High Ion Flux Plasma Nanostructures for Electrochemical Applications

Anja Bieberle-Hütter [1], R. Sinha [1], I. Tanyeli [1], R. Lavrijsen [2], M.C.M. van de Sanden [1,3]

[1] DIFFER – Dutch Institute for Fundamental Energy Research

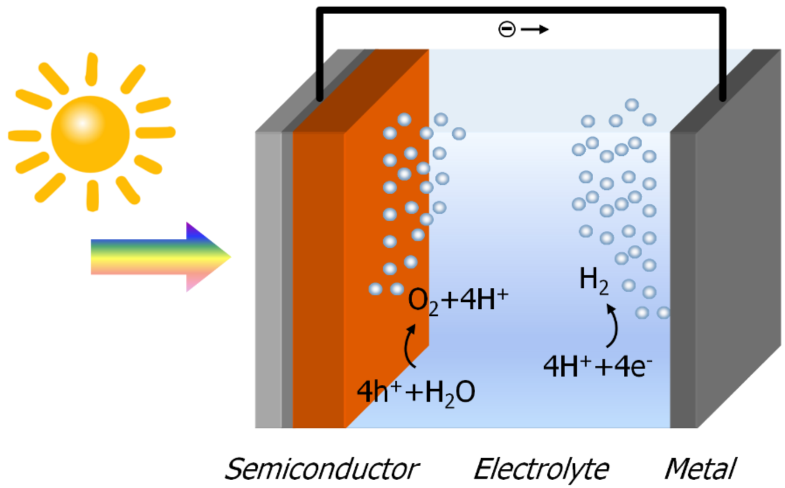
[2] Physics of Nanostructures and center for NanoMaterials (cNM), Applied Physics, Eindhoven University of Technology (TU/e)

[3] Plasma and Materials Processing, Department of Applied Physics, Eindhoven University of Technology (TU/e),

Eindhoven, the Netherlands

Electrochemical Energy Applications

Photo-electrochemical water splitting



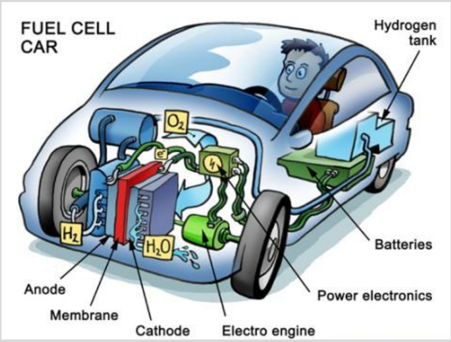
Krol and Graetzel (2012).

direct use

storage

transformation into liquid fuel

Fuel Cells

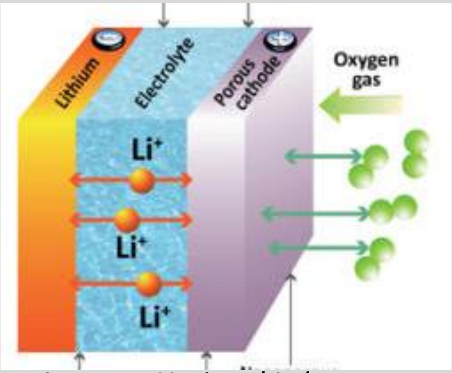


www.imageproduction.nl

Electrolyser

www.wikipedia.com

Batteries



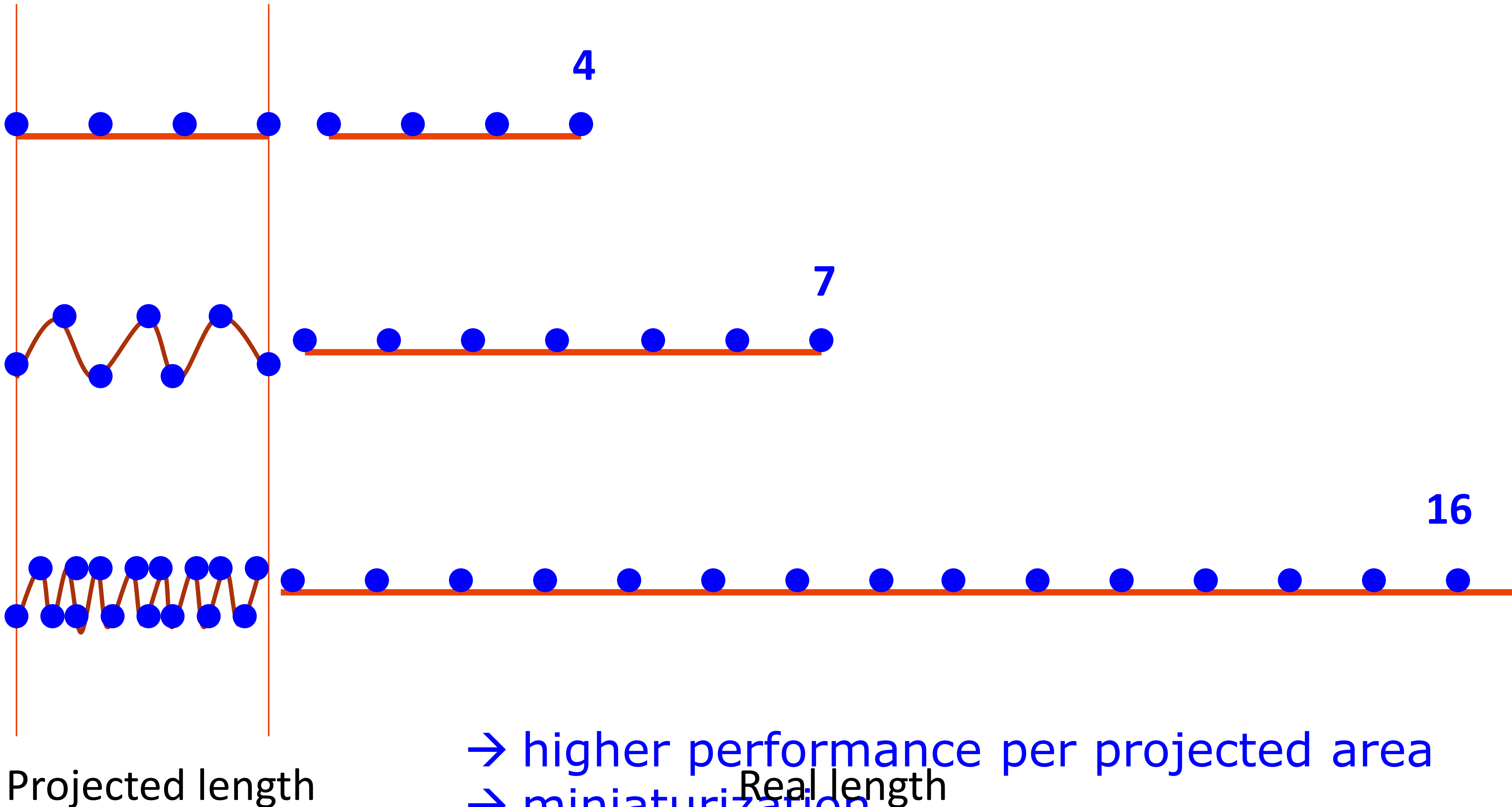
Argonne National Laboratory

Electrochromic windows

www.greengeek.ca

Progress in performance is required → large surface area

The Importance of Large Surface Area

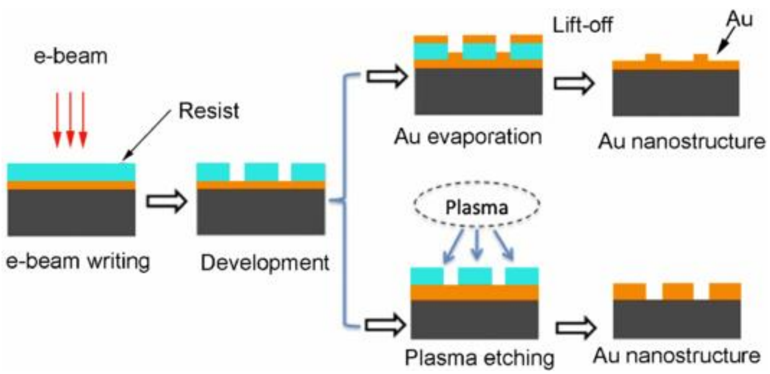


→ higher performance per projected area
→ miniaturization

Fabrication of Large Surface Area Thin Films

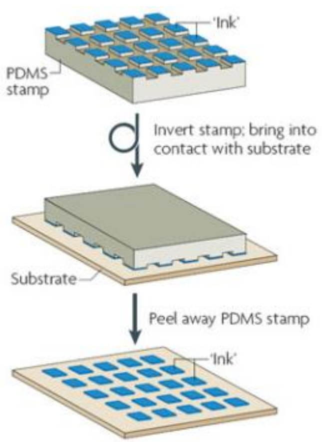
Top down

E-beam lithography



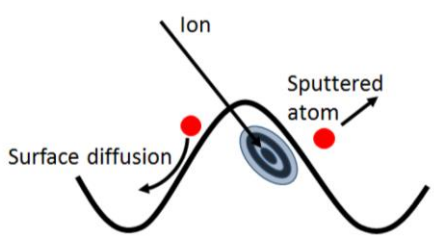
Yue et al., J. Micromech. Microeng. (2012)

