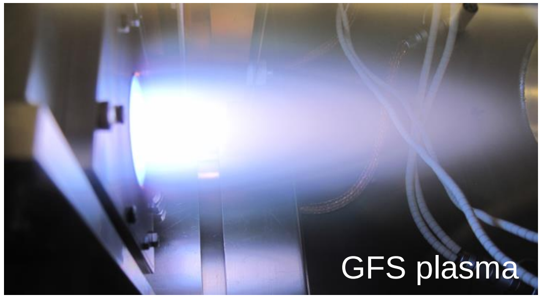

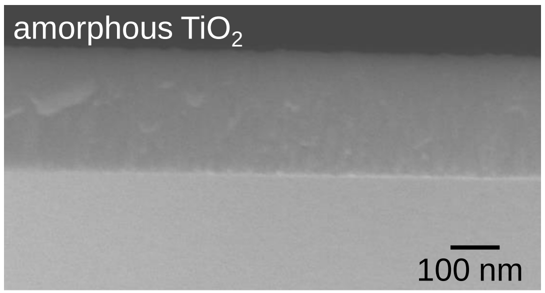

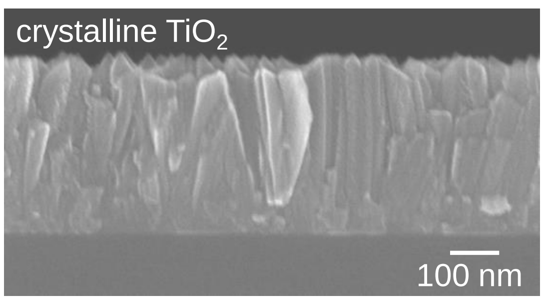

Towards **sustainable catalytic coatings** – *merits & challenges* of **hollow cathode gas flow sputtering** as a *potentially* **large scale / high volume** coating technology

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TRUMPF Hüttinger, Zielonka, Poland

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Outline

1 **GFS**
- Principle
- Equipment at TU-Berlin

2 **TiO_2 films**
- Optical properties, issues
- Photocatalytic properties

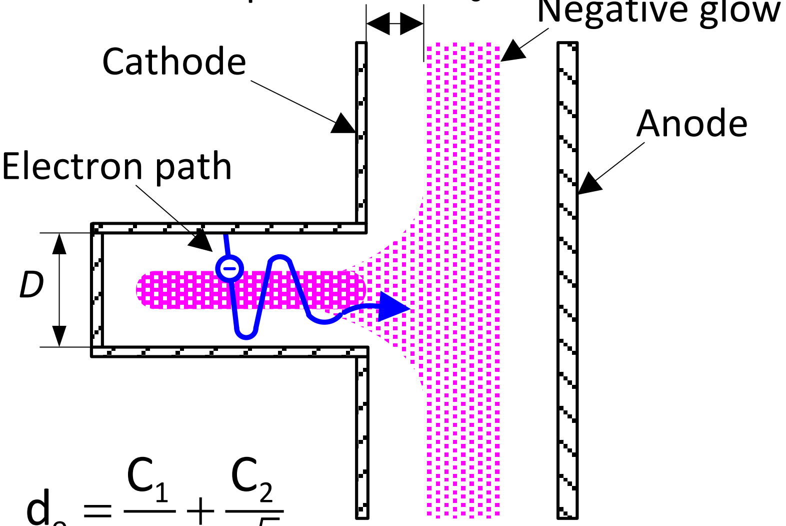
3 **Simulations**
- State-of-the-art
- Way to improve

4 **Summary & Outlook**

Hollow cathode glow discharge is…

- a DC plasma im mbar-range w/o assistance of magnetic field

* plasma pushes into a hollow space if $\boldsymbol{D} > 2\mathbf{d}_0$:



$$d_o = \frac{C_1}{p} + \frac{C_2}{\sqrt{j}}$$

pressure *current density*

1. **Oscillating electrons** being emitted by a cathode are reflected on the other side by a dark space
2. **Narrow cathode sheath:** lesser collisions at higher currents → higher energy of down going charged species → higher sputter yield
3. **Plasma entrapping:** positive ions are retained in a negative glow → viability of the plasma remote deposition via magnetic field shielding
4. **Multiple-excitation** owing to high plasma density

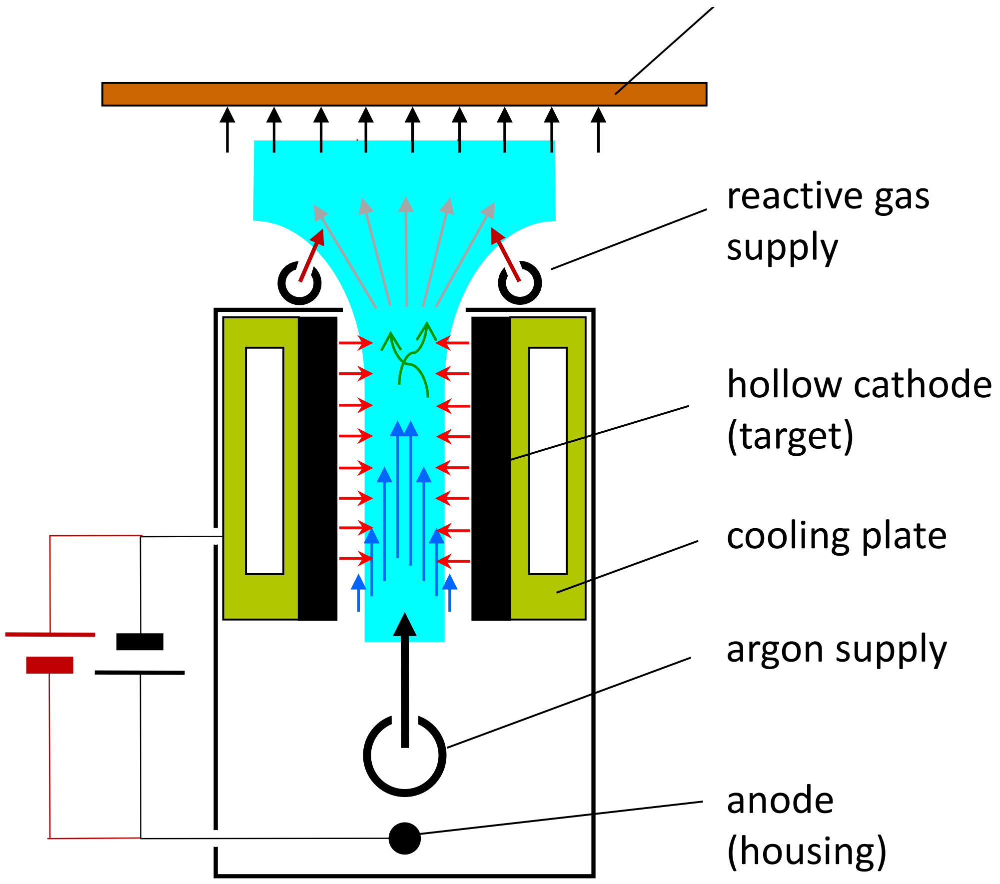
G. Schäfer, K. H. Schönbach. Basic mechanisms contributing to the hollow cathode effect. In: Physics and Applications of Pseudosparks, Plenum Press, New York, 1990 p. 55-76

Processes of GFS

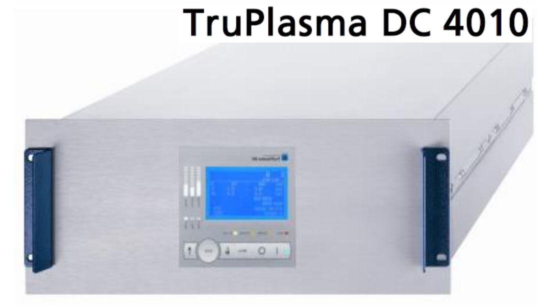
Controlled modulation of a plasma potential allows extracting of energetic ions to the substrate

