemical composition) – easily recognizable
- Thin and low roughness needed



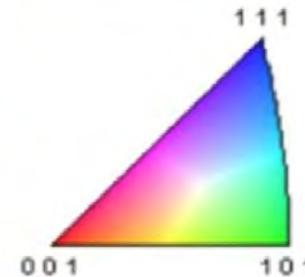
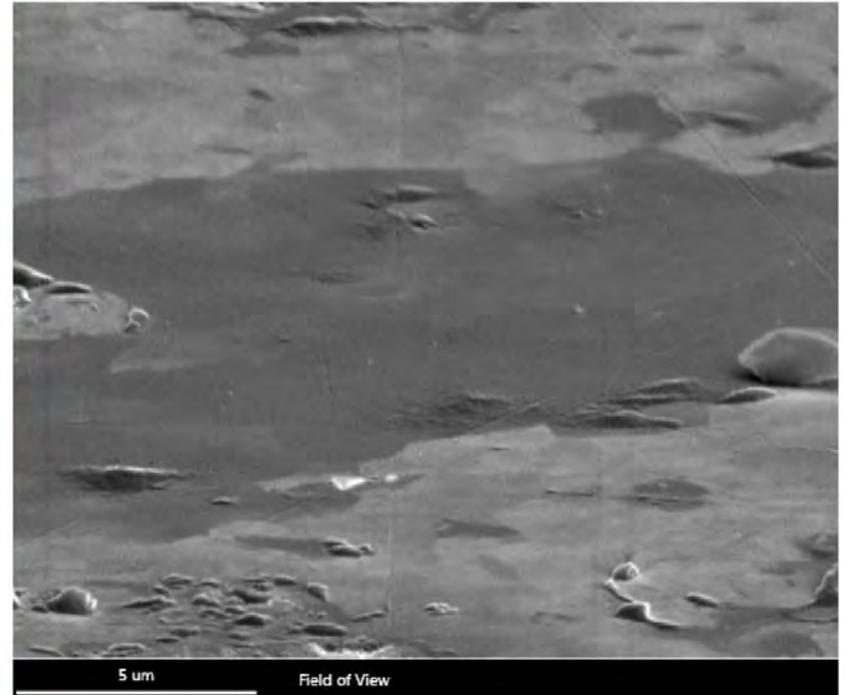
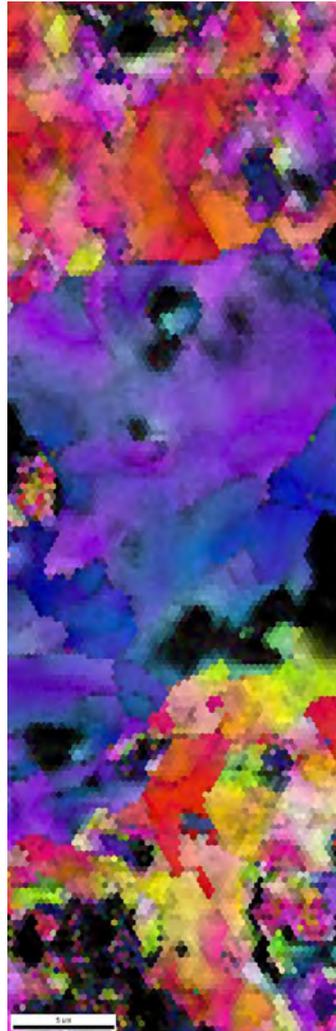
Tungsten flats

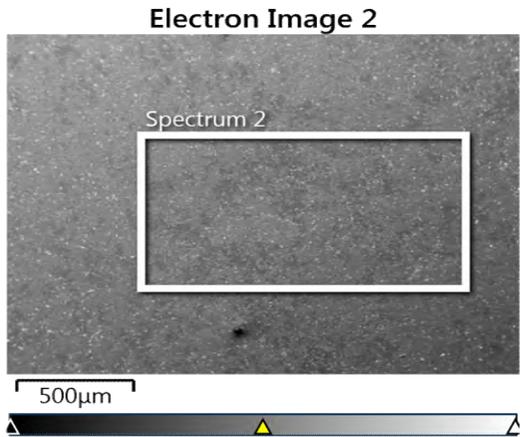


Better shape for testing properties, before termoxidize the tips



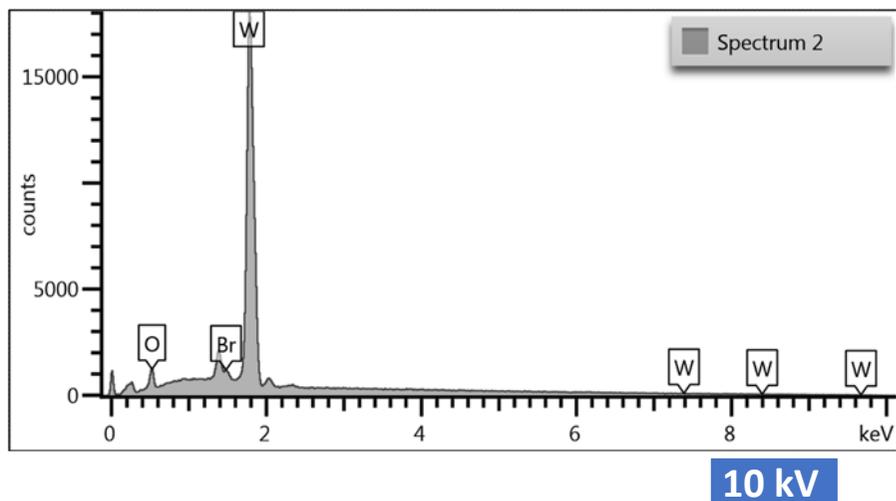
Crystalline structure (polycrystal - affordable)





EDS characterization of the reference.

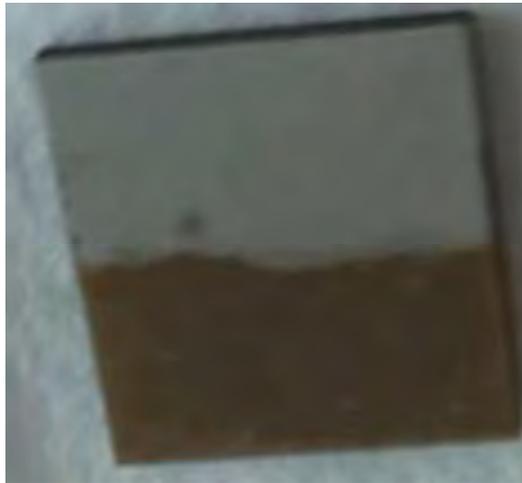
- Native oxide
- Contamination around 1%



Element	Wt%	Wt% Sigma	Atomic %
O	3.23	0.12	27.45
Br	1.07	0.10	1.81
W	95.70	0.15	70.74