Soft lithography



https://ninithi.com

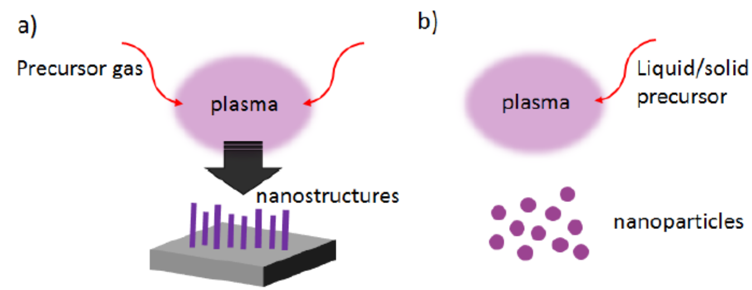
Ion beam sputtering



Thesis Tanyeli (2016)

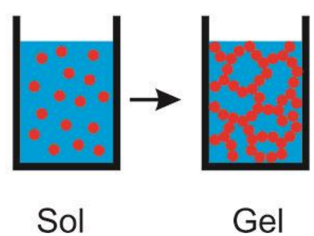
Bottom up

Vapor methods



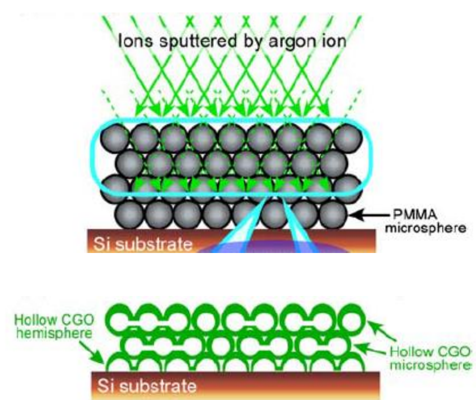
Thesis Tanyeli (2016)

Sol gel



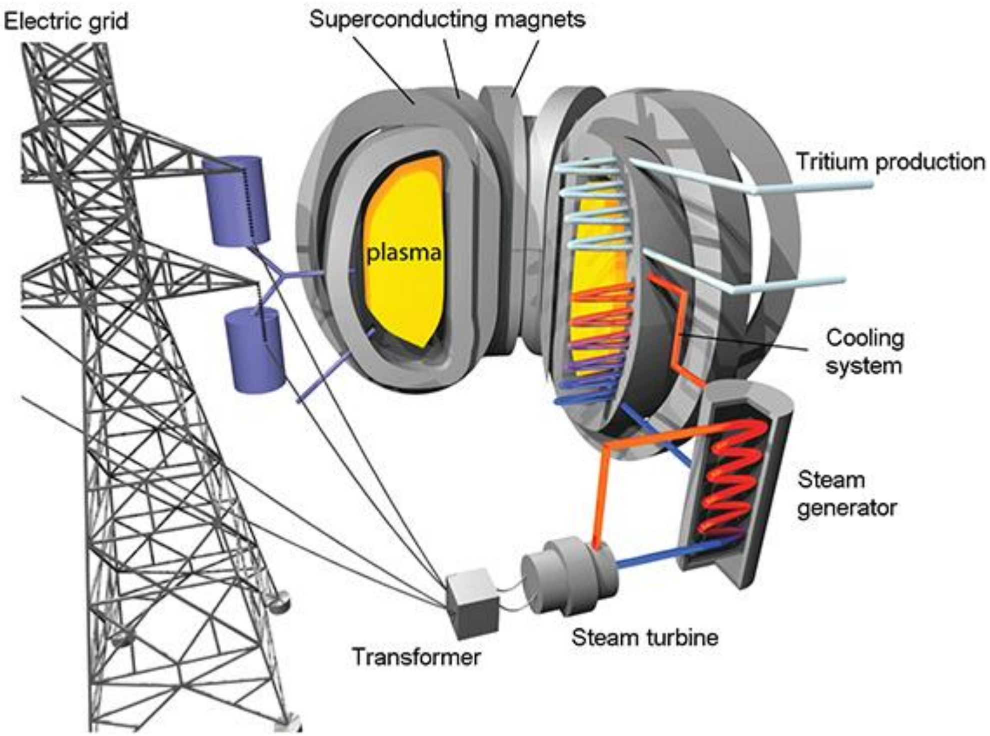
http://soft-matter.seas.harvard.edu/

Self-assembly



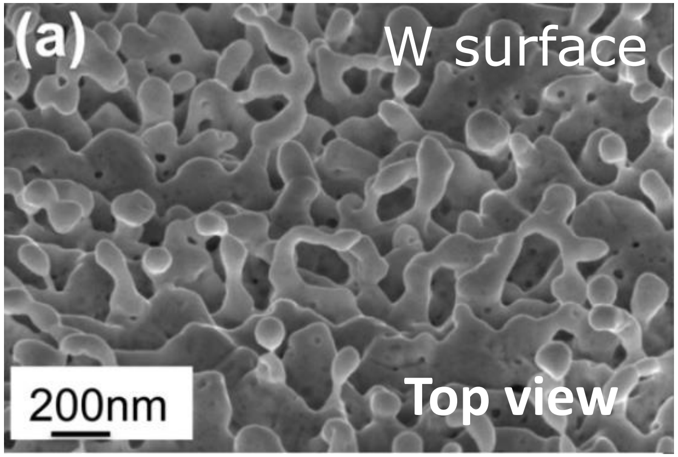
Hyodo, ABH et al., J. Electroceram. (2006).

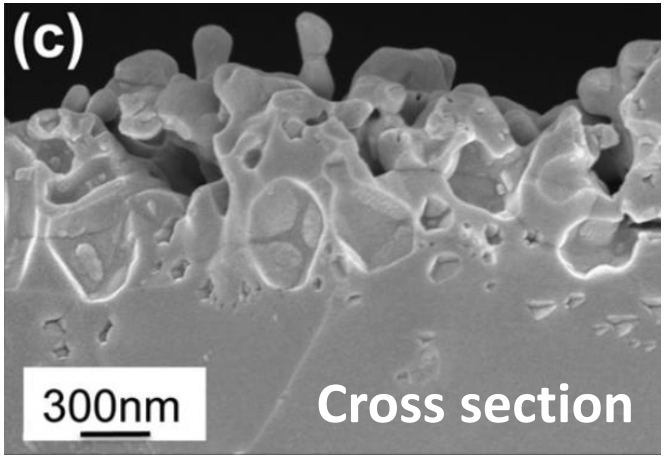
High Ion Flux He Plasma Nanostructuring: Nanofuzz in Fusion