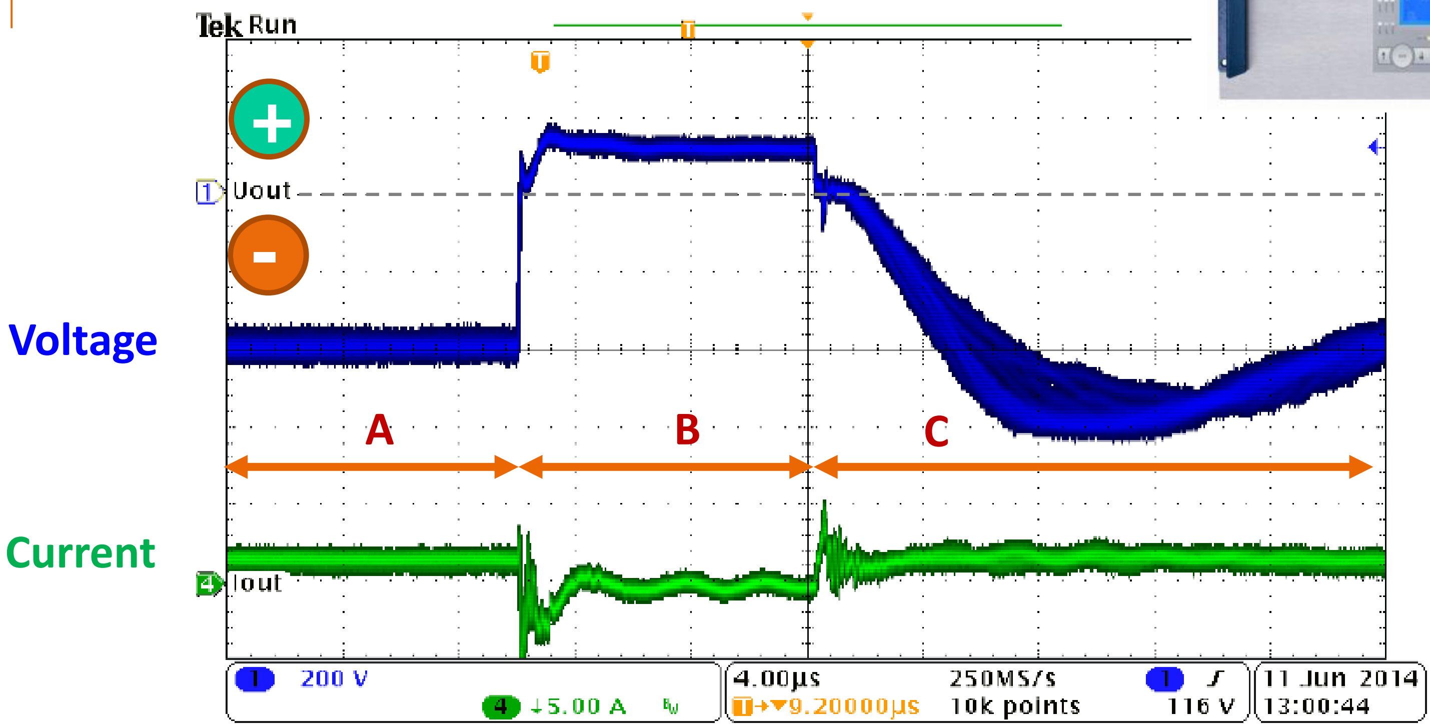
Processes

1. Laminar gas-flow
2. Hollow cathode glow discharge
3. Sputtering of the inner cathode surface
4. Thermolisation
5. Material transport outwards by (argon) gas flow
6. Addition of reactive gases (e. g. oxygen) outside of the hollow cathode
7. Diffusion to the substrate surface



Unipolar pulsing with reverse voltage





TRUMPF

- Operation of the GFS source at 10 kHz / 10 µs pulse time and 30 % reverse voltage.
- Region **A**: negative voltage applied, sputtering process
  B: 10 µs reverse voltage pulse
  C: restart of sputtering

Comparison with other sputter-techniques

	DCMS ceramic	RF/DC MS ceramic	TwinMag reactive	GFS reactive	GFS modified
ratio Ion flux : metal flux	1:100	< 1:5	1:10	< 1:1	1:1 ... 1:1000
plasma density [cm^{-3}]	5×10^8	$< 3 \times 10^9$	$< 2 \times 10^9$	$< 1 \times 10^{10}$	$10^7 \ldots 10^{10}$
ion energy [eV]	5 … 10	5 … 70	< 200	kT	kT
UV	--	--	--	--	+
fast electrons	+	+	+	-	+
negative ions	-	+	-	+	+

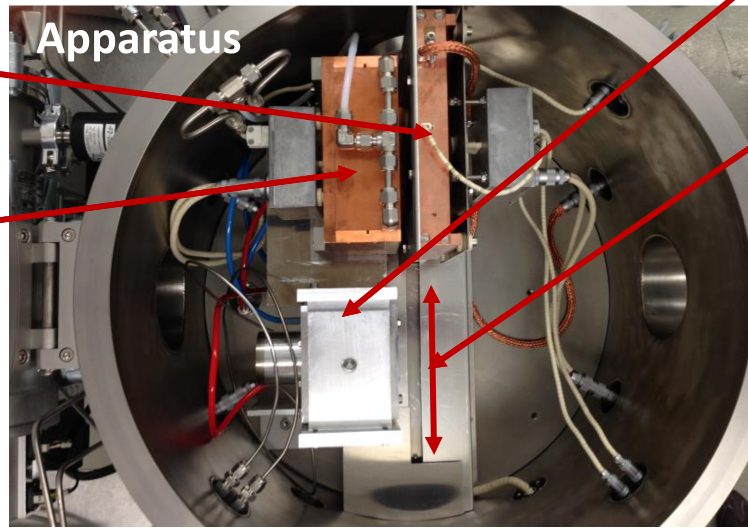
Deposition apparatus at TU Berlin

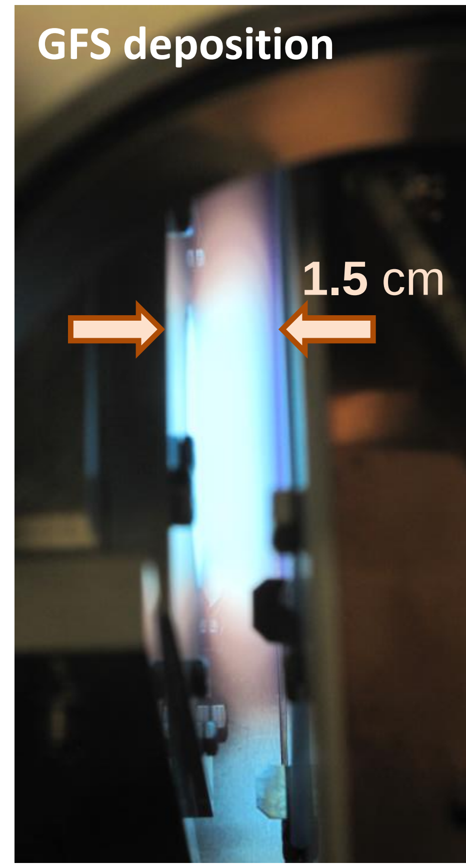
GFS source

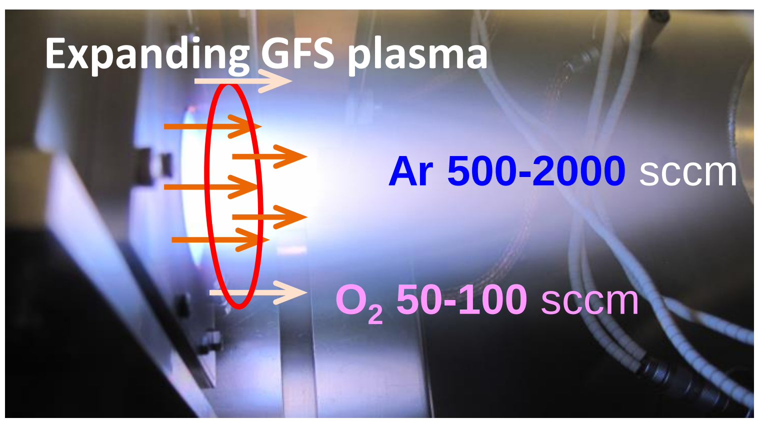
Heatable substrate holder

Pretreatment & heating section

Deposition zone (static deposition or oscillating by +/- 50 mm)







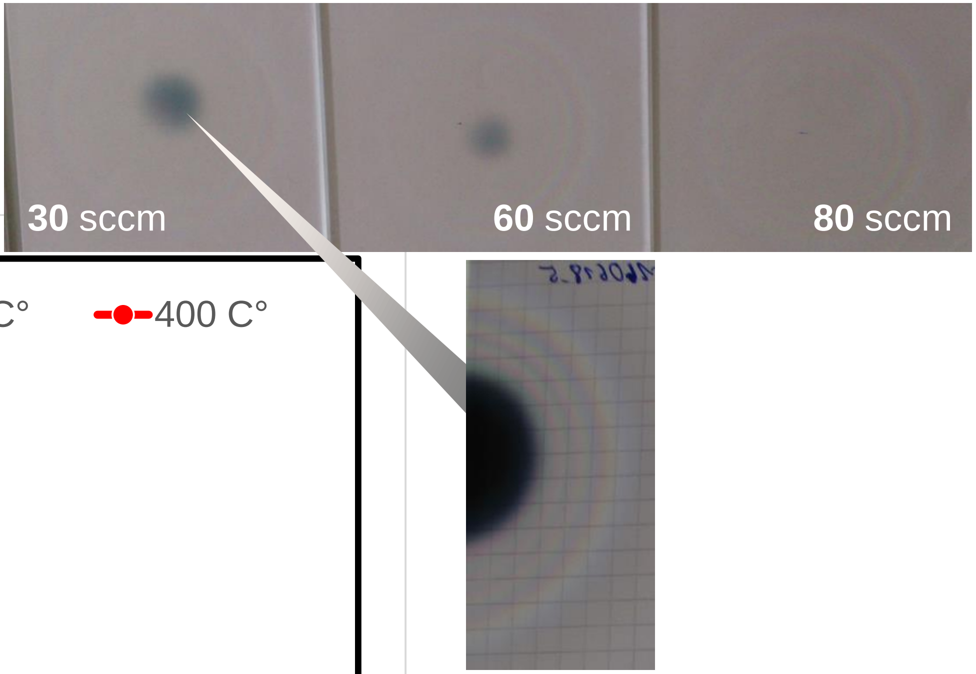
Change of the refractive index *n* with *T*-*p*(O_2)