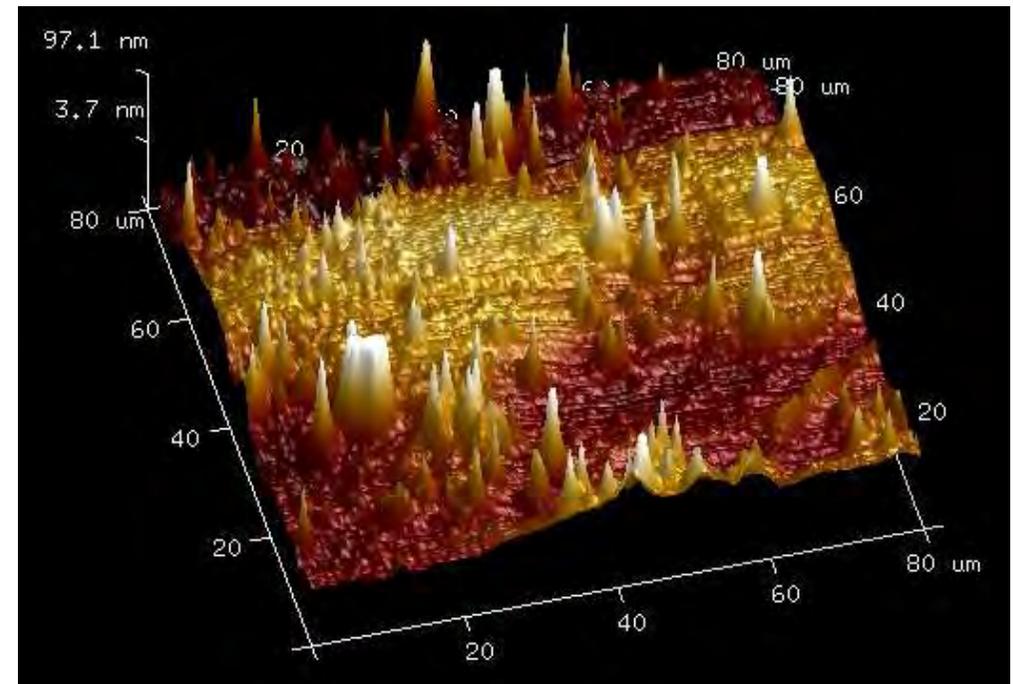
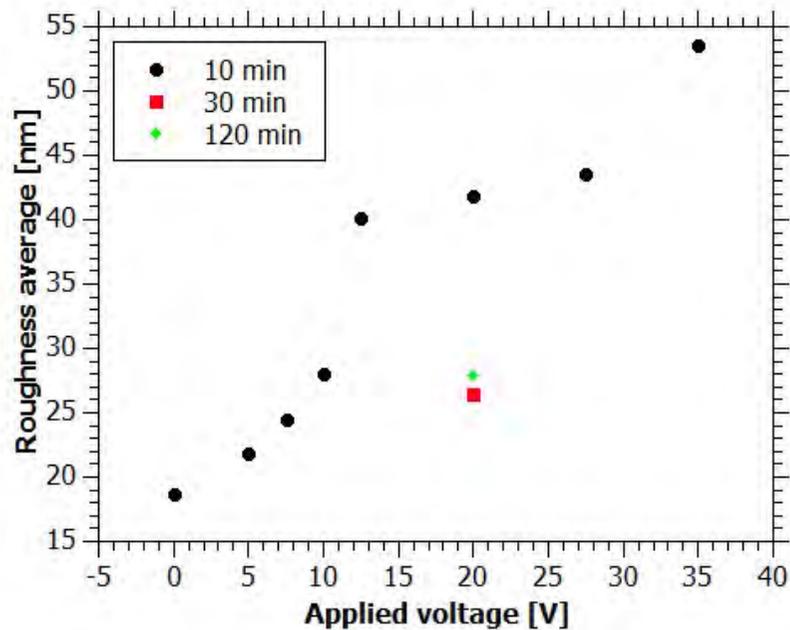
Optimization of anodization conditions

- From 5 V to 35 V (in increments of 7.5 V)
- At 20 V - 30 and 120 minutes
- With increasing anodization voltage, the layer becomes bluer, and the layer is thicker.

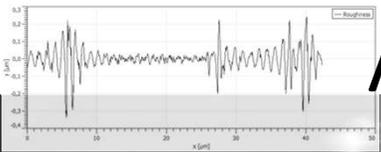


AFM characterization

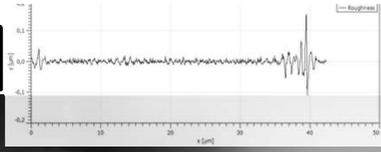
- From AFM - Ra value
- Time reduced roughness, but extending deposition time after 30 minutes had no significant impact.
- The dependency is approximately linear.



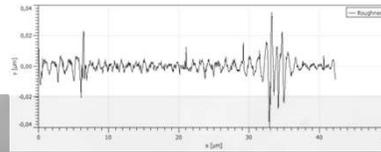
AFM



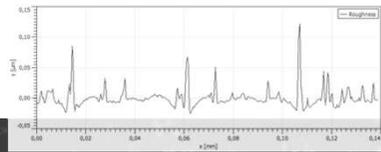
750°C short



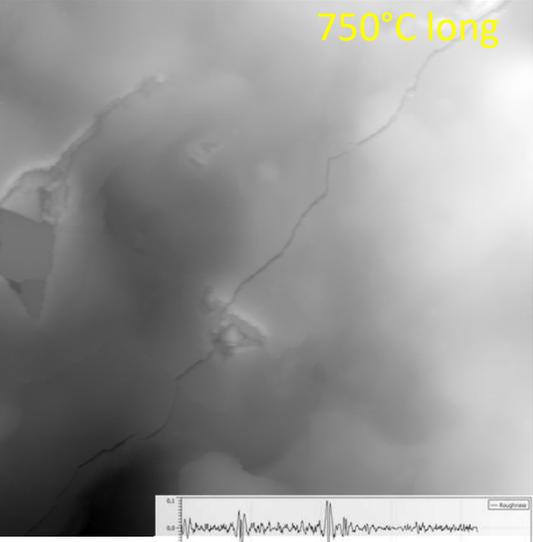
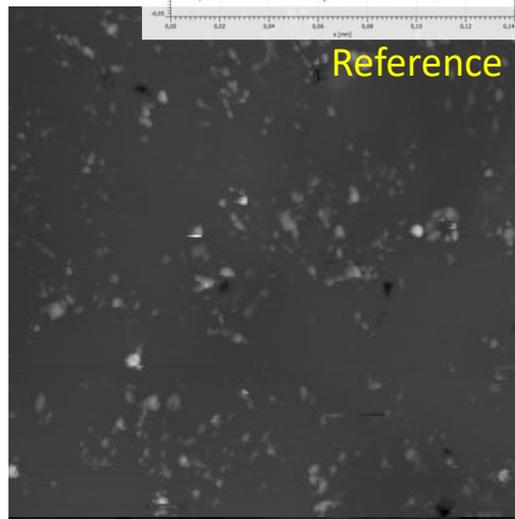
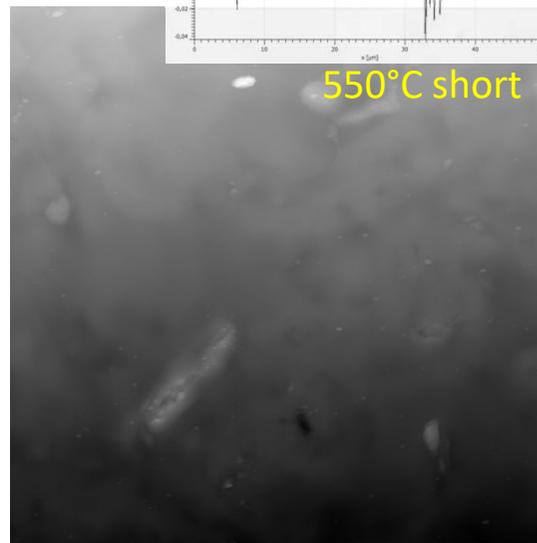
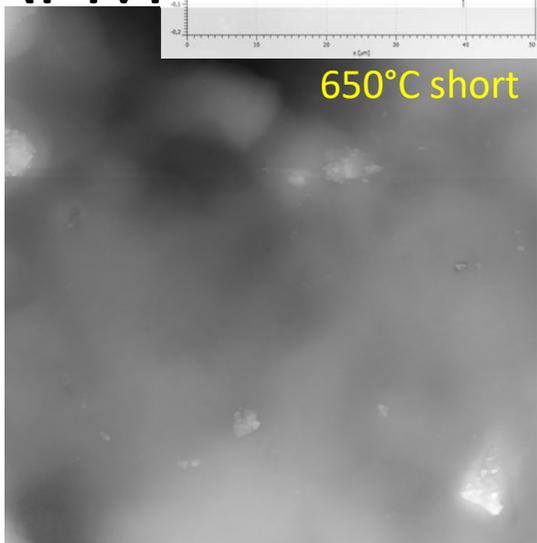
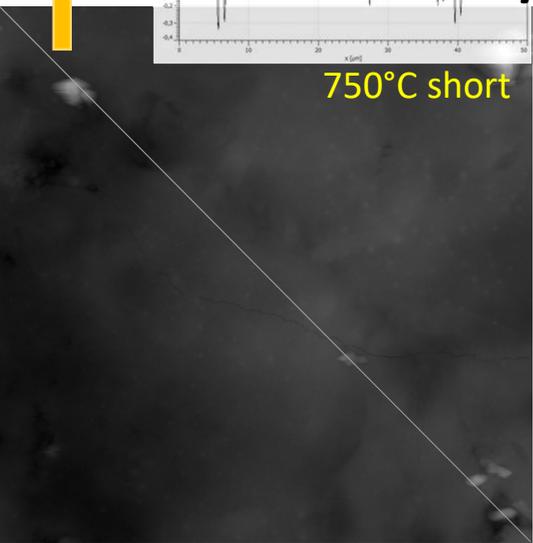
650°C short