[1] *Baldwin and Doerner, Nucl. Fusion 48 (2008) 035001.*

[2] *Kajita et al., Appl. Phys. Express, 3 (2010) 085204.*

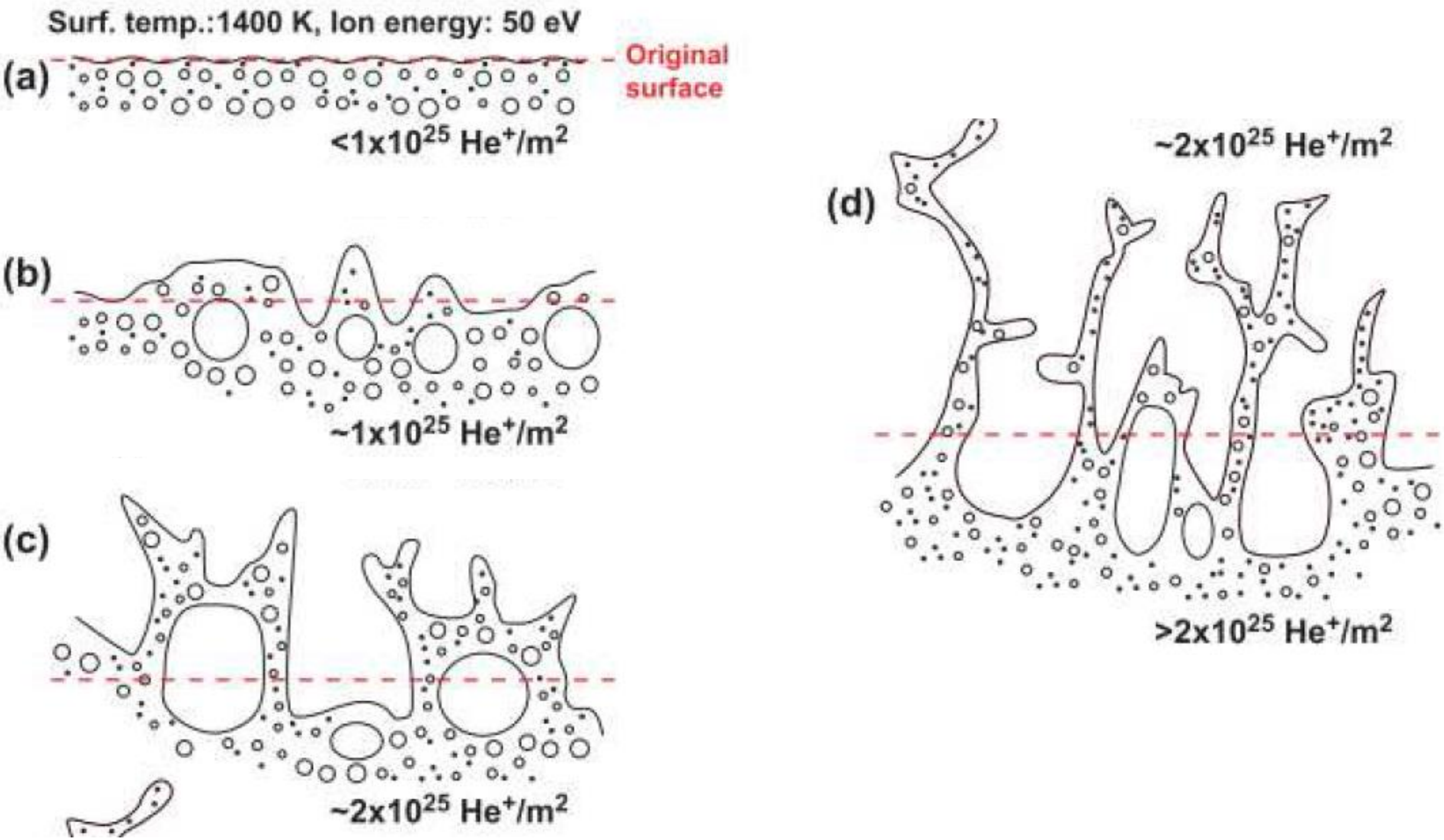




De Temmerman et al., J. Vac. Sci. Technol. A (2012).

New method of making nanostructured surfaces:
High Ion Flux Plasma Exposure

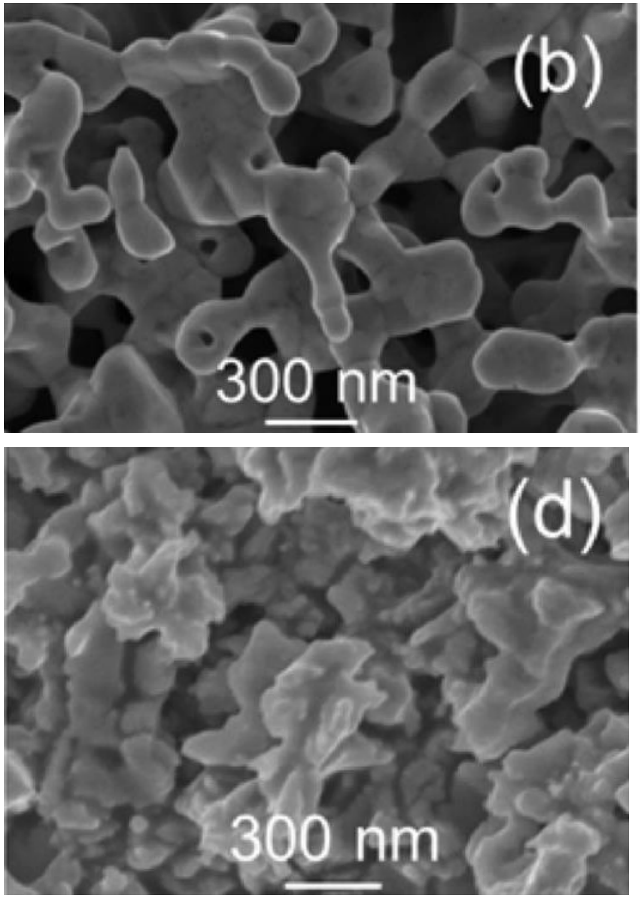
Mechanism of Nanostructuring



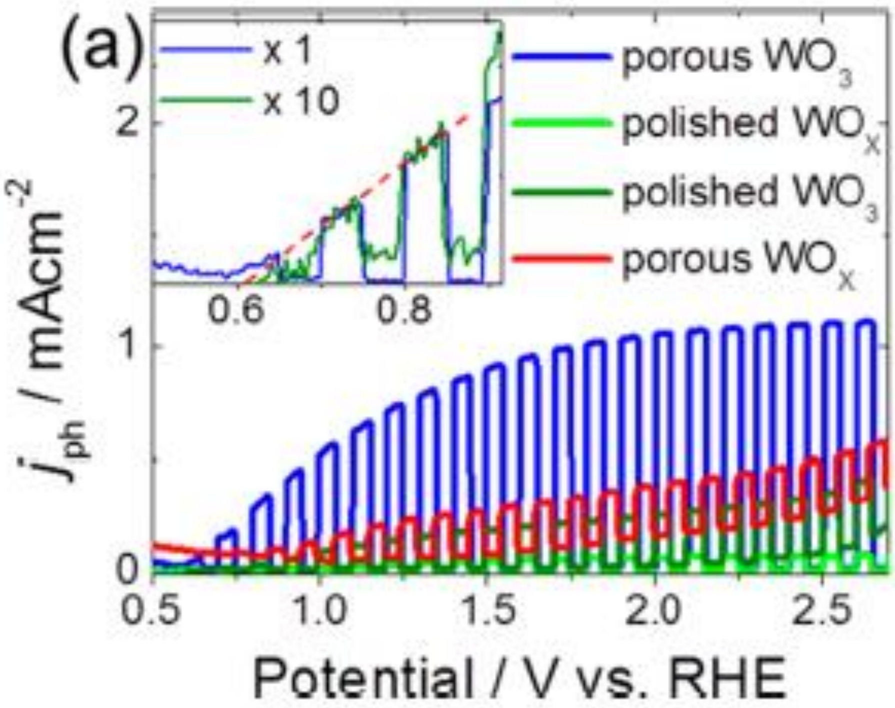
Kajita et al., J. Nucl. Mater. 418 (2011) 152.