DC-Process

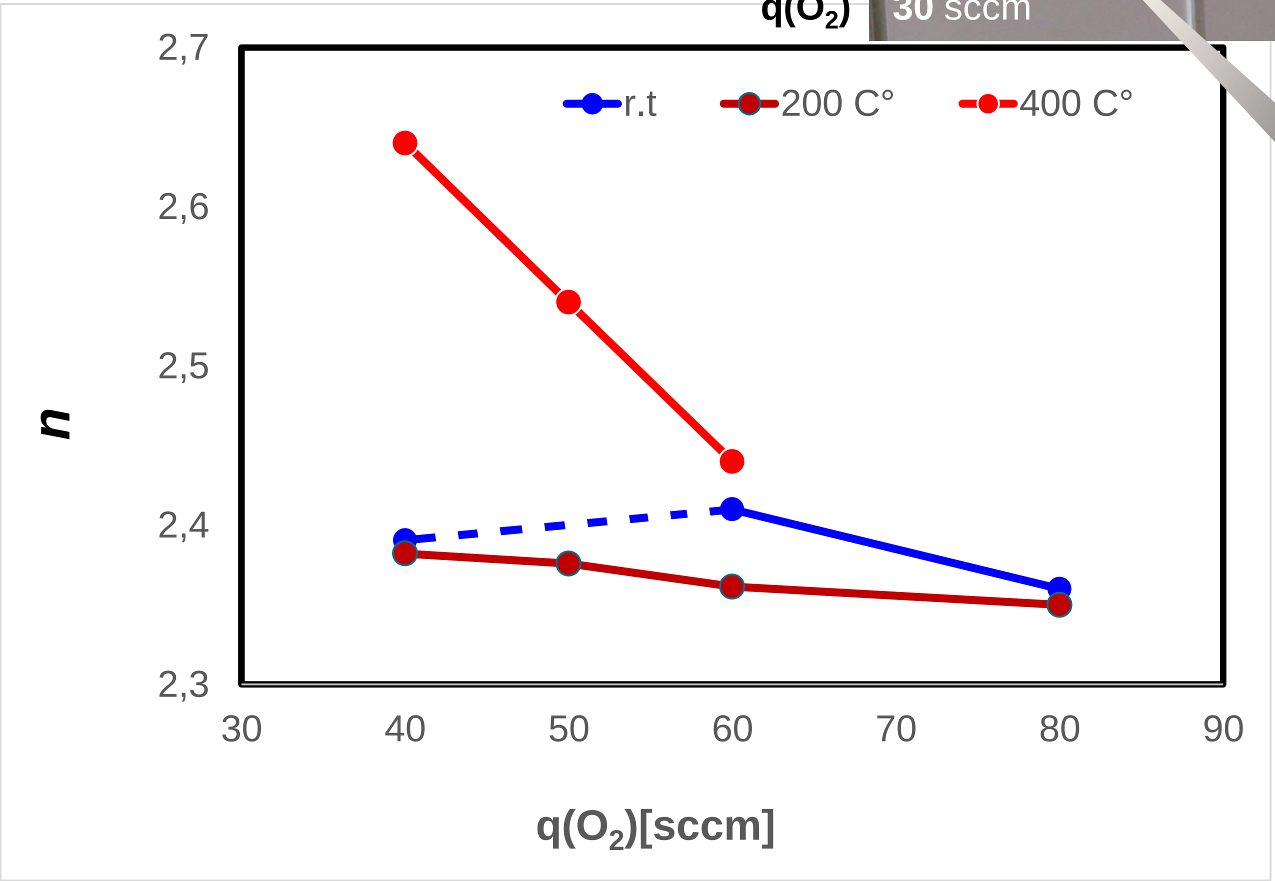
photographs

r.t.

q(O_2)

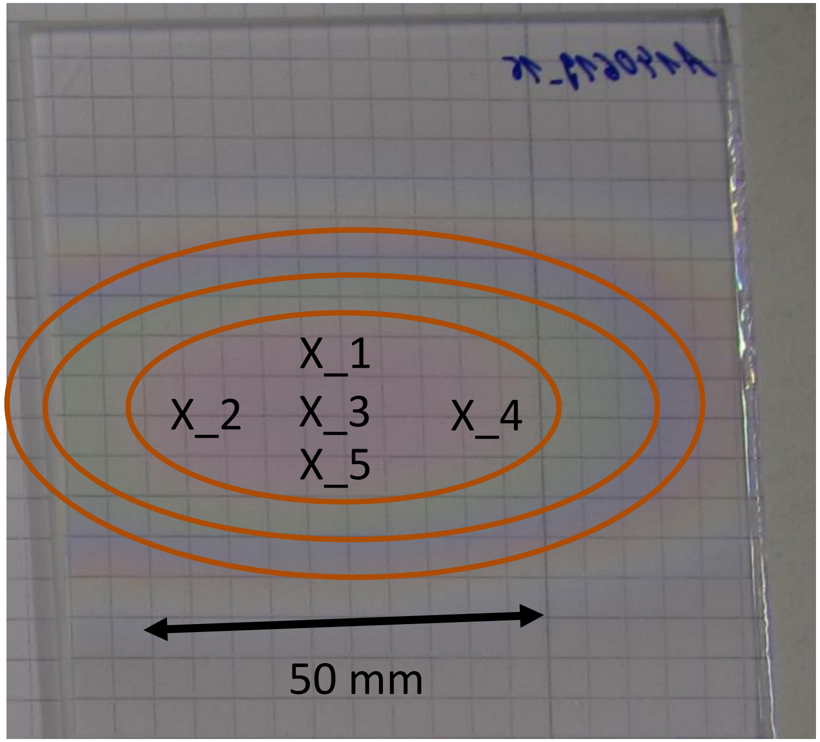


* from ellipsometry (*Sentech SE850*)
made in the middle



- **substoichiometric growth**
- **interference fringes**

Dynamic GFS process



	X_1	X_2	X_3	X_4	X_5	Static
n	2.24	2.22	2.25	2.27	2.23	2.41
d [nm]	280.9	299.9	303.2	294.7	292.6	

Experiment:

- Oscillation by +/- 50 mm in front of the source (6 Oscillations, 100 mm / 13 s)

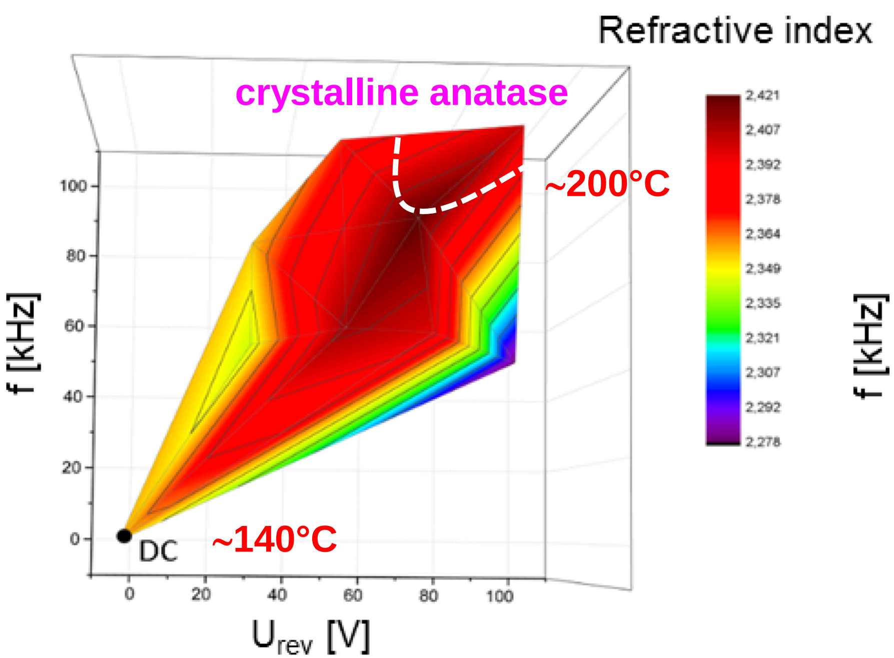
Observation:

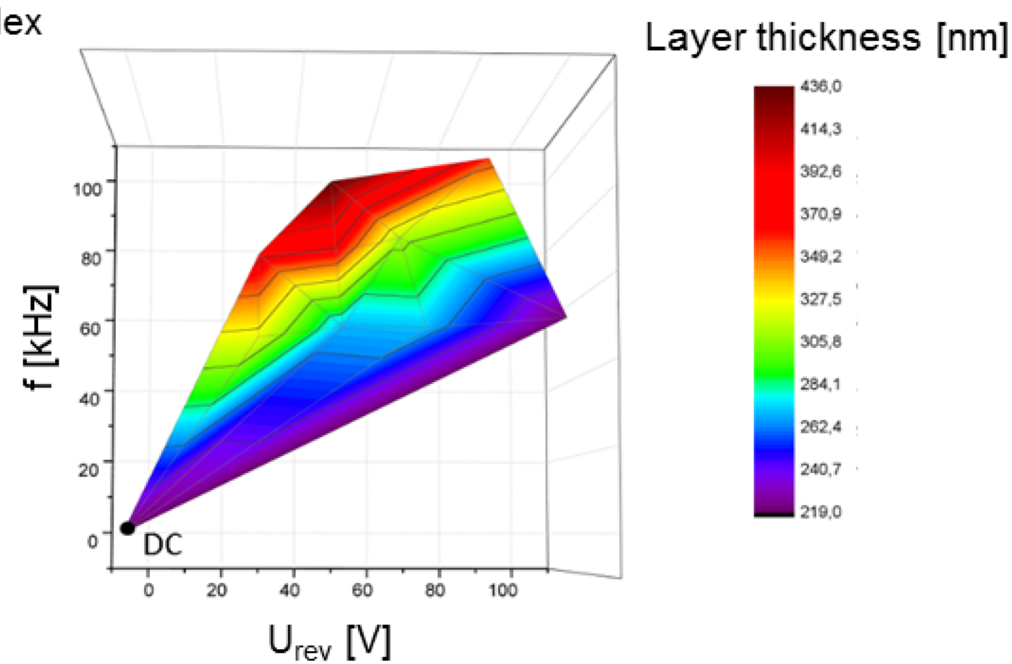
- Oscillation limits the growth of dense films:
- ***n* (static) = 2.41 -> *n* (dynamic) = 2.25**
- On 50 x 20 mm^2, homogeneity of $\Delta d/d < 5$ % is achieved

Issue:

- static process cannot be 1-to-1 transferred to the dynamic one

Impact of the pulse operation (r.t.)

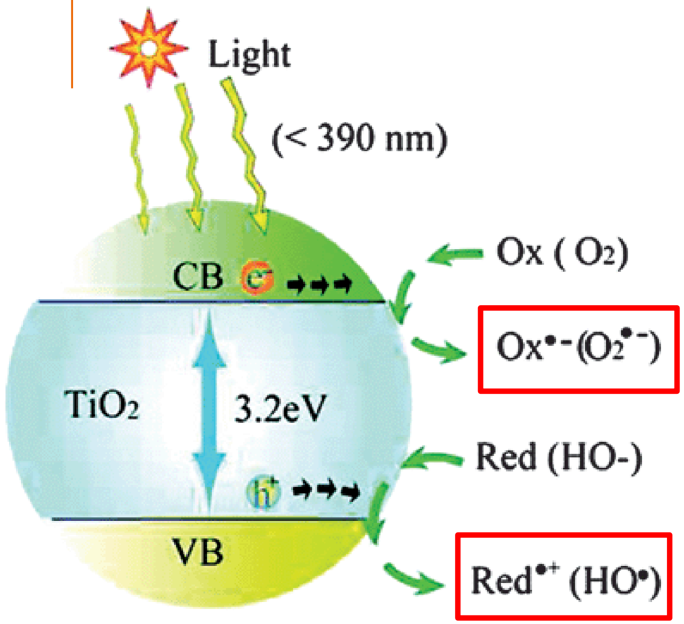


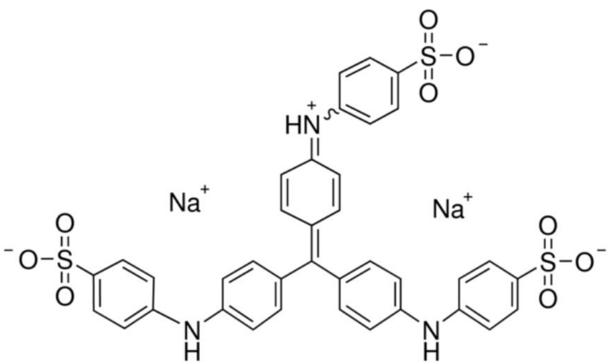


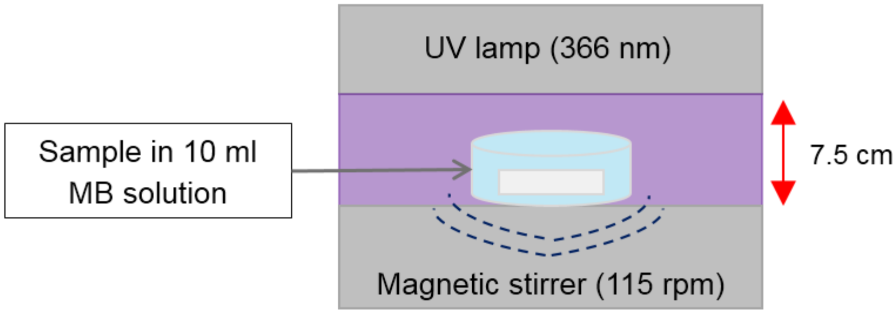
- TiO_2 on glass
- T_{depo} ≈ 25 °C
- q(Ar) = 1000 sccm
- $q(O_2)$ = 80 sccm
- P = 500W
- t_{dep} = 150s

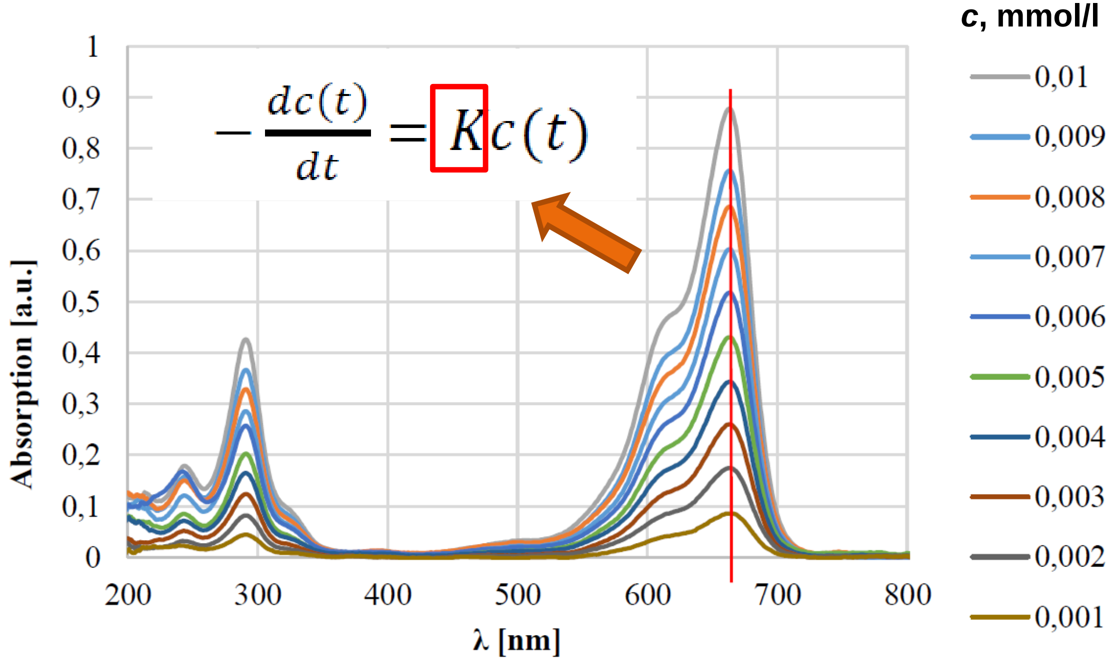
- higher $\boldsymbol{U_{rev}}$ **&** $\boldsymbol{f}$ -> higher refractive index
- higher frequencies -> thicker films
- higher $\boldsymbol{U_{rev}}$ @ f=const -> thinner films

