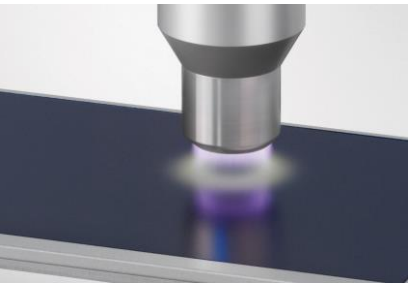
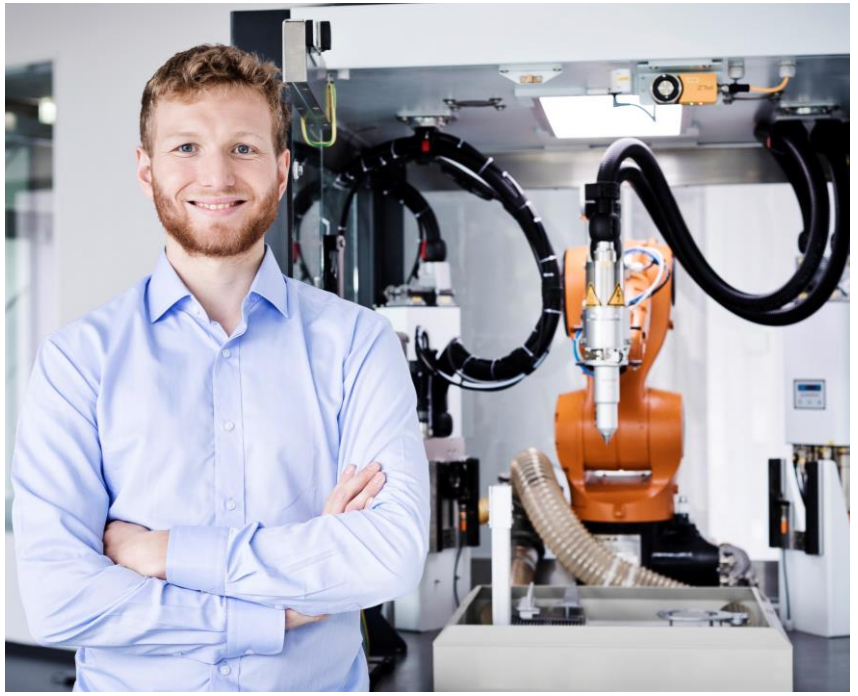
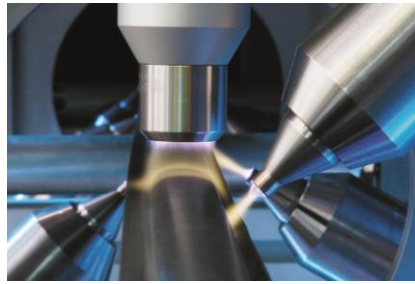
AutoProtect Webinar-Series # 2
Regulatory Requirements for Antimicrobial Surfaces
Plasma-based antimicrobial coatings

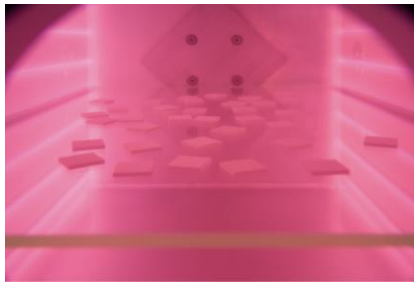
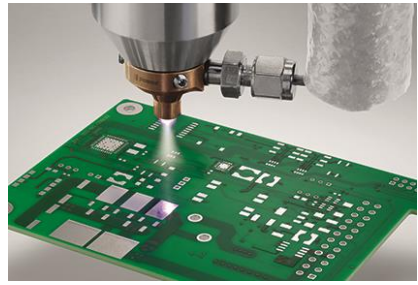
plasmatreat

20th of May 2021 – Dr D. Ben Salem







We are surface specialists and leading supplier for
atmospheric plasma technology as well as experts for
low pressure plasma processes