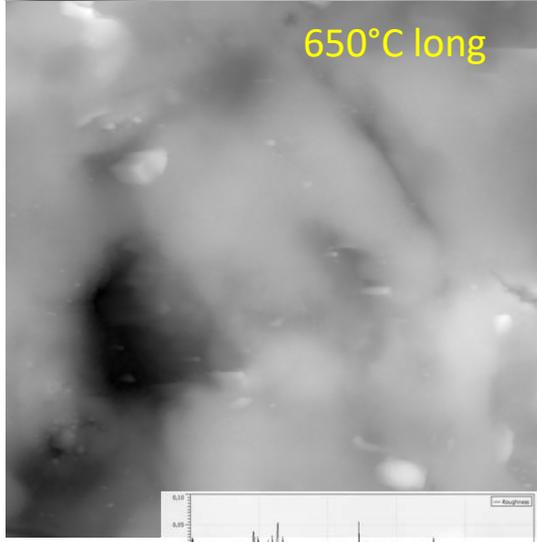
550°C short



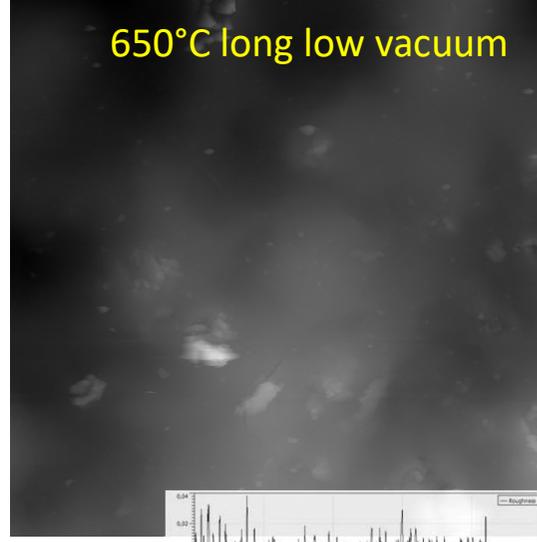
Reference



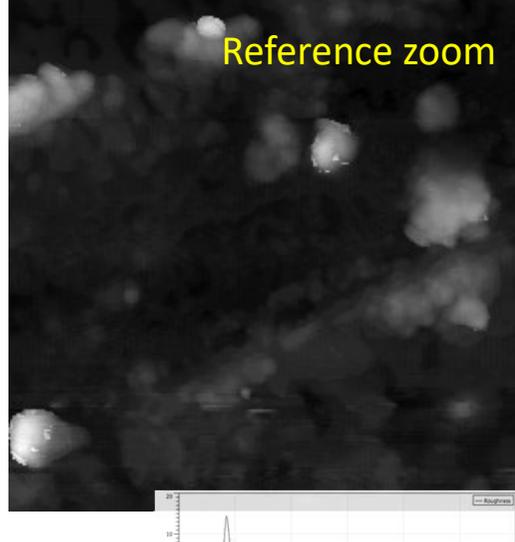
750°C long



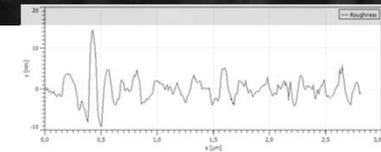
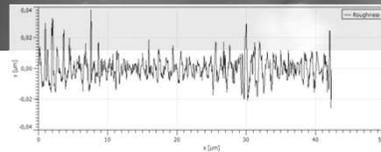
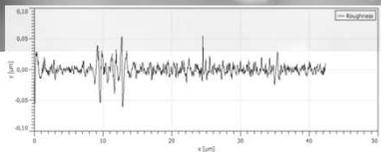
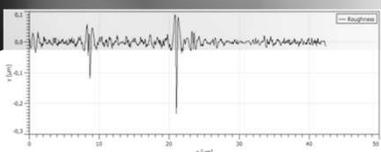
650°C long