Plasma Nanostructuring for Electro-chemical Applications

Example: Photoelectrode for water splitting



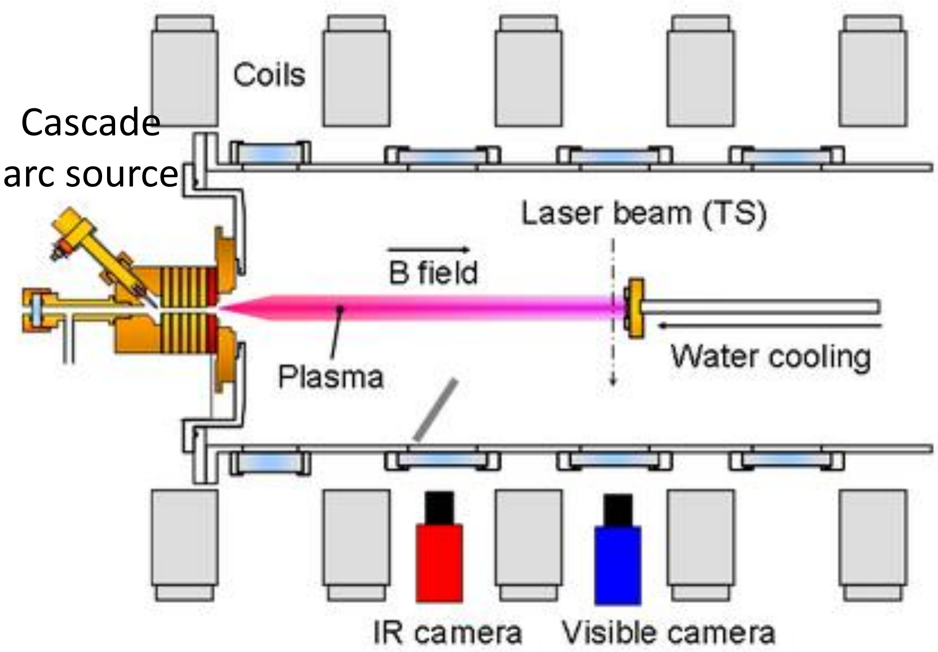
Bulk material



De Respinis et al., ACS Appl. Mater. Interfaces 5 (2013) 7621.

High Ion Flux He Plasma Exposure

Magnetic coils (1.6 T max.)



Typical plasma treatment parameter	
Gas	He
Electron density	$0.4–30*10^{22}$ m^{-3}
Ionisation energy	Few eV-60 eV
Ion flux (max.)	10^{25} m^{-2} s^{-1}
Magnetic field	< 1.6 T
Temperature	~ 1000°C
Discharge current	150-250 A
He flow rate	1.4-2 slm

High ion flux plasma exposure of thin films
→ parameter evaluation

De Temmerman et al., J. Vac. Sci. Technol. A (2012).

Challenges for Thin Films

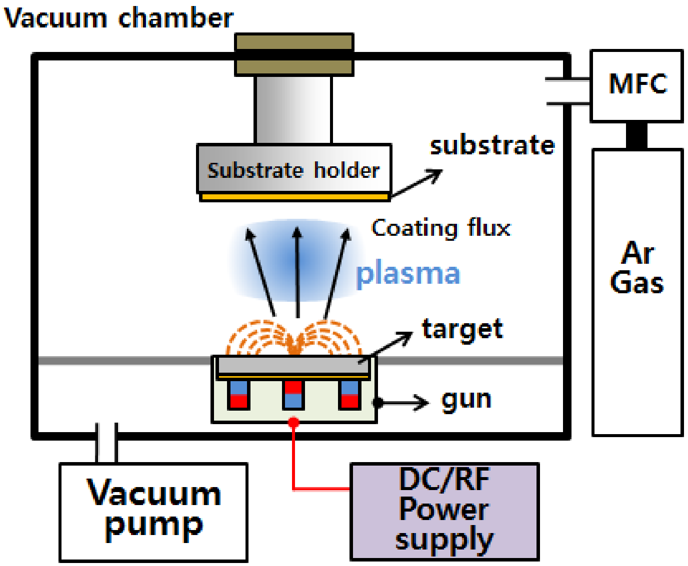
- **Substrate – thin film interface**
  - Thermal stability
  - Delamination
  - Interdiffusion
  - Penetration depth

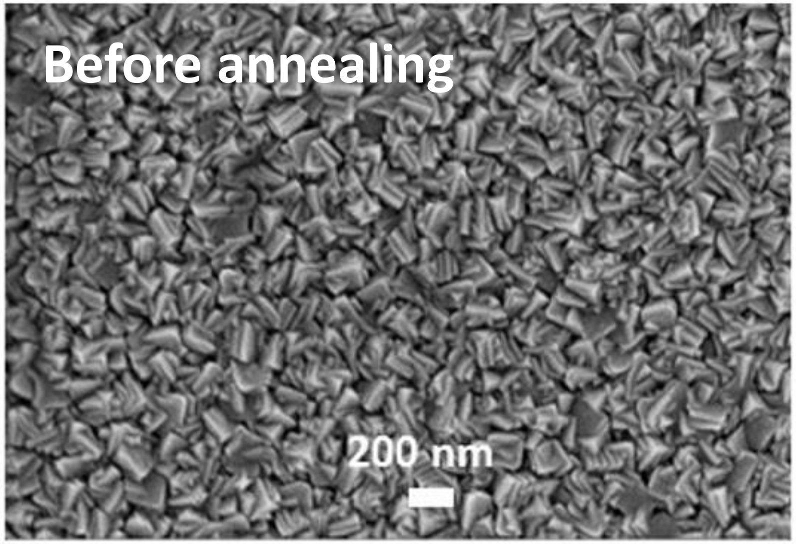
- **Substrate**
  - Thermal stability
  - Undesired nanostructuring of substrate

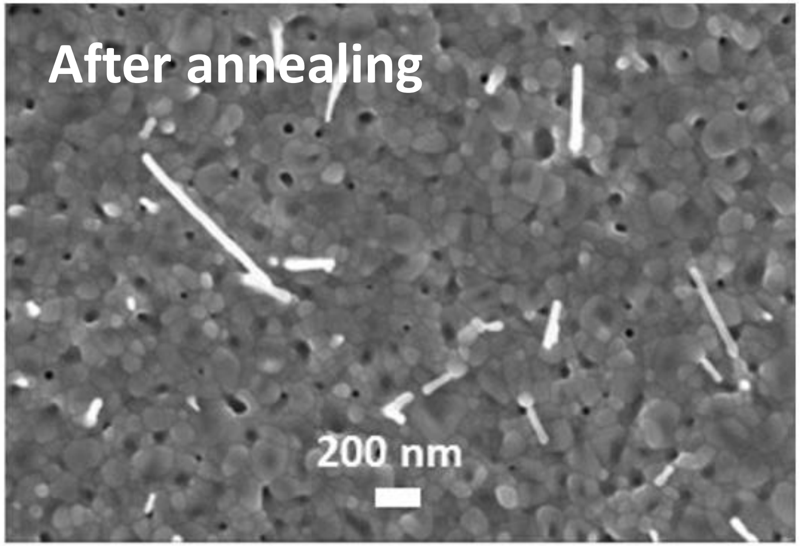
Bieberle-Hütter, Tanyeli, Lavrijsen, Koopmans, van de Sanden
Thin Solid Films (2016) submitted.

DC Sputtering of Fe Thin Films

http://marriott.tistory.com/97

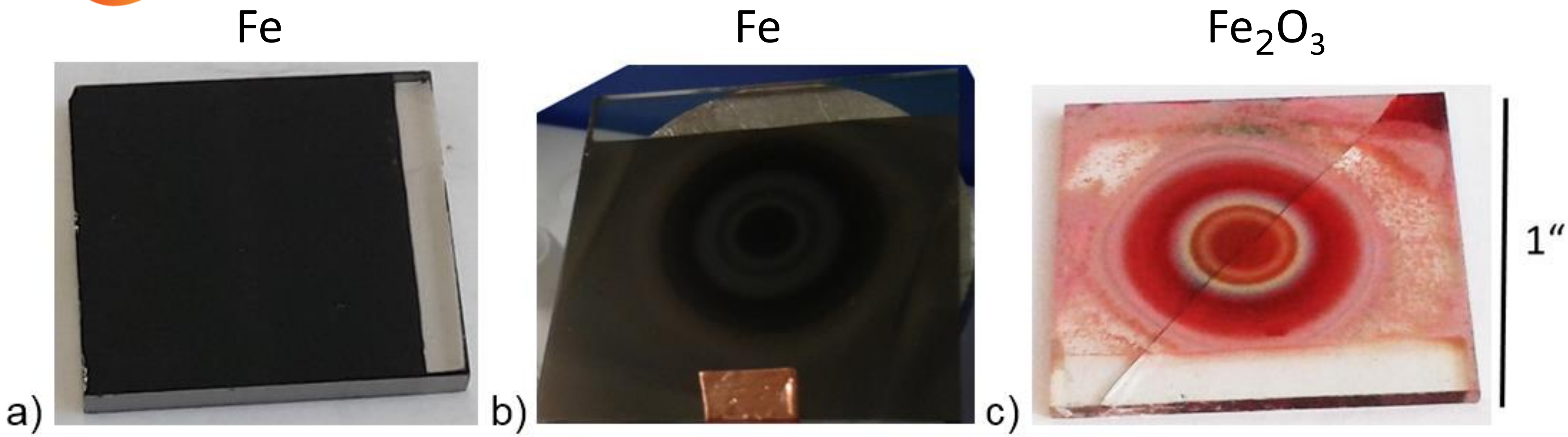


a) 

b) 

Bieberle et al., Thin Solid Films (2016) submitted.