Methylene-blue test



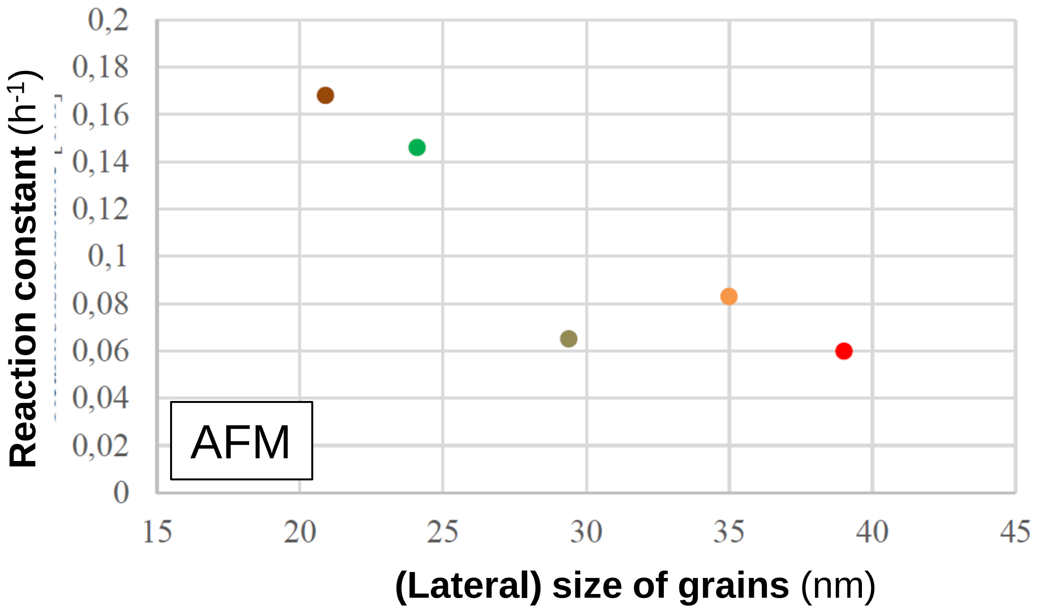


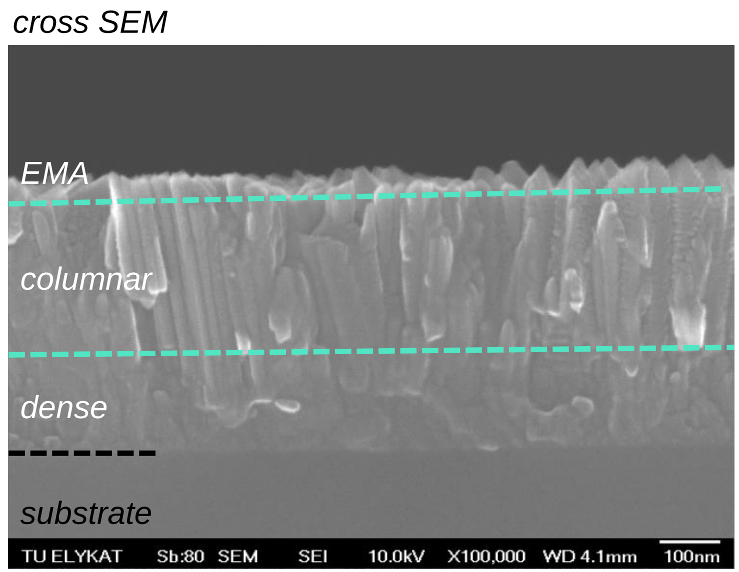


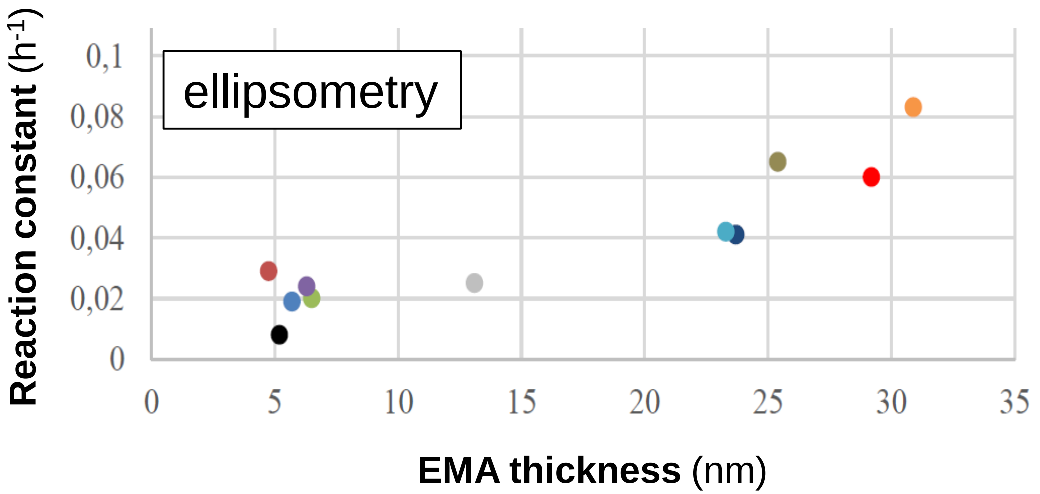


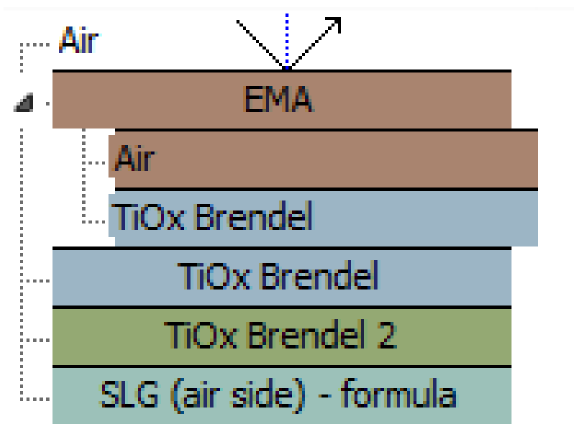
O. Lorret, D. Francová, G. Waldner und N. Stelzer, Applied Catalysis B: Environmental 91 (2009) 39–46