650°C long low vacuum

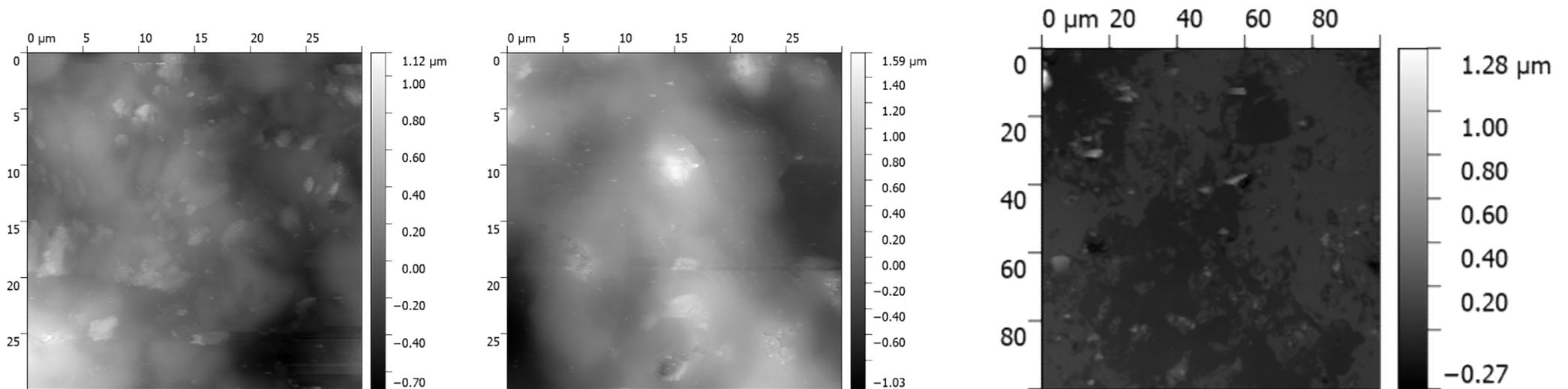


Reference zoom

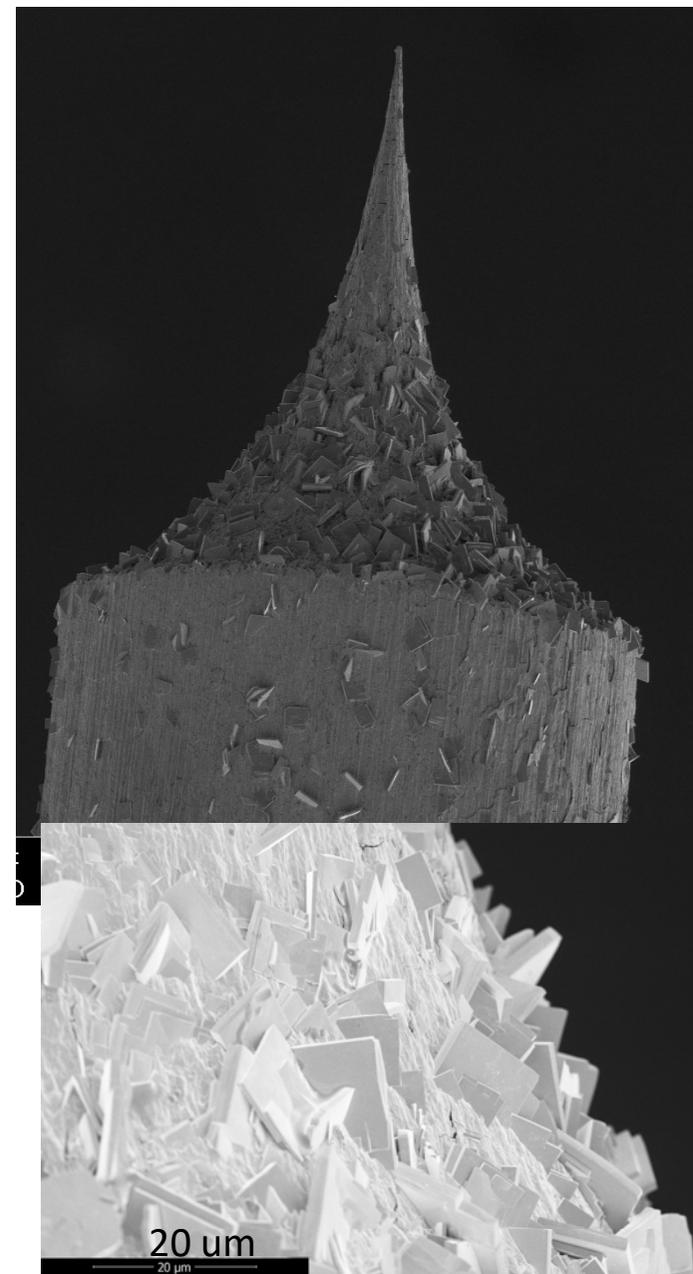
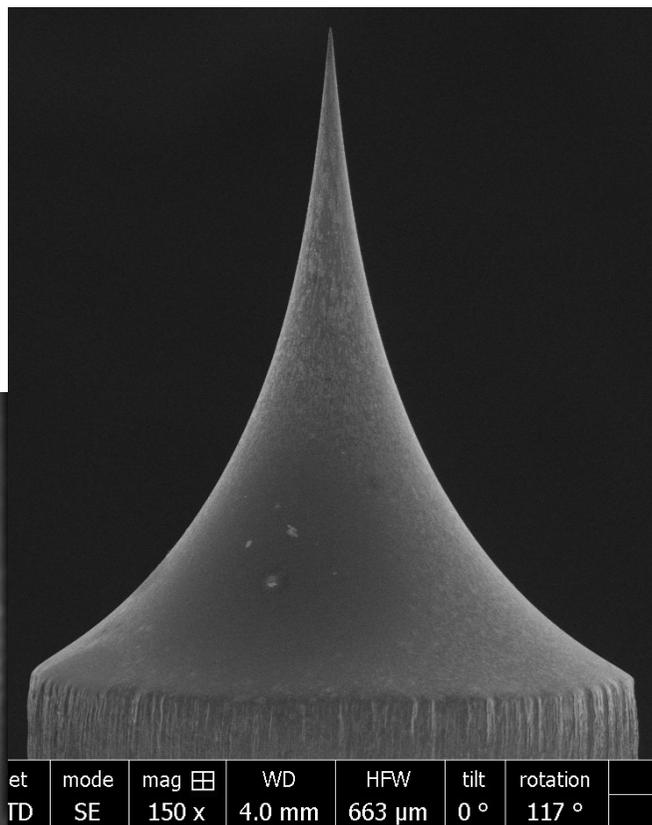
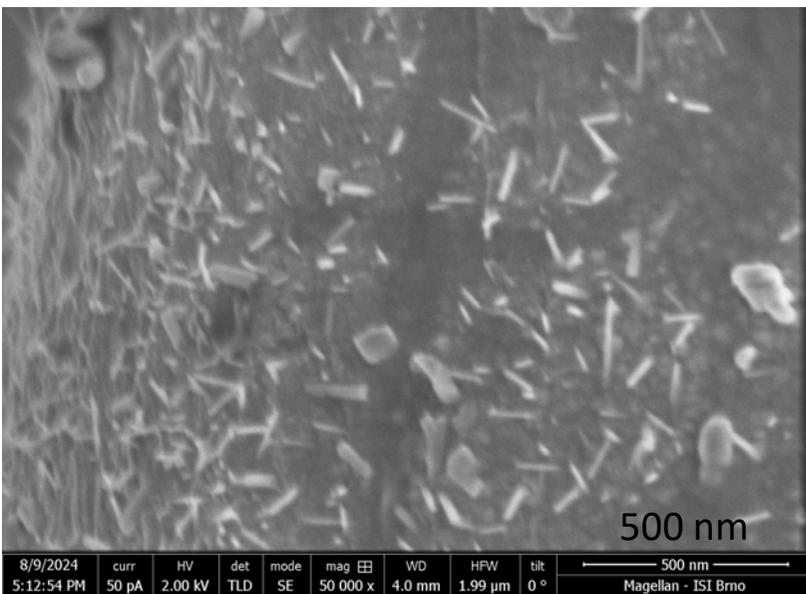


Comparison with thermooxidation

- Pores may form during anodisation, visible small sharper areas
- Thermooxidation tends to produce grains

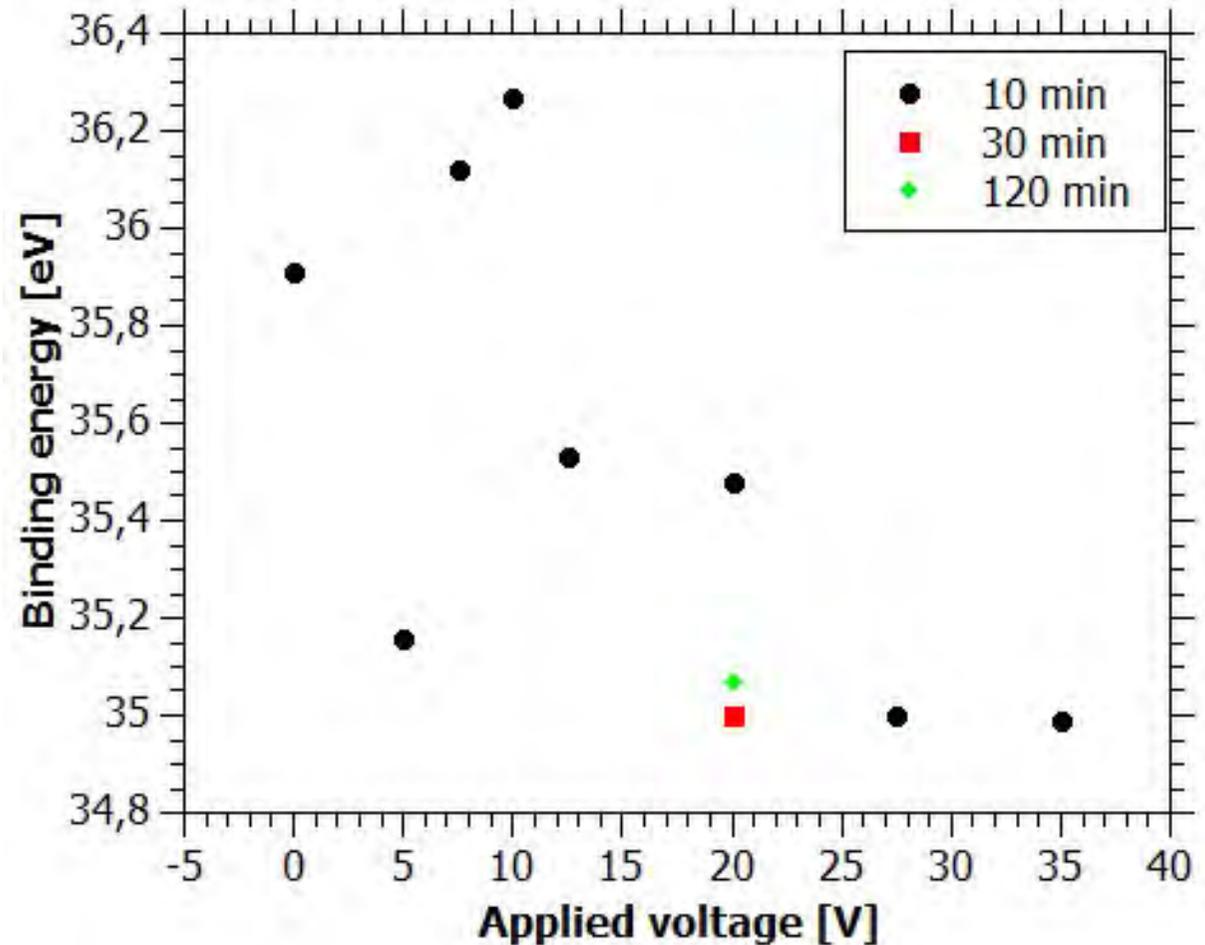


Crystals after anodization



XPS characterization Anodization

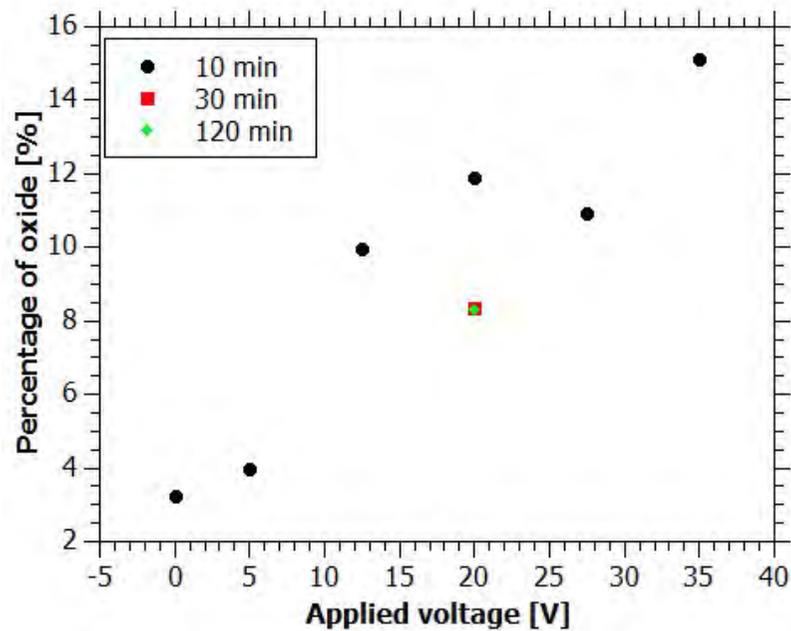
- Binding energies help determine the composition of the WO_2 or WO_3 layer.
- Samples at 7.5 V and 10 V were added later because this voltage range seemed promising.