Plasma Exposure of Thin Films



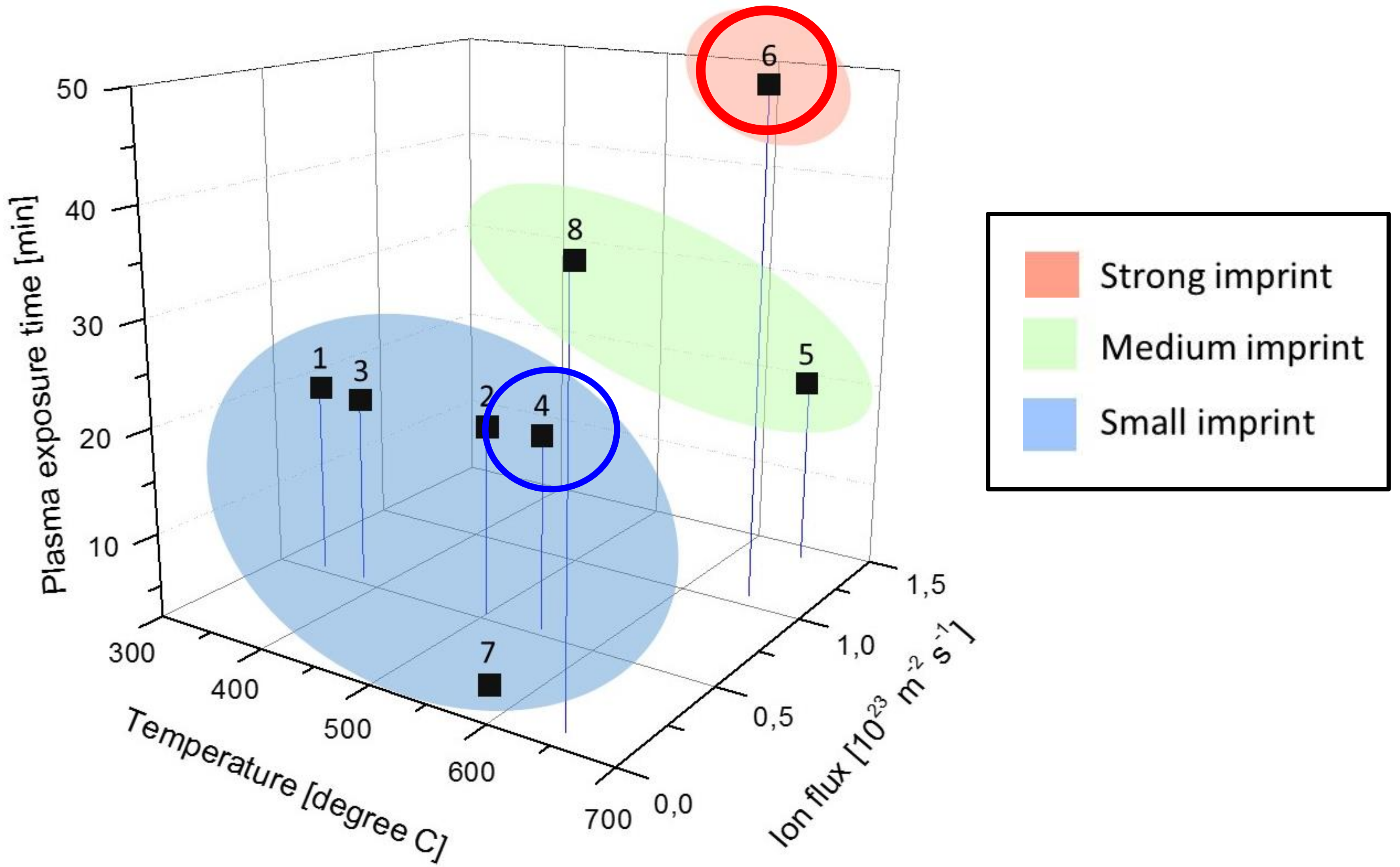
As-deposited

After plasma exposure

After plasma exposure and annealing

- Using bulk plasma conditions (high T, high current)
  → samples break
- Using mild plasma conditions → no imprint
- Never found delamination of the thin films
- Strong interplay of many exposure parameters: T, t, current, bias, He flow rate