Impact of the microstructure



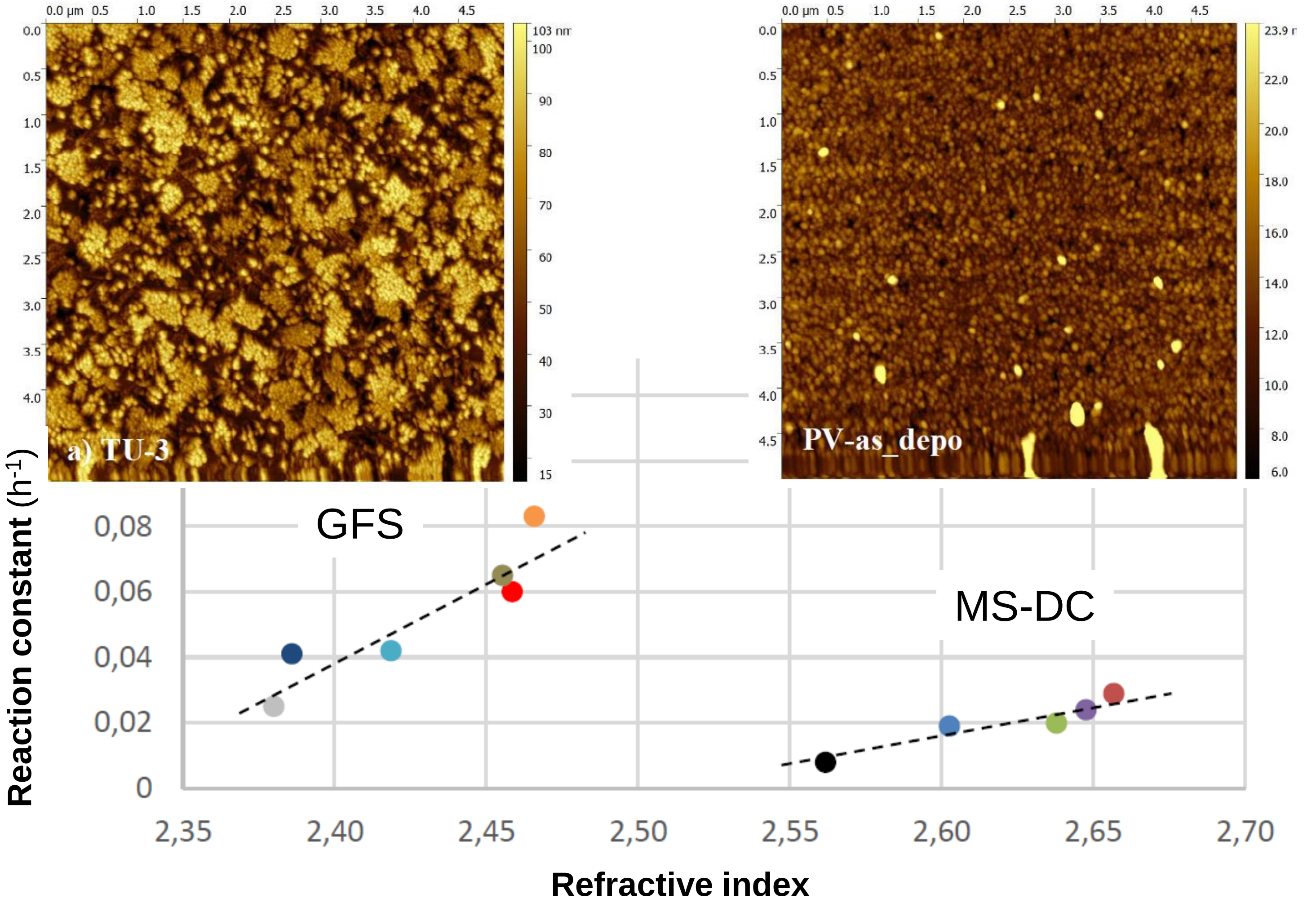






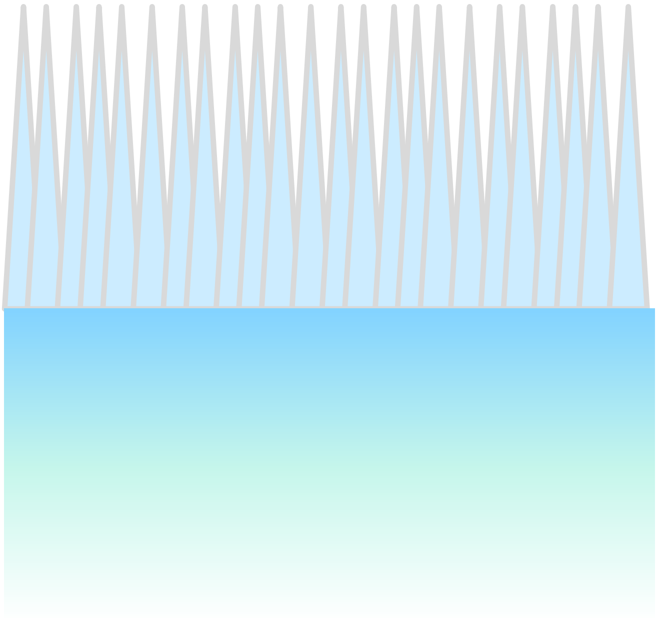
Crystalline photocatalytic TiO_x films

comparison with the MS



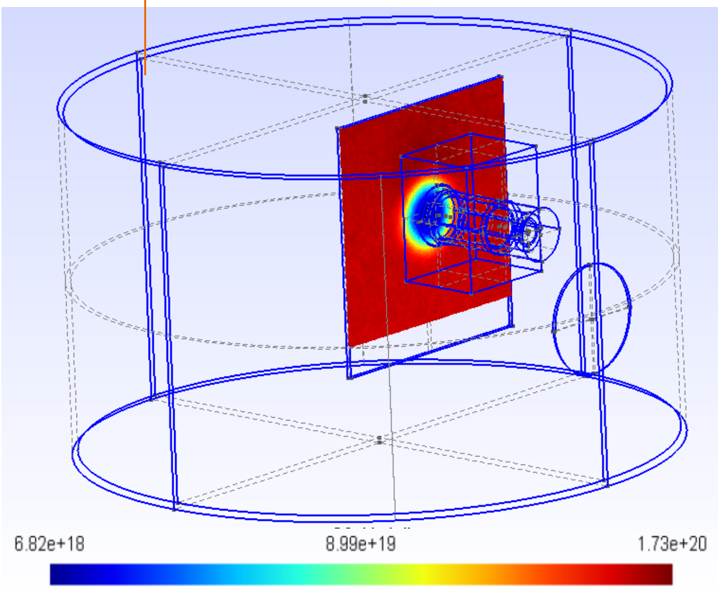
IDEAL PHOT-CAT TiO_2 FILM is…

a nano-comb?



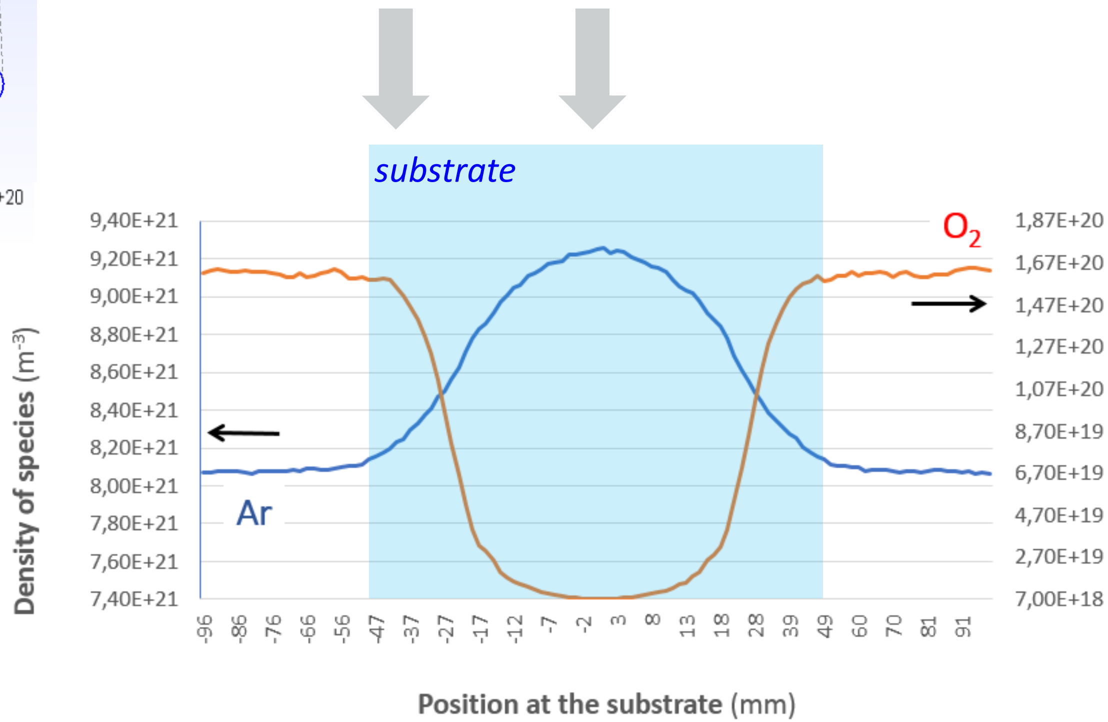
Monte-carlo simulations: state-of-the-art

made based ON **Cluster @ TU Berlin**
the work of **Dr. Andreas Pflug** (Fraunhofer IST)