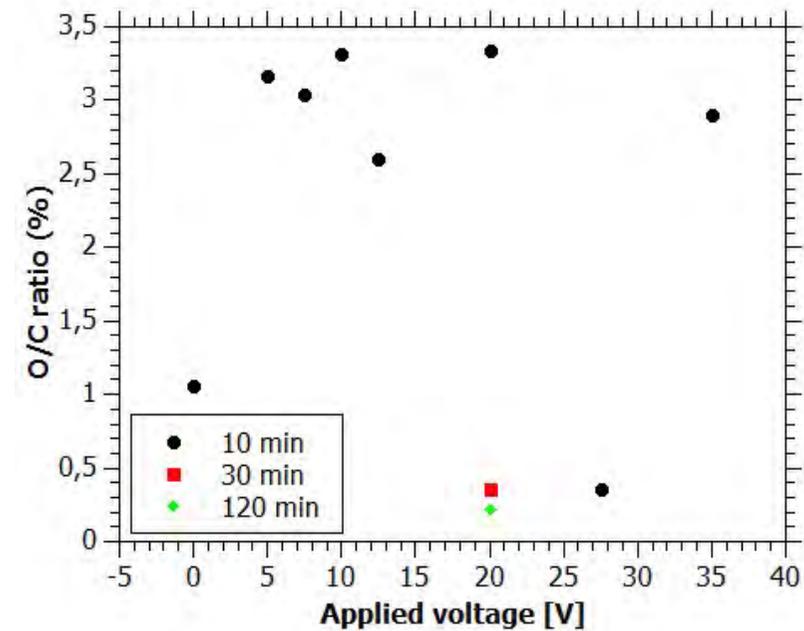
Chemical composition

- The O/C ratio of XPS seemed to be similar, but EDS showed an increased proportion of oxide (with an approximately linear dependence).
- The EDS results may also depend on the thickness of the oxide layer.
- Longer anodization time decreased both the O/C ratio and the percentage of

EDS

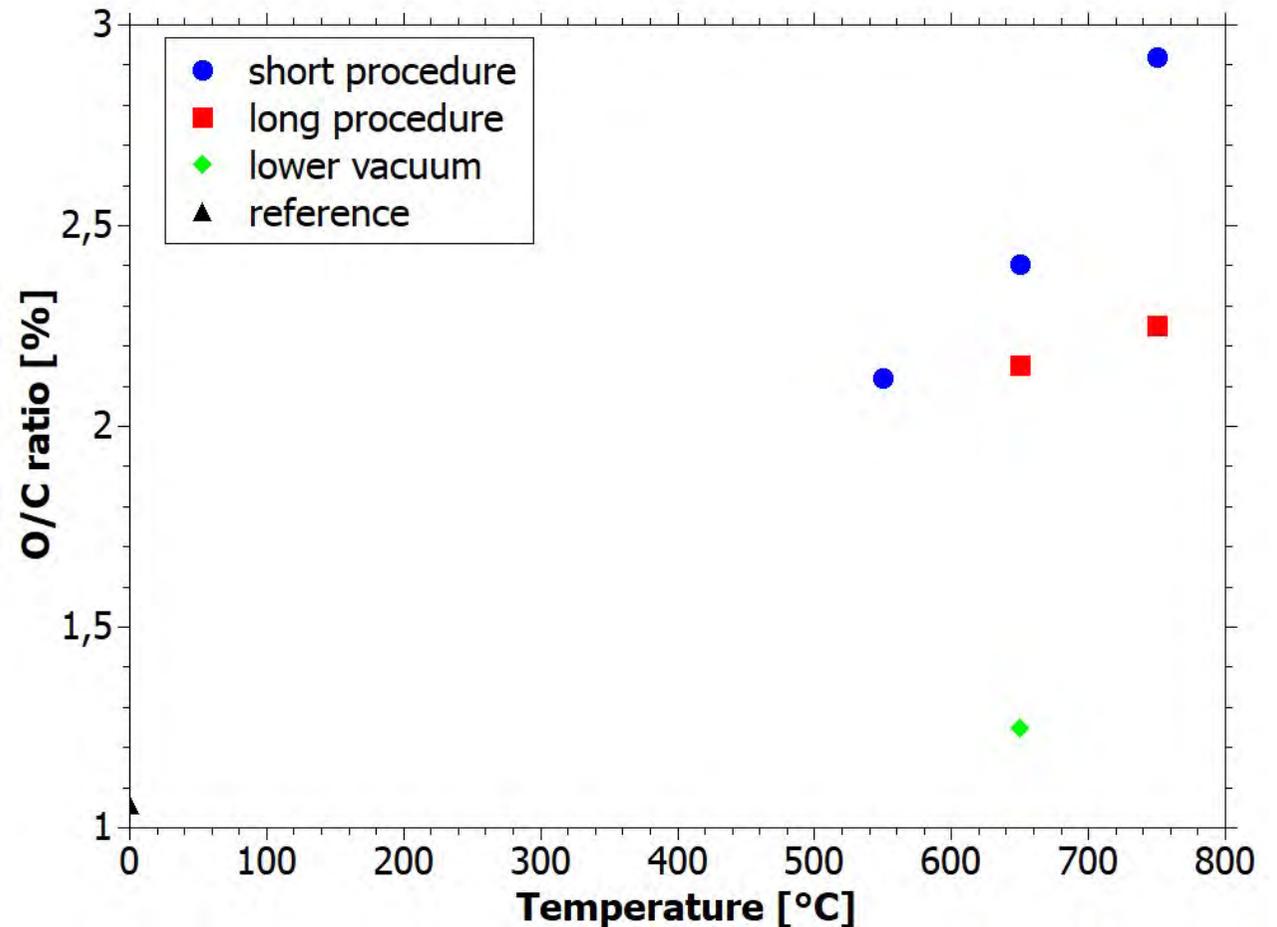


XPS



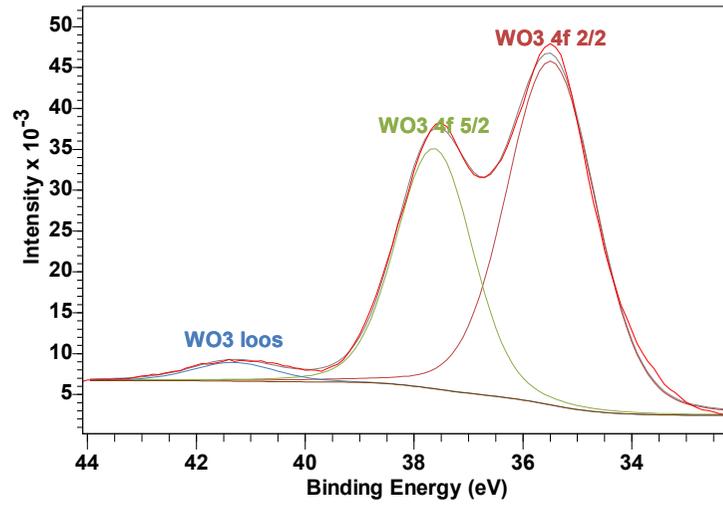
Chemical Analyses Termooxidation

- Lower vacuum – similar O/C ratio to reference
- In longer procedure, increasement in O/C ratio is not very large