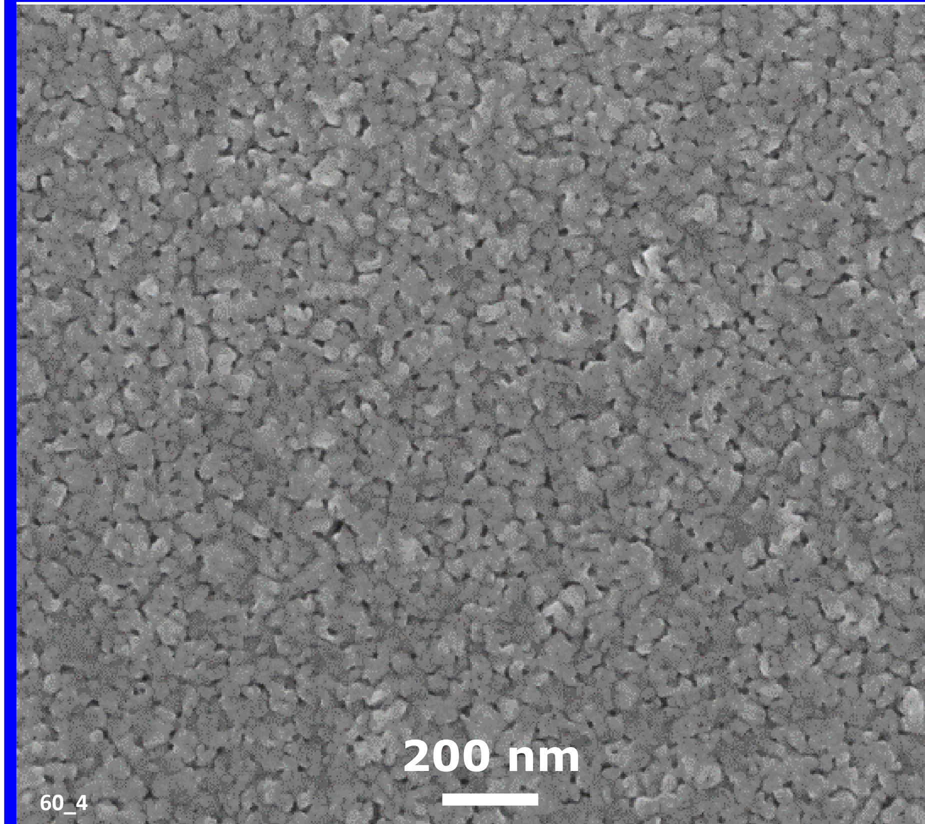
Plasma Nanostructured Iron Oxide Films

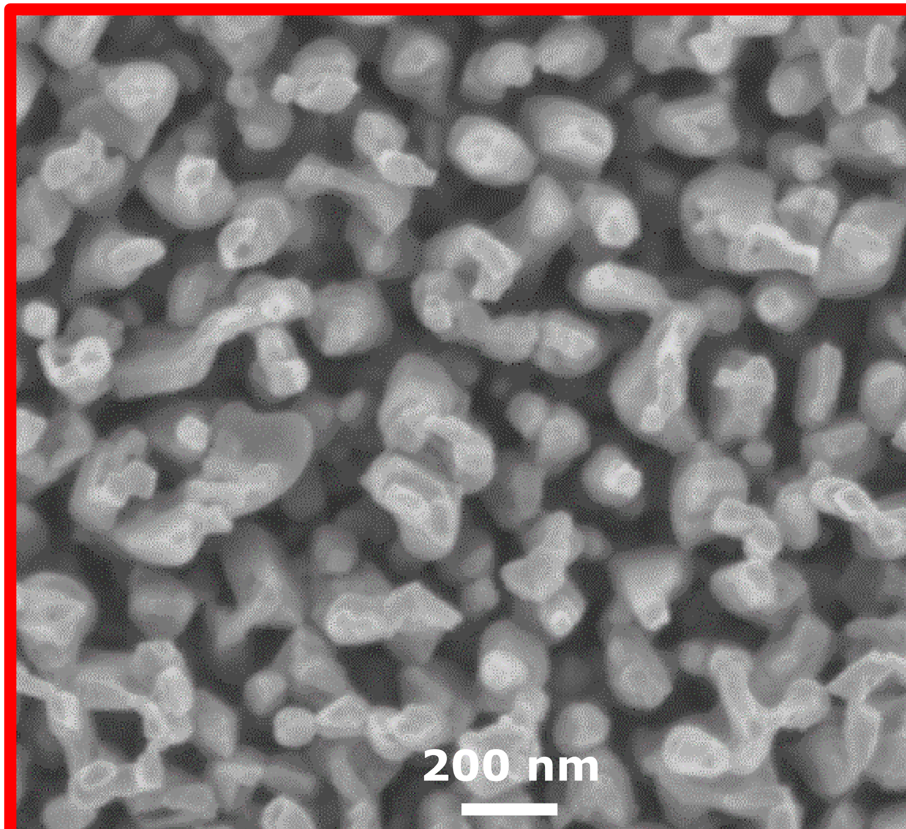


Bieberle et al., Thin Solid Films (2016) submitted.

Nanostructure Formation

Before annealing, top view SEM





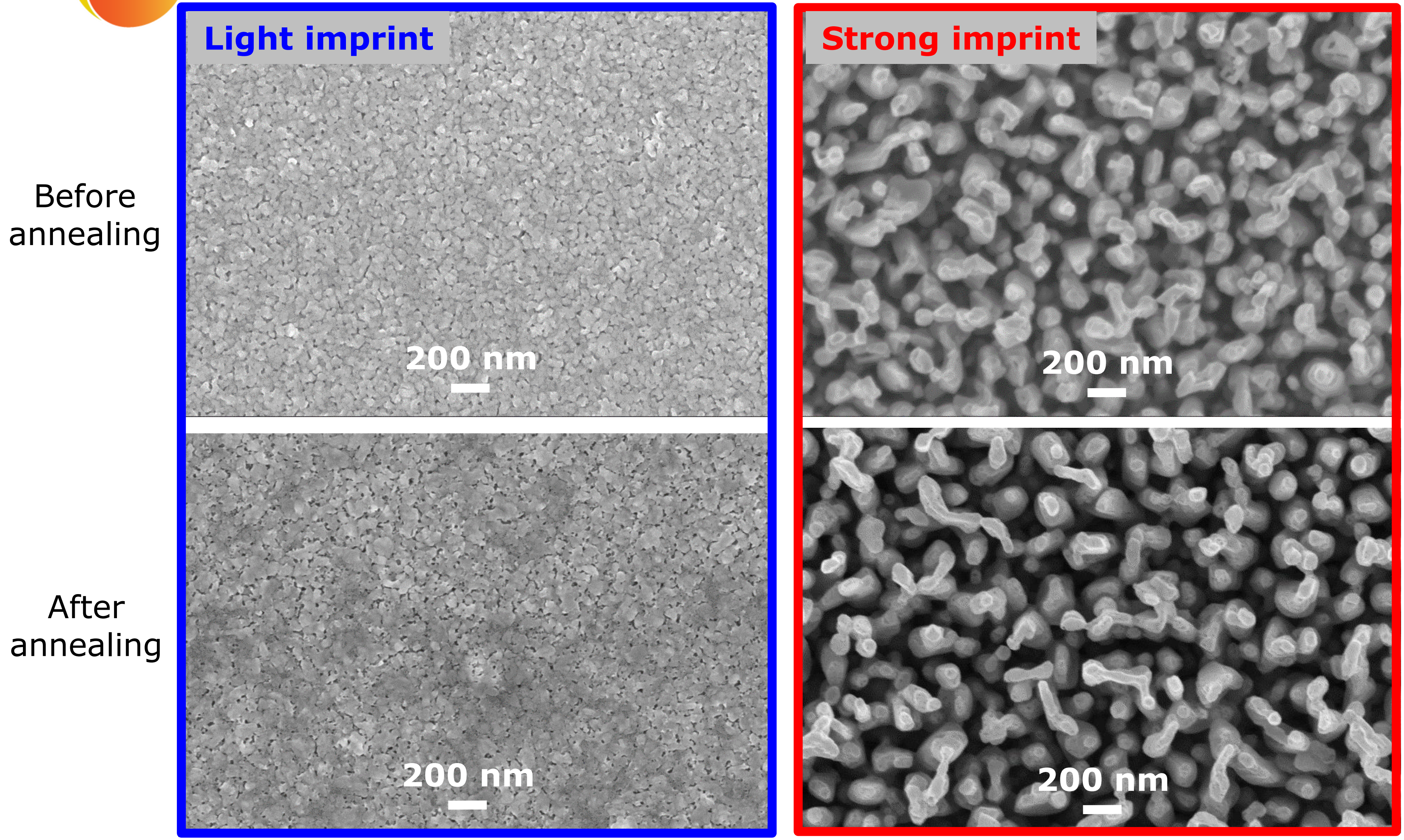
No nanostructuring for light imprint.

Nice nanostructure for strong imprint.

No nanowires.

Bieberle et al., Thin Solid Films (2016) submitted.