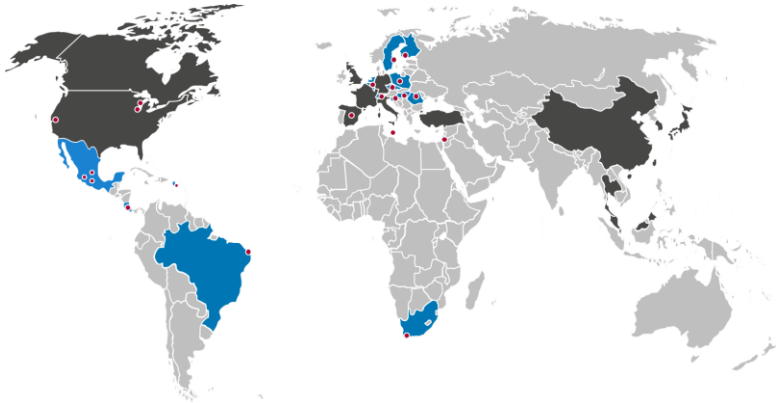
Market leader in Openair-Plasma® Technology

Global Presence

- HQ in Germany
- Production sites in Germany, China & USA
- 17 subsidiaries & Technology Centers in 11 Countries
- 15+ agents in ROW

Family Owned Business

- Founded in 1995
- 225 employees worldwide
- Consolidated turnover: €45 Million

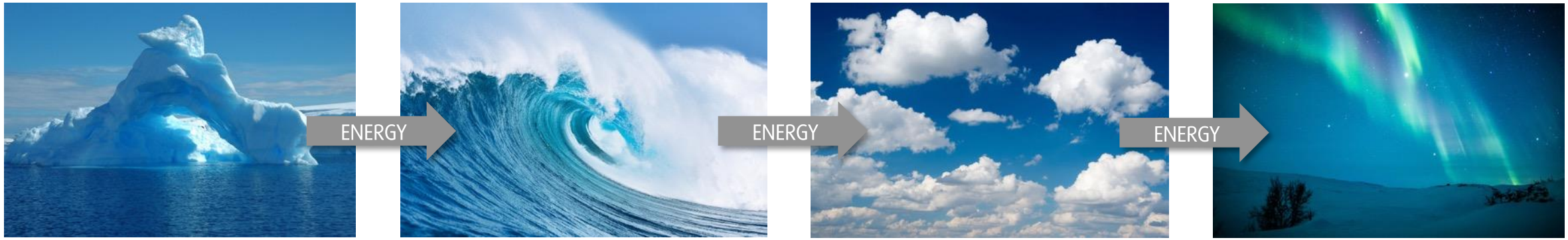


Milestones

1995: Invention of Openair-Plasma®
2007: PlasmaPlus® coating
2019: Opening of the HQ Technology Center
2020: Plasmatreat Academy

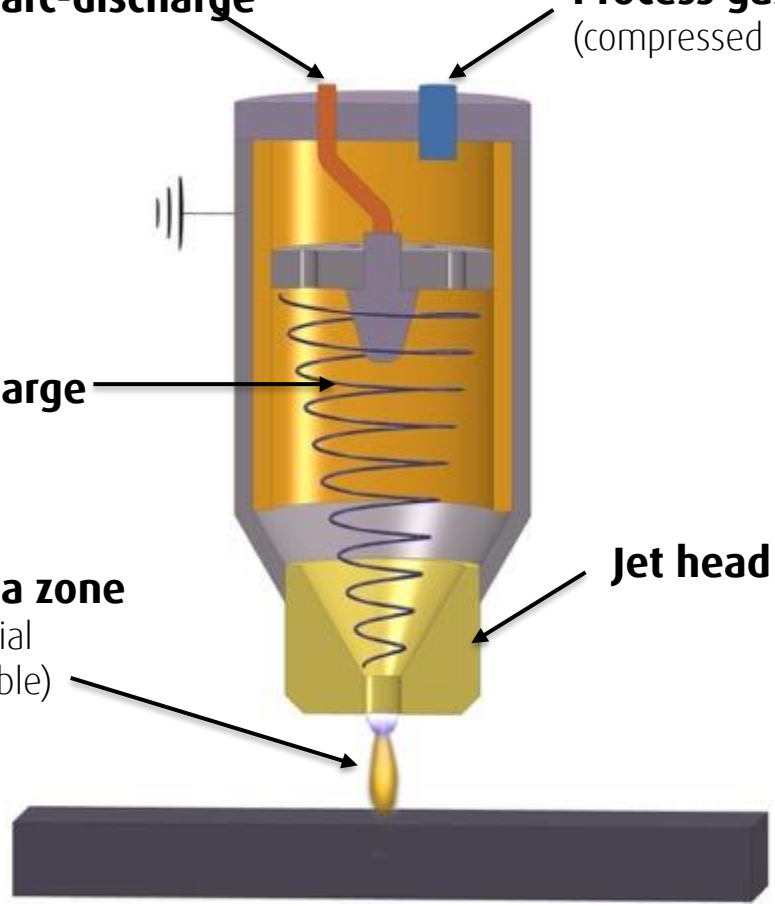
What is Plasma?