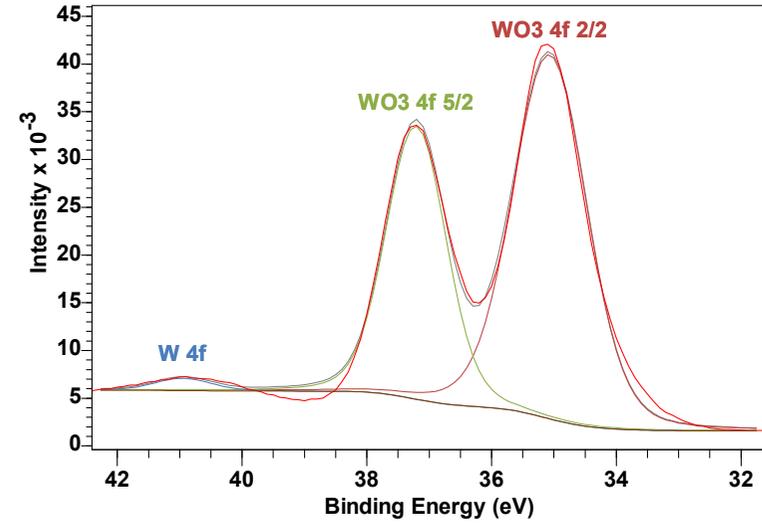


XPS spectra

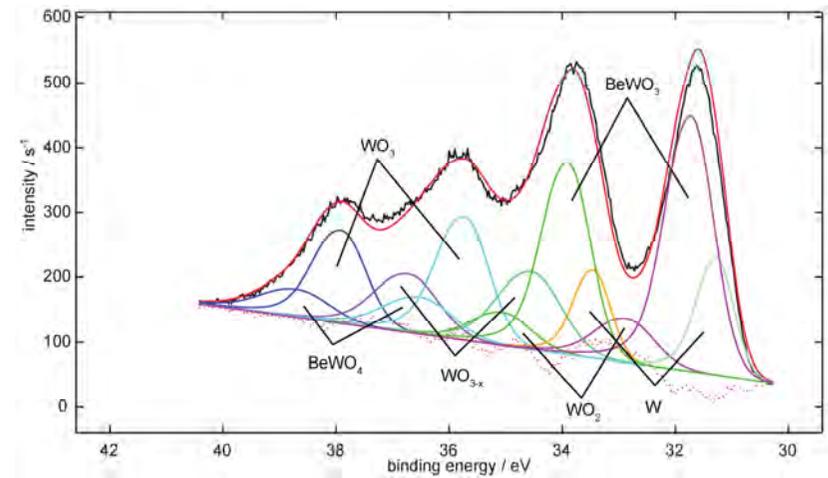
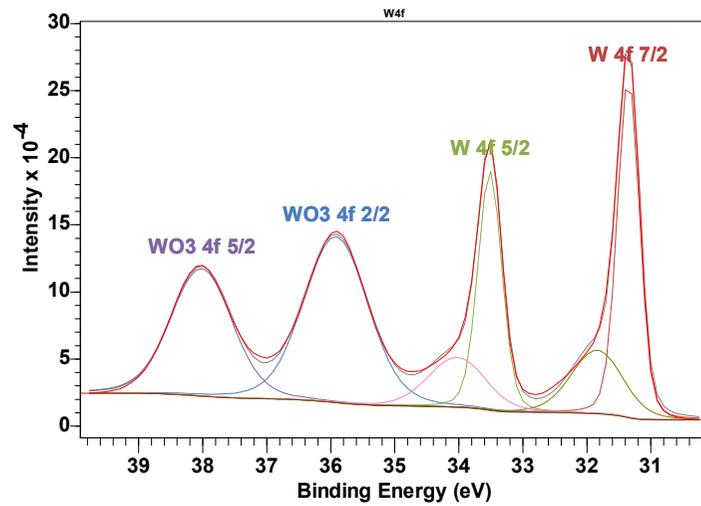
10 min



120 min

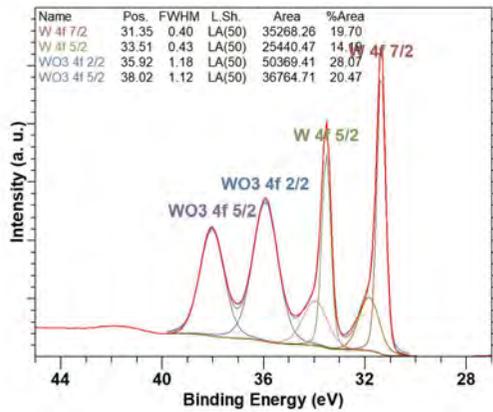
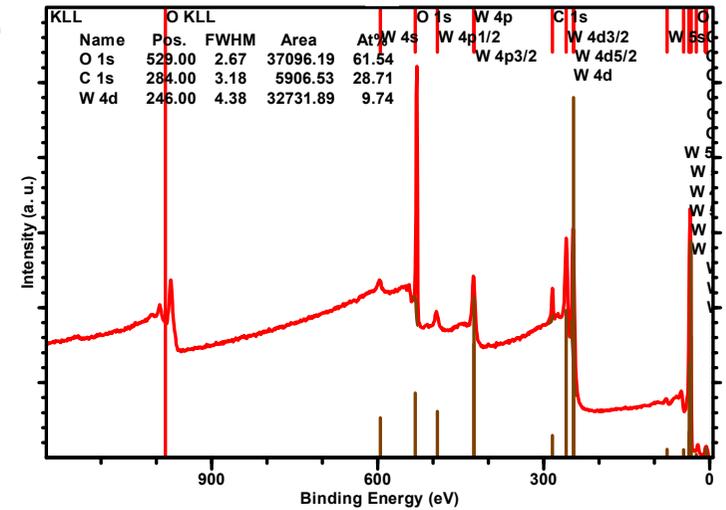


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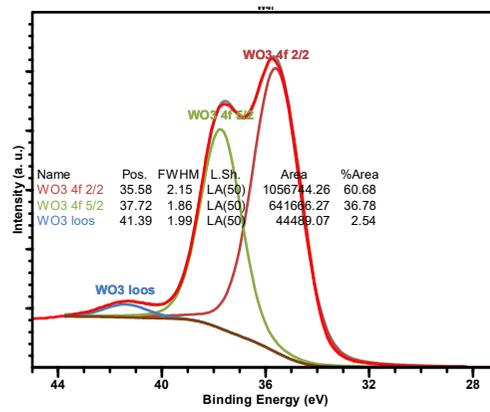


Termooxidation spectra from XPS

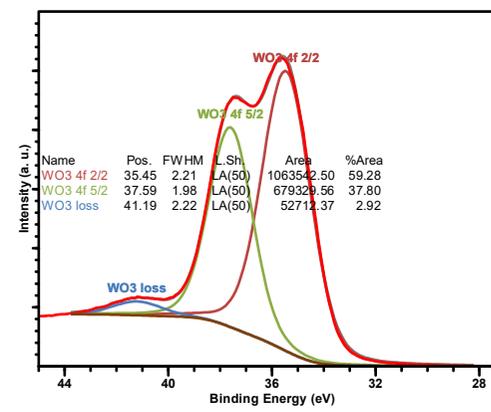
- Native oxide on reference sample
- Negligible impurities (traces of nitrogen and copper were found on some samples)