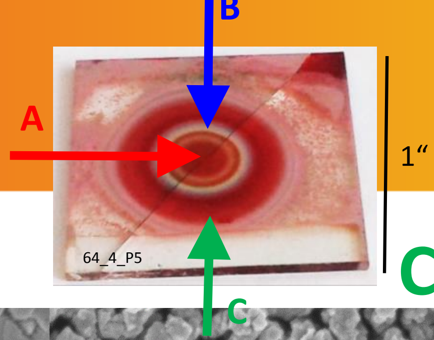
Stable Microstructure After Annealing



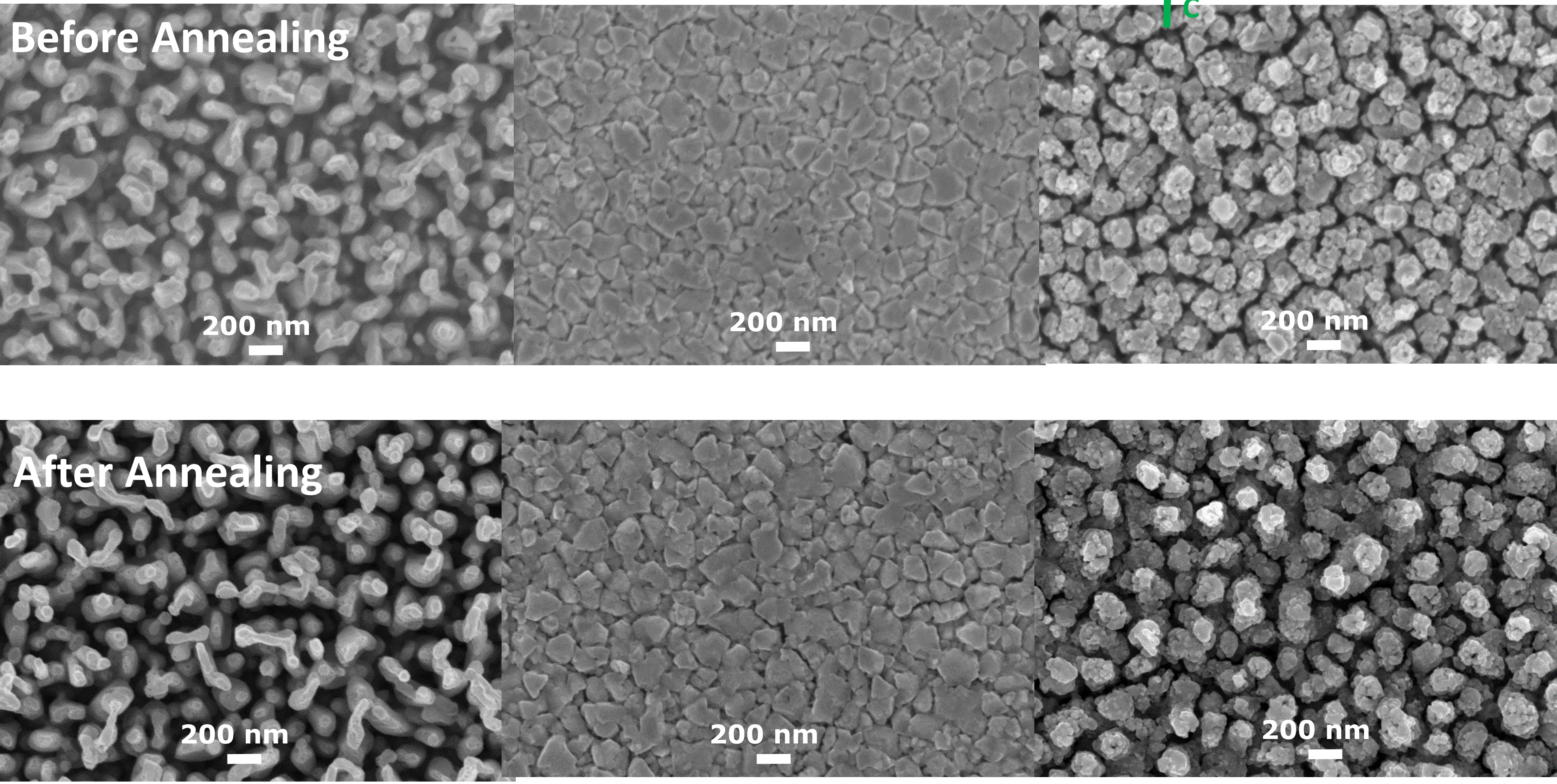
Bieberle et al., Thin Solid Films (2016) submitted.

Stable nanostructure after annealing; no nanowires.

Spatial Distribution of Nanostructure Formation



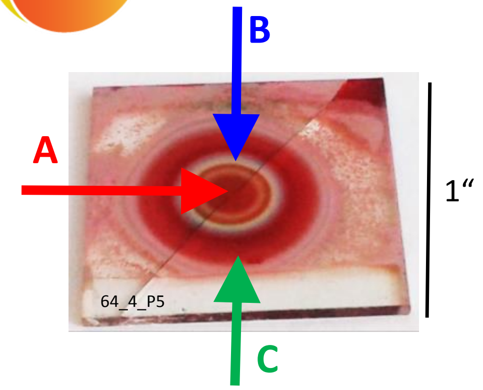
A B C



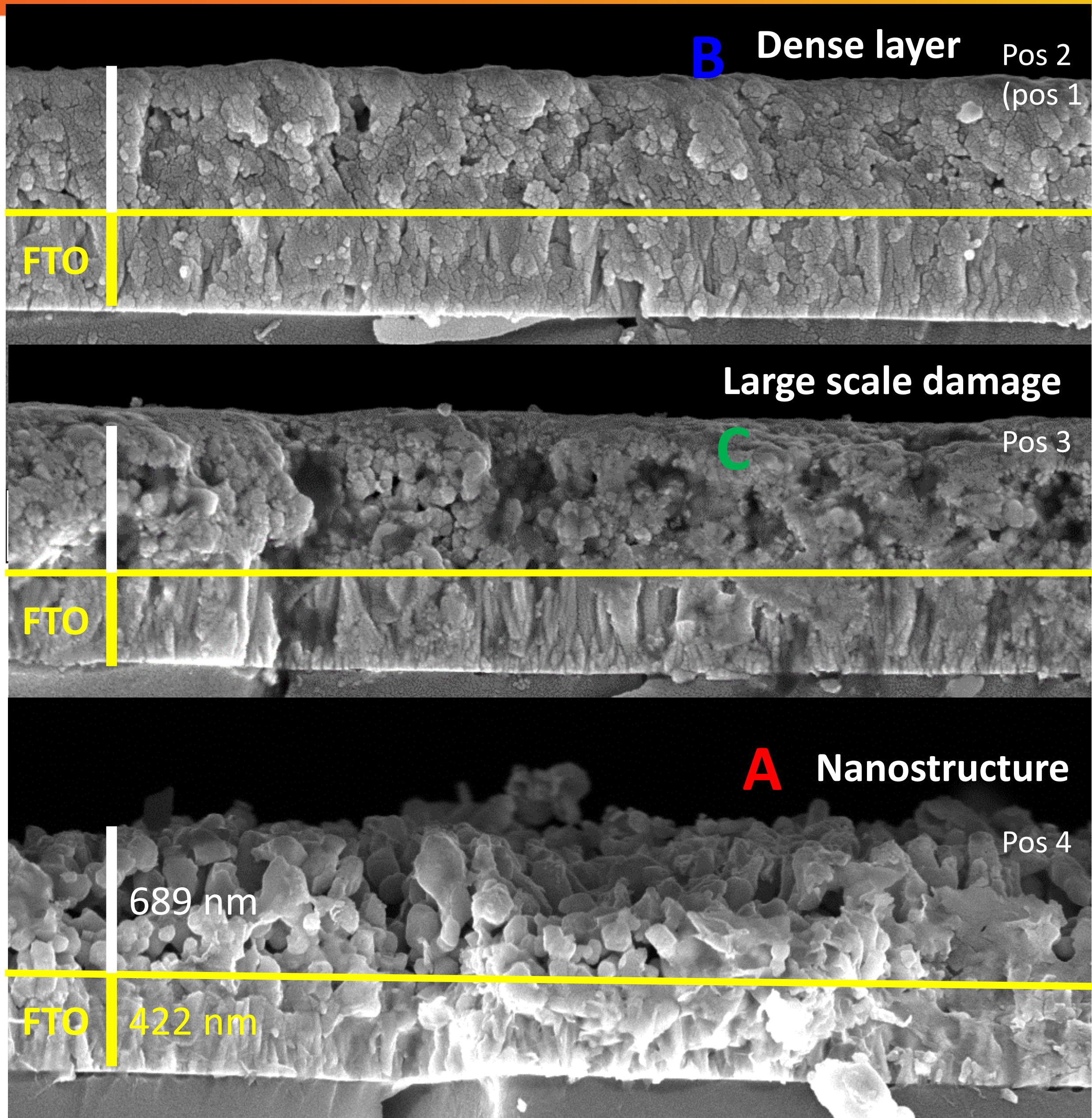
- Best nanostructure formation in the middle of the sample.
- No significant difference due to annealing.

Bieberle et al., Thin Solid Films (2016) submitted.

Cross Section (after PEC)