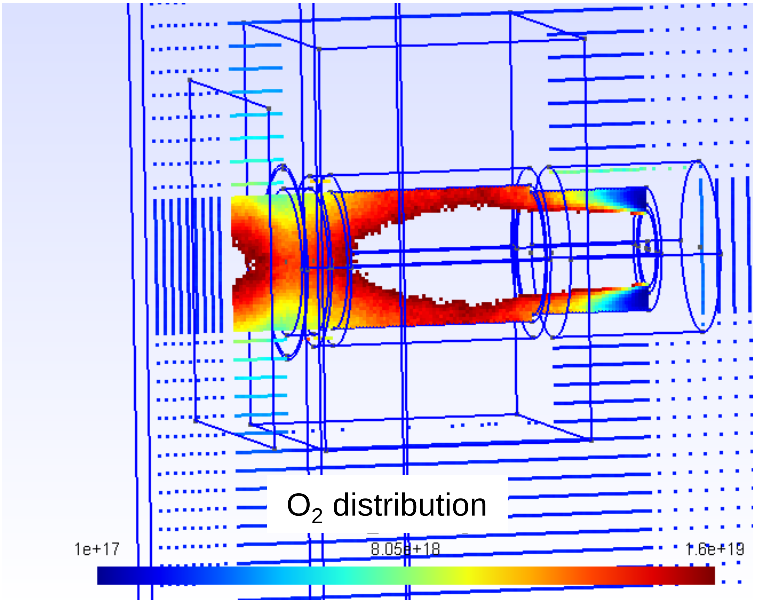
distribution of oxygen

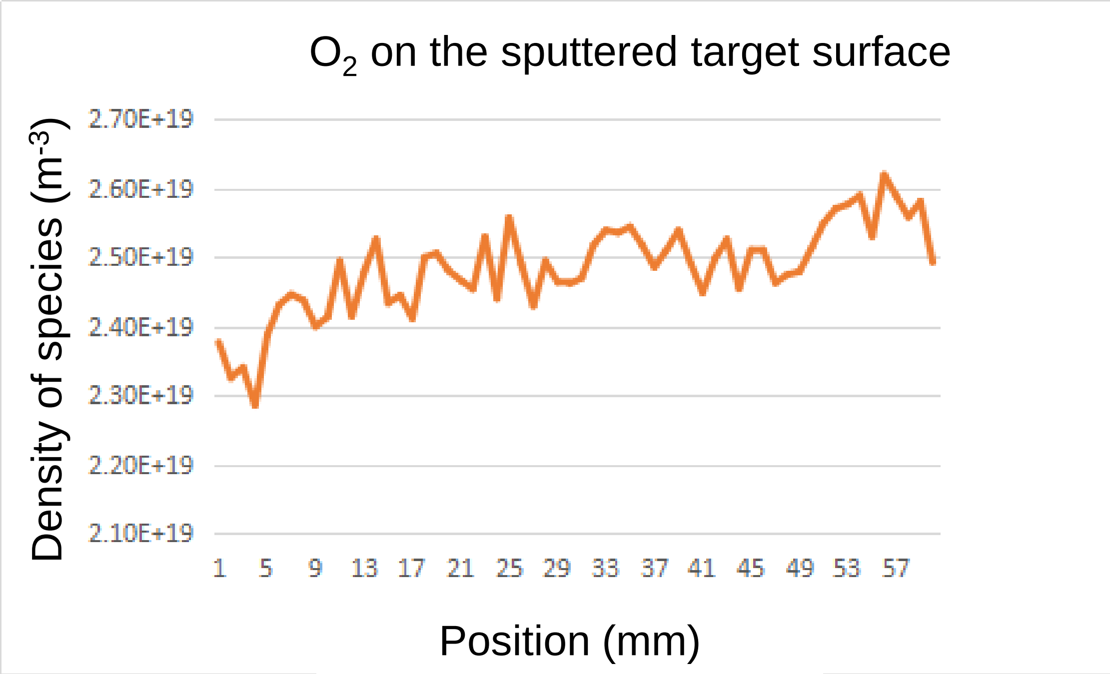
Ar/O_2	~53	~1300



- q(Ar) = 1000 sccm
- $q(O_2)$ = 20 sccm

Oxygen inlet behind the target





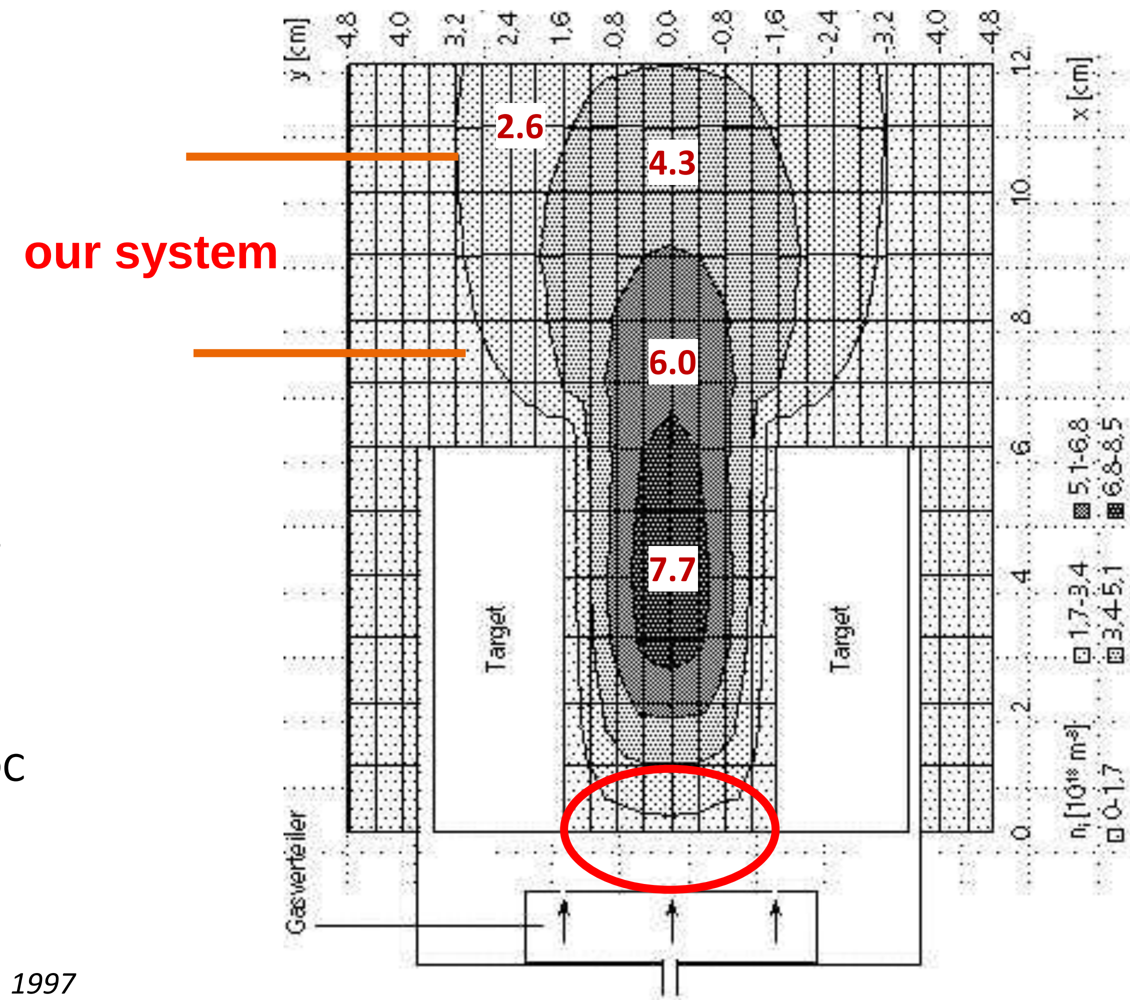
- $q(Ar) =$ 750 sccm
- $q(O_2) =$ 8 sccm

target poisoning

Plasma density distribution

from the Langmuir probe measurements

(unit: 10^{12} cm^{-3})

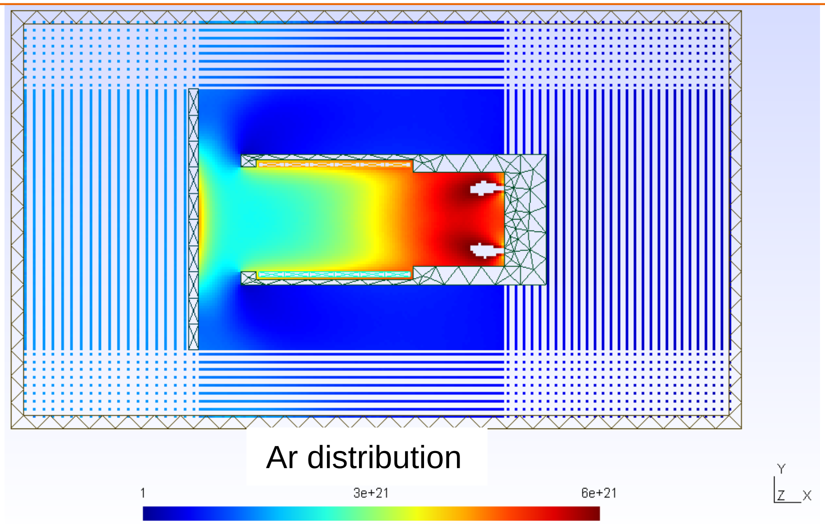


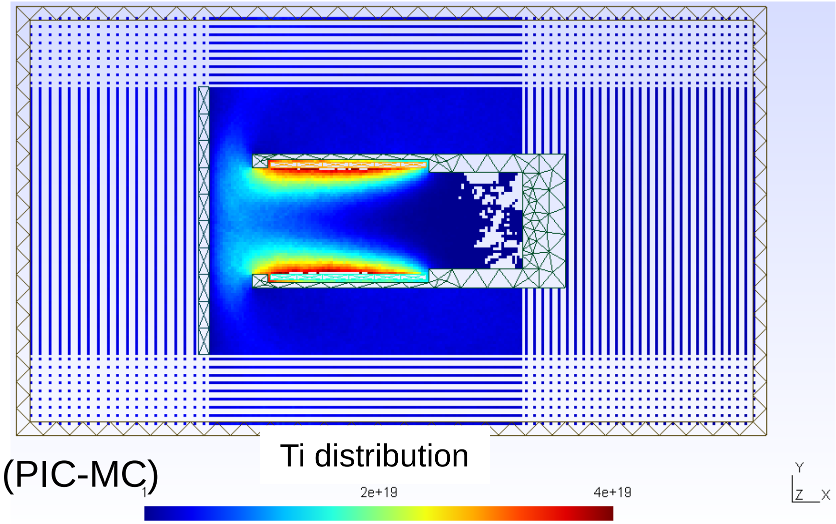
Linear GFS source

Target length	25 cm
Working gas	Argon
Total pressure	0.3 mbar
Gas flow	3.5 slm
Gas velocity	27 m/s
Electric power	1.5 kW DC