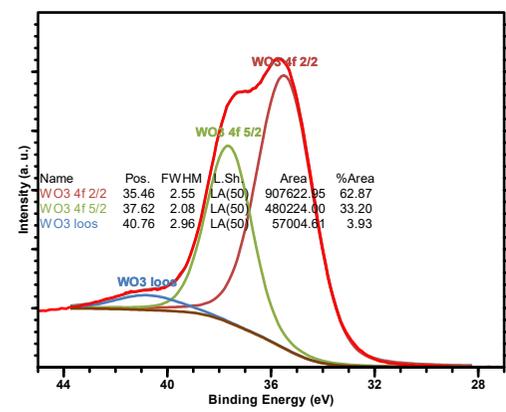
Reference



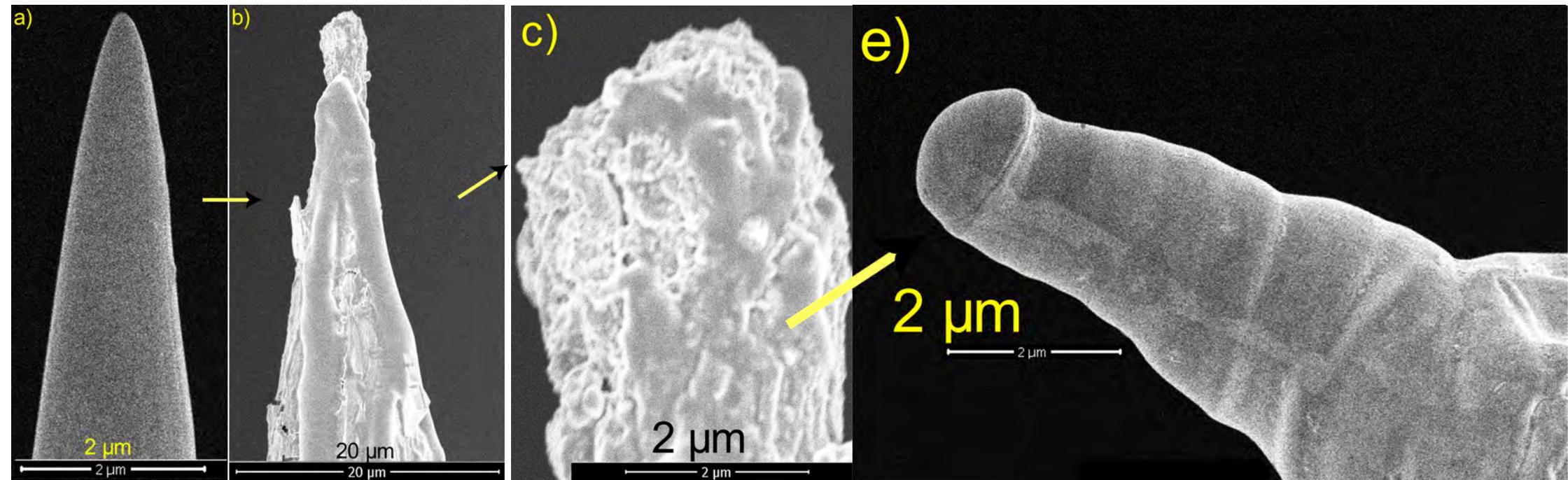
Longer 650 °C



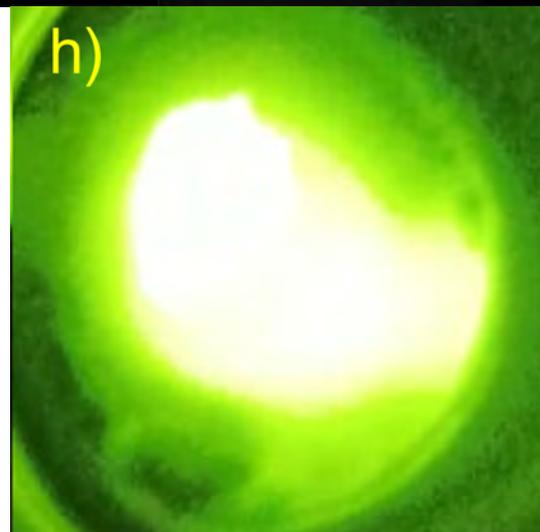
Shorter 650 °C



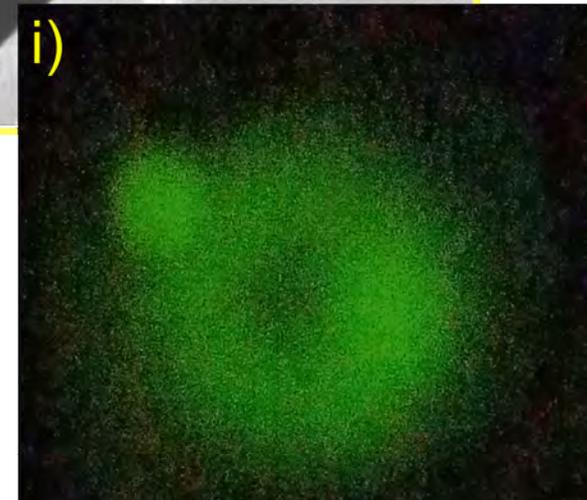
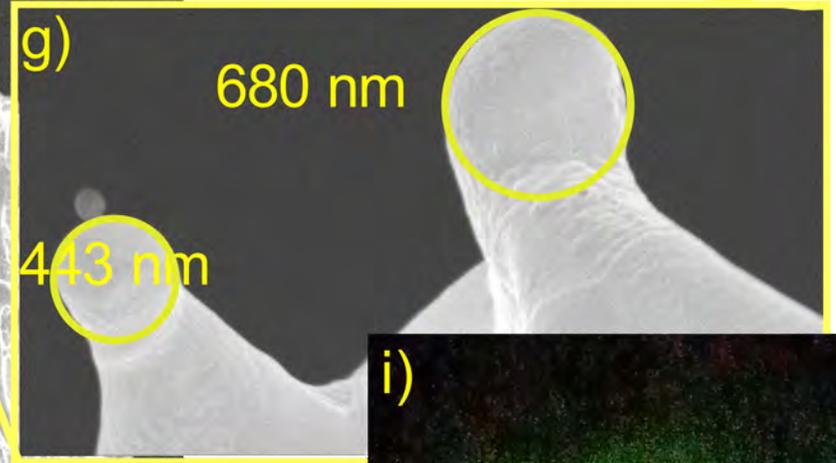
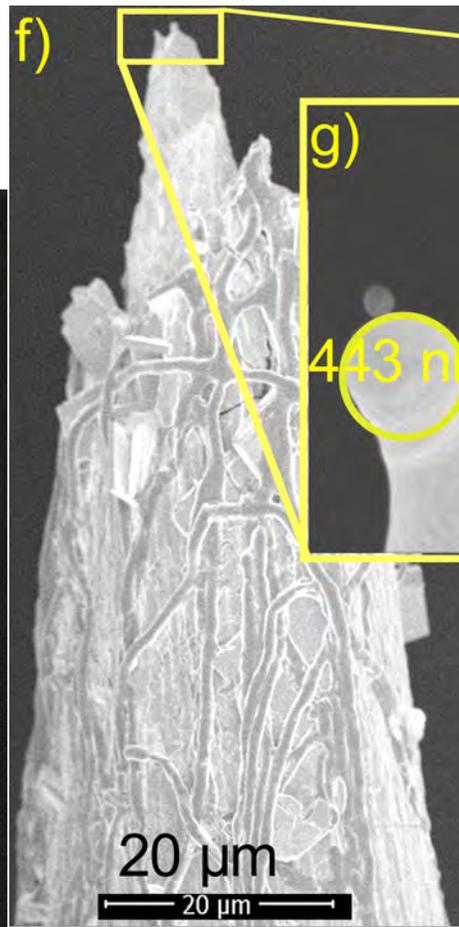
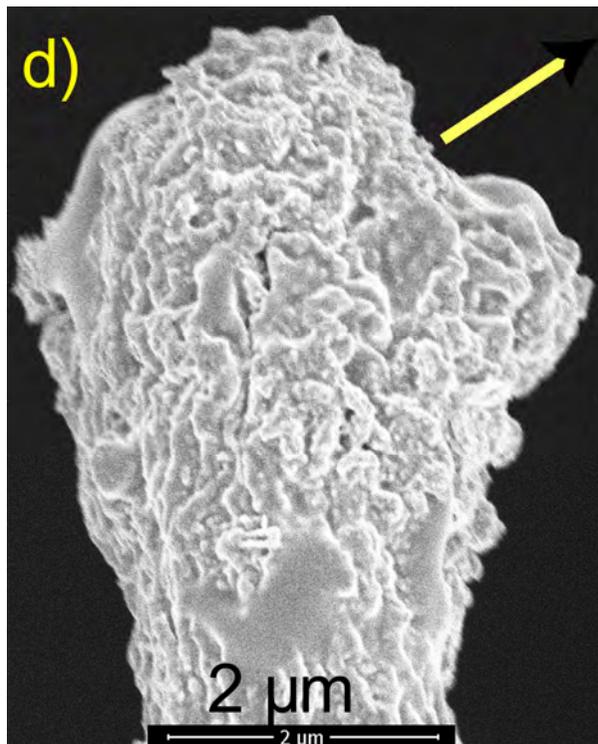
Longer 650 °C low vacuum