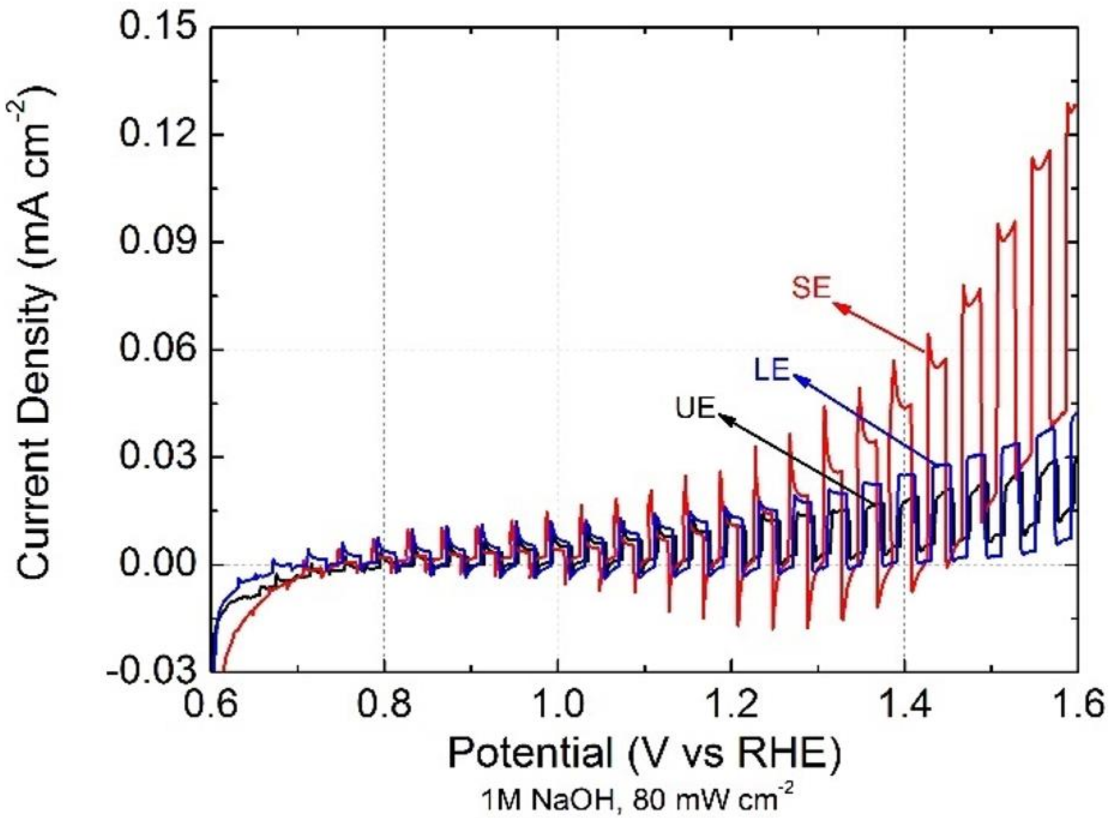


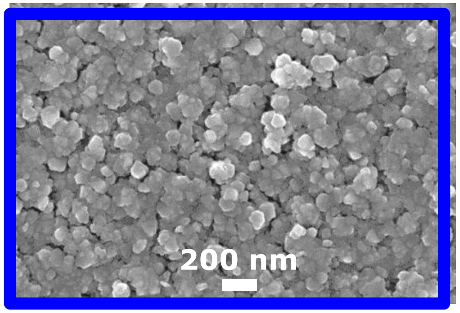
- Same features seen as in top view.
- No thickness change due to plasma exposure.
- No delamination at the Fe_2O_3-FTO interface.
- Damage of FTO?

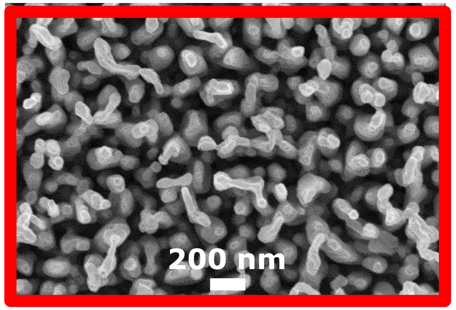


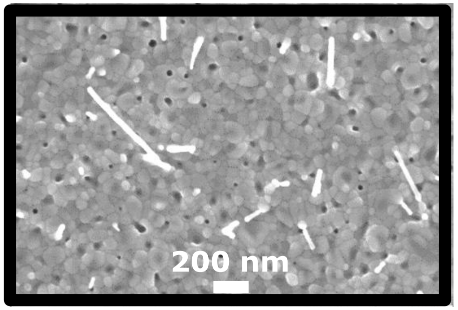
Bieberle et al., Thin Solid Films (2016) submitted.

Photo-electrochemical Characterization









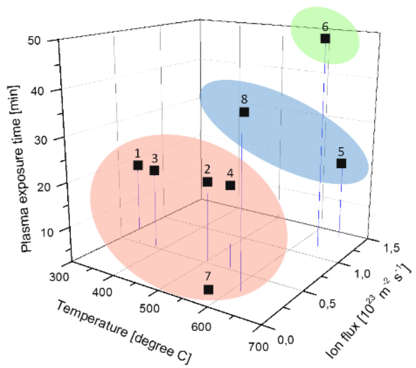
- Low overall photocurrent due to very thick films.
- 2-5 times increase in photocurrent after plasma exposure.
- Less structured material has a higher performance.

Sinha, ABH et al., under preparation.

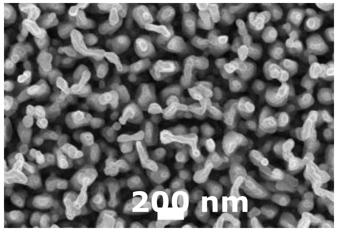
Bieberle et al., Thin Solid Films (2016) submitted.

Summary

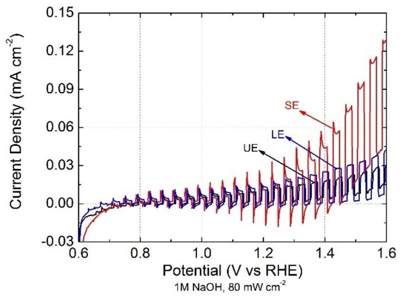
Fe/Fe-oxide model system on glass substrate (water splitting):



Thin films on glass can be nanostructured by high ion flux plasma.



Highly porous and **stable** structure with **small features** formed.



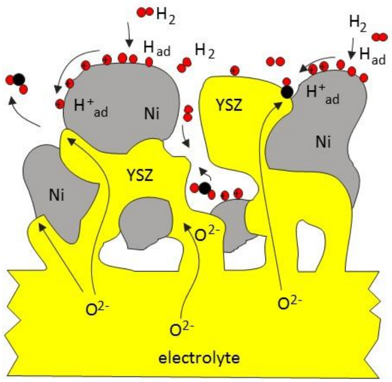
Nanostructure is **electrochemical active**.

Transfer to other applications?

Transfer to Other Applications: Opportunities and Challenges

Electrodes for fuel cells

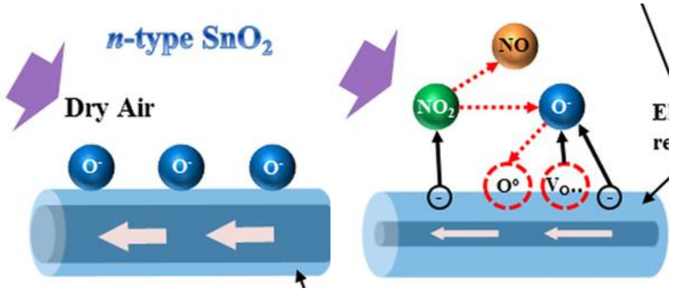
+ large surface area needed
+ interconnected structure → impregnation?
- plasma nanostructuring of complex oxides?
- impact on electrochemical performance?



Ni-YSZ SOFC anode

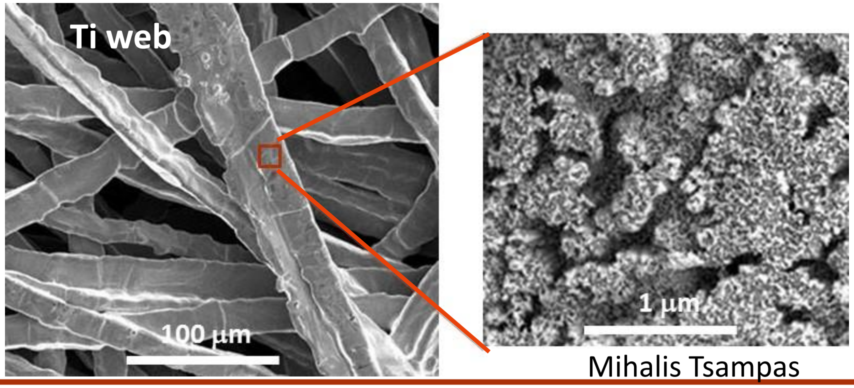
Metal oxide sensors

+ large surface area of up to 90%
- impact of impurities on sensing performance?



Large surface area substrates

+ large surface area of up to 90%
- reachable surface area?



Mihalis Tsampas

Outlook

- Investigate direct nanostucturing of oxide materials
- Relate structure and performance
- Study the impact of impurities from the plasma exposure process
- Other applications?
  - Large porosity (up to 90%)
  - Large surface area

Acknowledgment

Dr. I. Tanyeli

Dr. R. Lavrijsen

TU/e Technische Universiteit Eindhoven University of Technology

NWO
Netherlands Organisation for Scientific Research

nanoLabNL