M. Szameitat, Diploma Thesis, TU Braunschweig, 1997

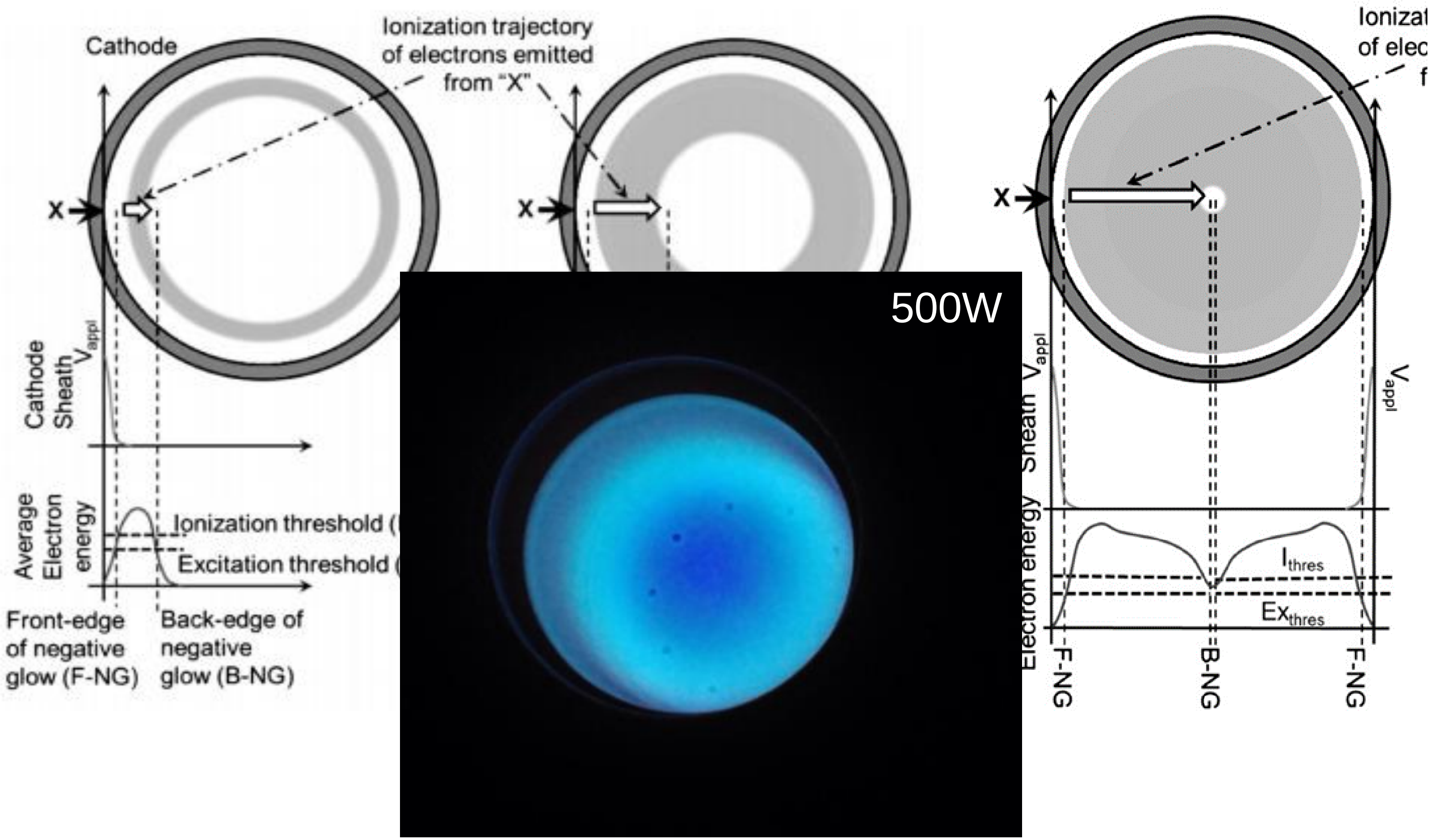
Laminar flow inside the hollow cathode





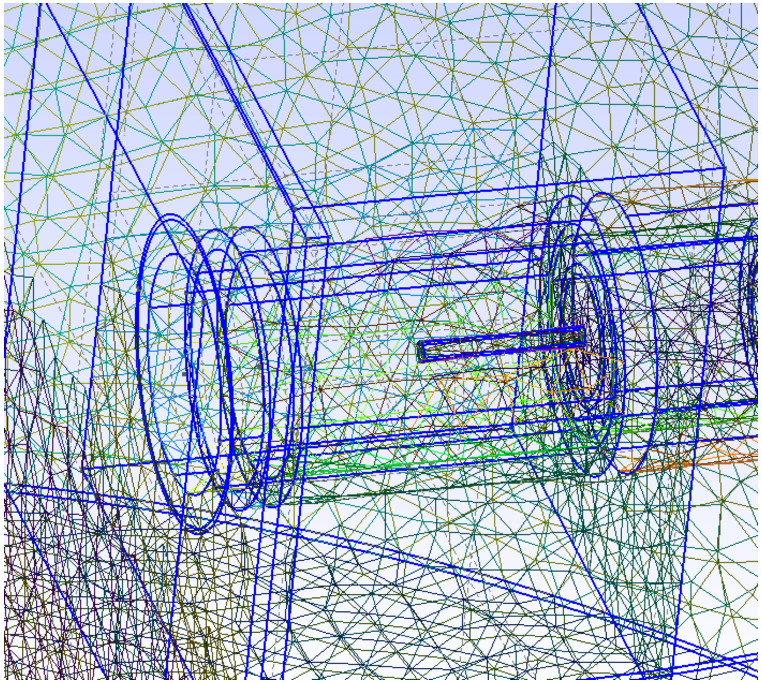
particle-in-cell Monte-Carlo (PIC-MC) emulation results

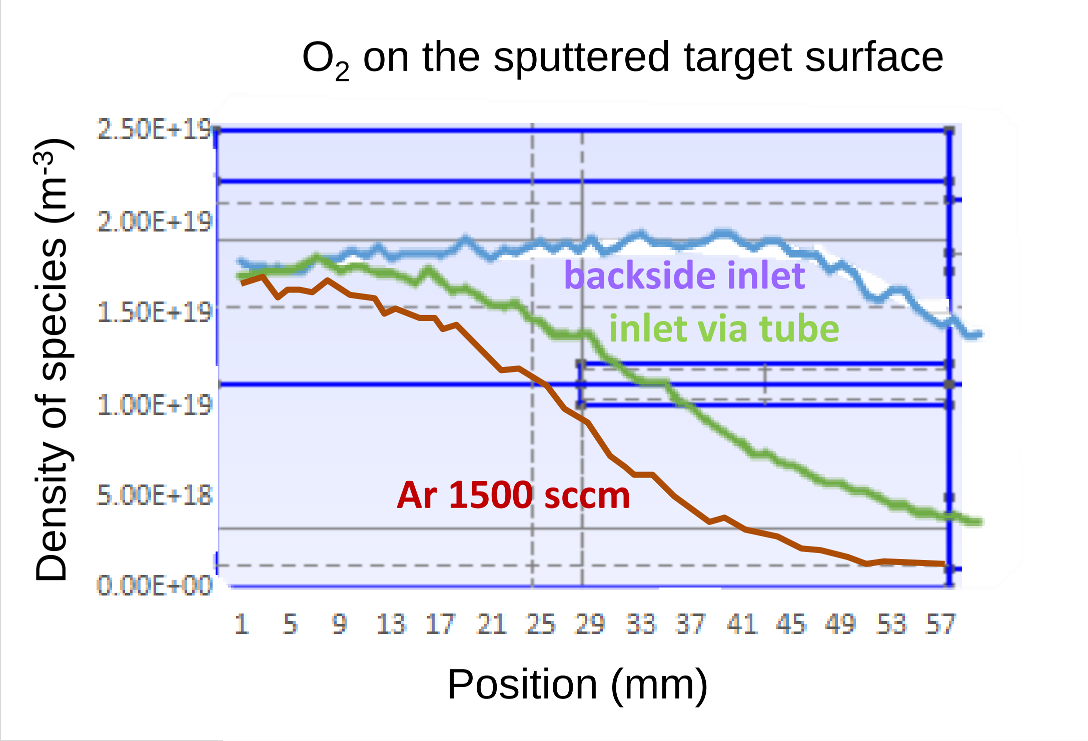
Dependence of the glow form on power



S. Muhl,, A. Pérez, The use of hollow cathodes in deposition processes: A critical review. Thin Solid Films 579 (2015) 174–198

Oxygen inlet inside the target





- $q(\mathrm{Ar})$ = 750 sccm
- $q(\mathrm{O_2})$ = 8 sccm

Summary & Outlook

IDEAL GFS is…

coming up next

Acknowledgements

Federal Ministry for the Environment, Nature Conservation and Nuclear Safety

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ORAMA

clear-up

Project “Spitzenforschung und Innvation in den neuen Ländern” funded by BMBF and SENBWF under grant no. 03IS2151

TRUMPF

INTERPANE Glass for Life

https://ruben.verborgh.org/blog/2014/12/31/thank-you-for-your-attention/