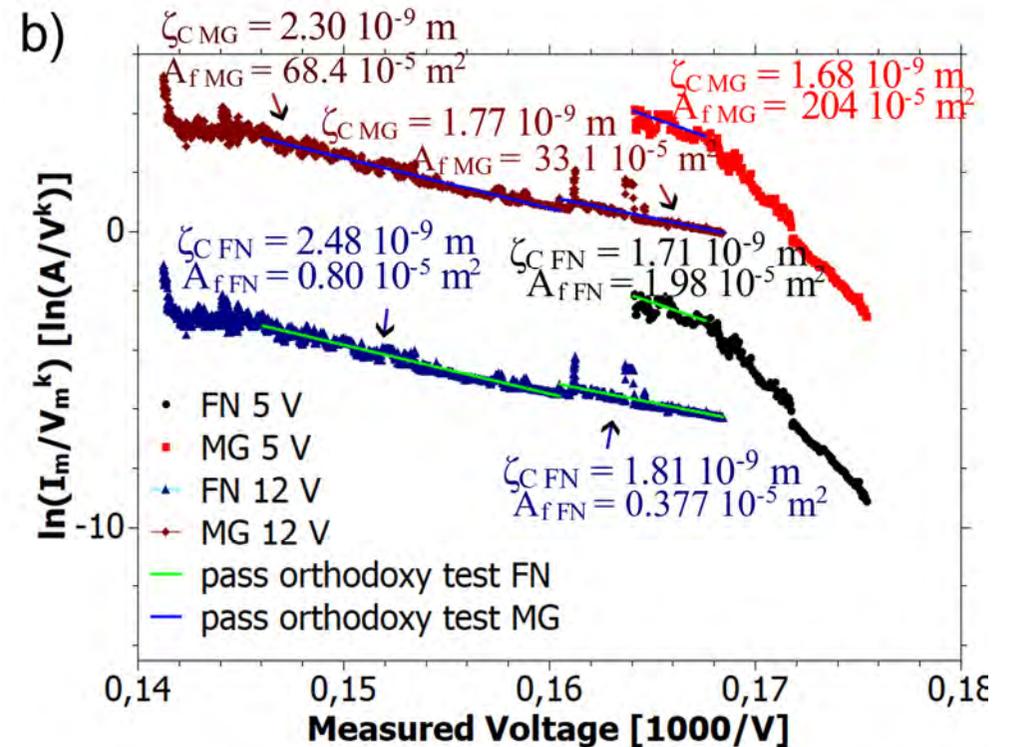
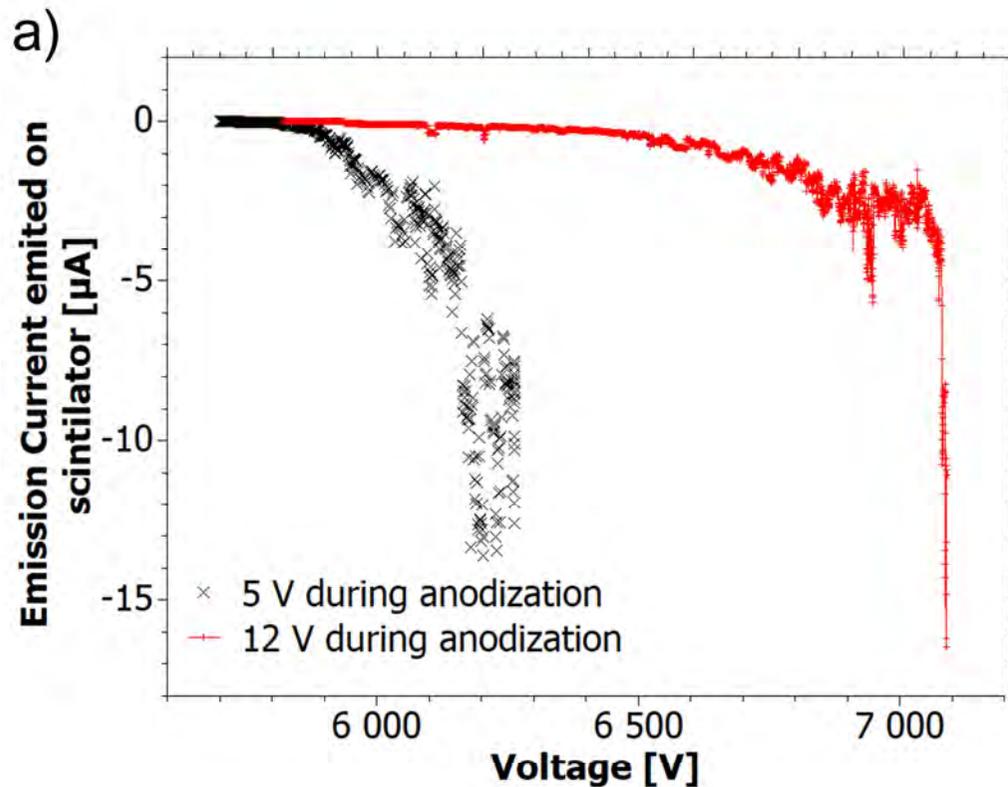
- Shape of oxidised head has impact on the final shape - depending on how the change of state takes place



if it expands it can create more stable „circles“ at the end



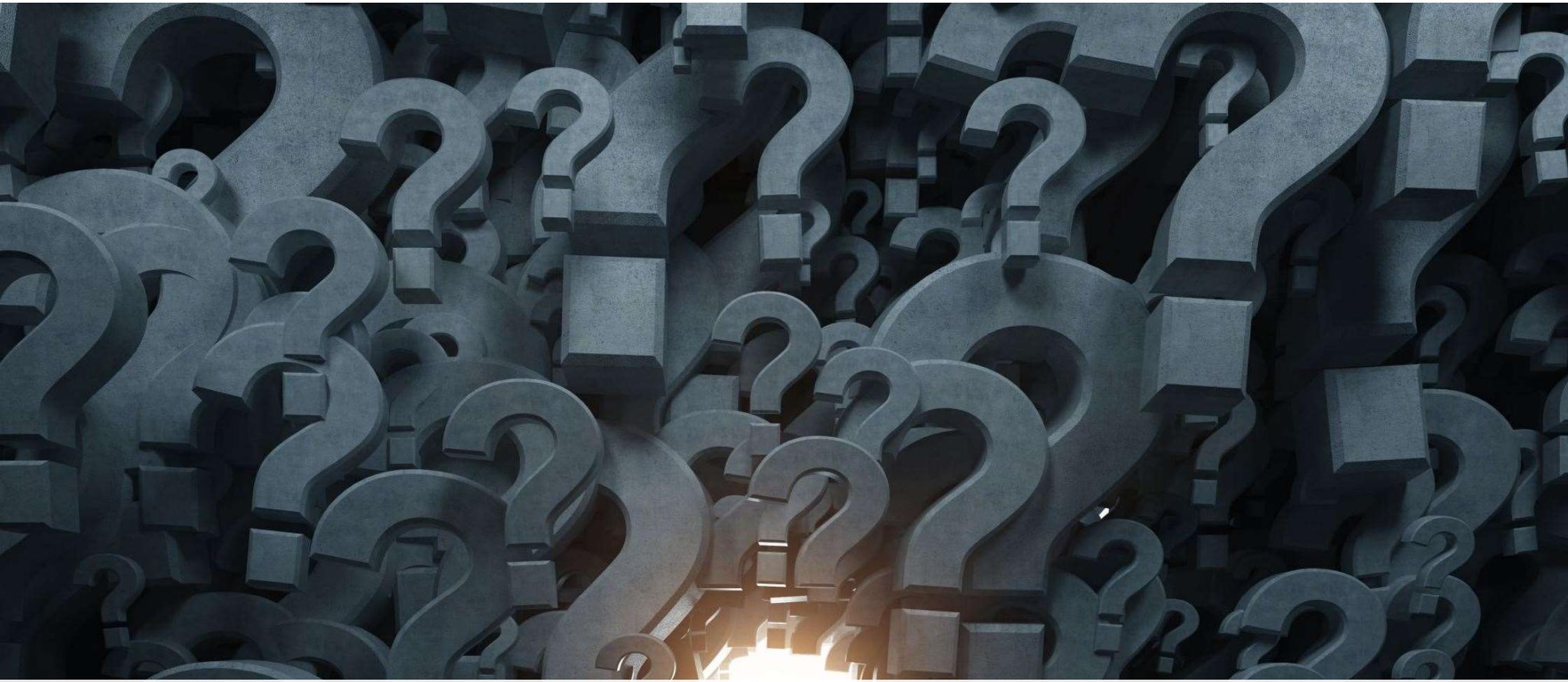
Emission current + Fowler–Nordheim and Murphy-Good plot



Conclusion

- Anodization – large crystals, the explosive electron emission occurs
- Thermo-oxidized tips - I expect more stable
- Oxide layer evaporation, often considered undesirable, can sometimes provide useful and stable tip shapes after explosive electron emission.
- Applicable for biosensors – only tips will remain sensitive for conduction





Questions