Plasma is formed when additional energy is supplied to the gas by electrical discharge. Plasma is an ionized gas with electrical conductivity which is electrically neutral. It is also called 4th state of matter.



SOLID LIQUID GAS PLASMA

Operating principle Openair-Plasma®

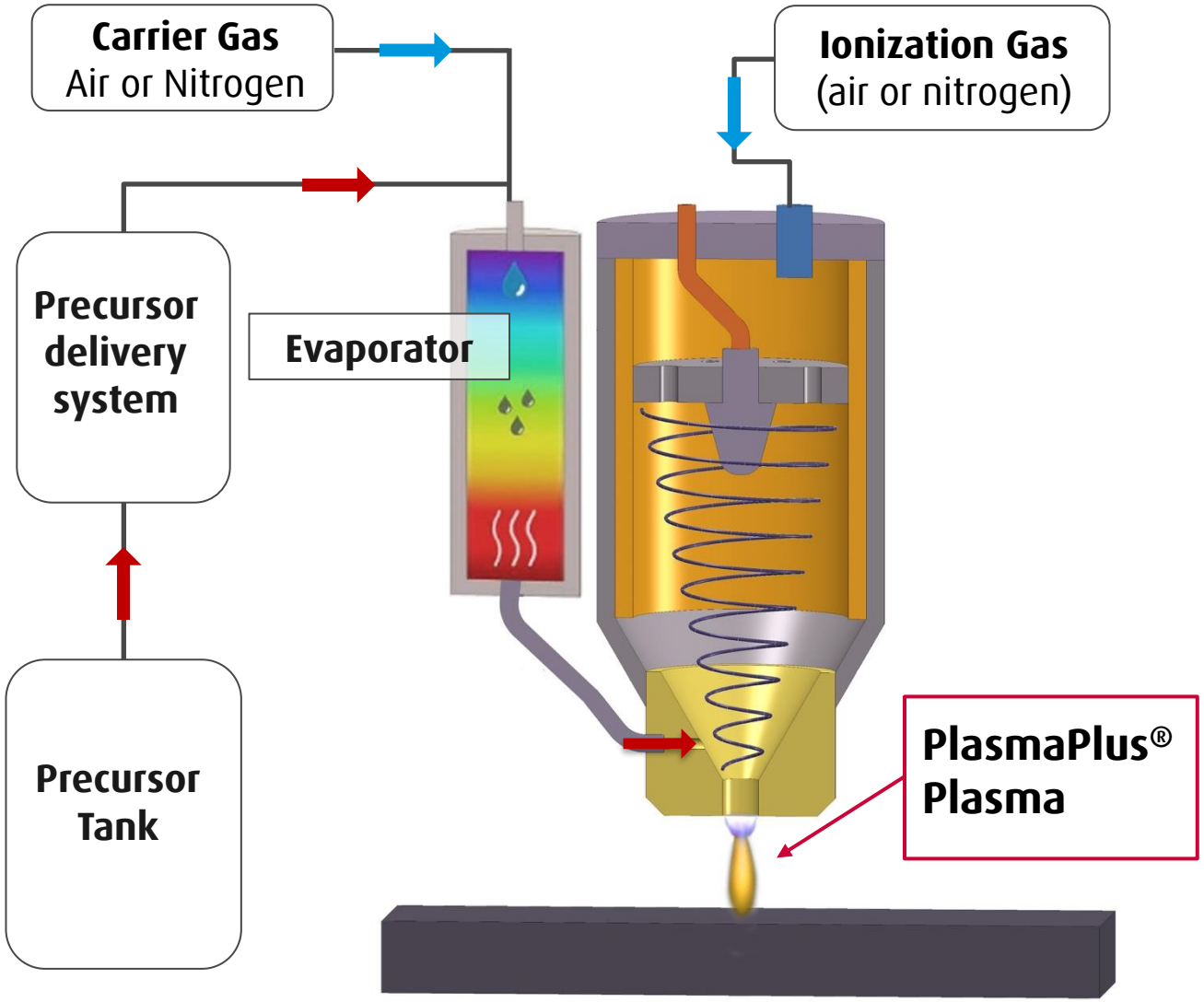


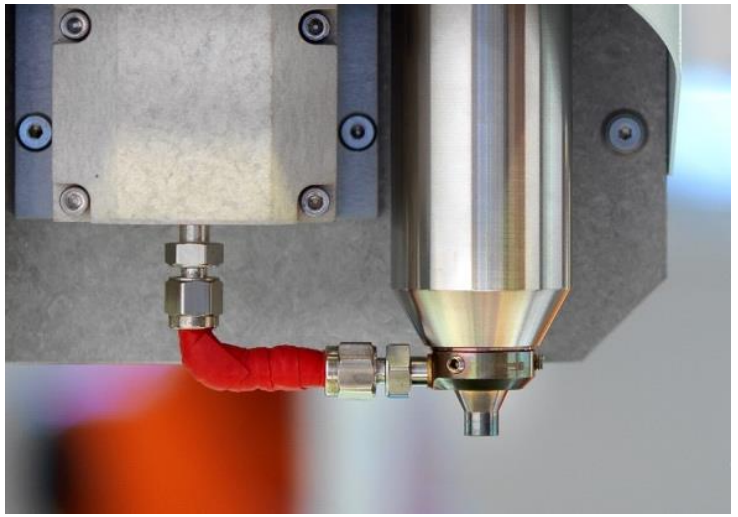
Static (higher speed) →

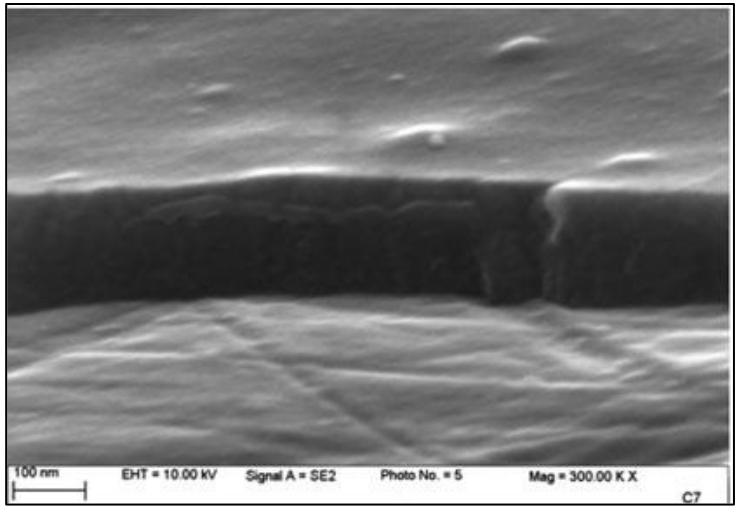
Rotating (larger width) →

Double rotating (largest width) →

Operating principle PlasmaPlus®

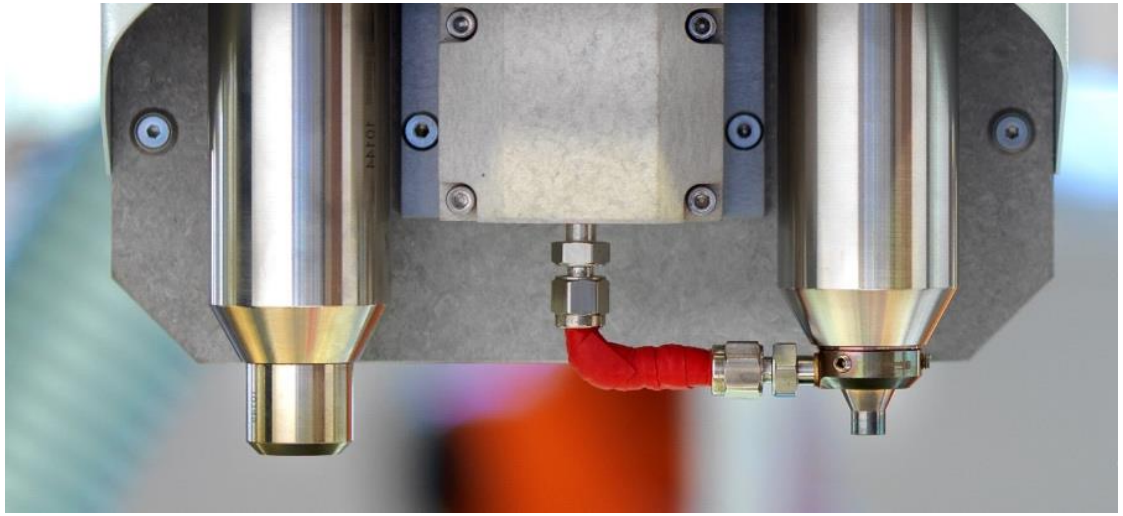


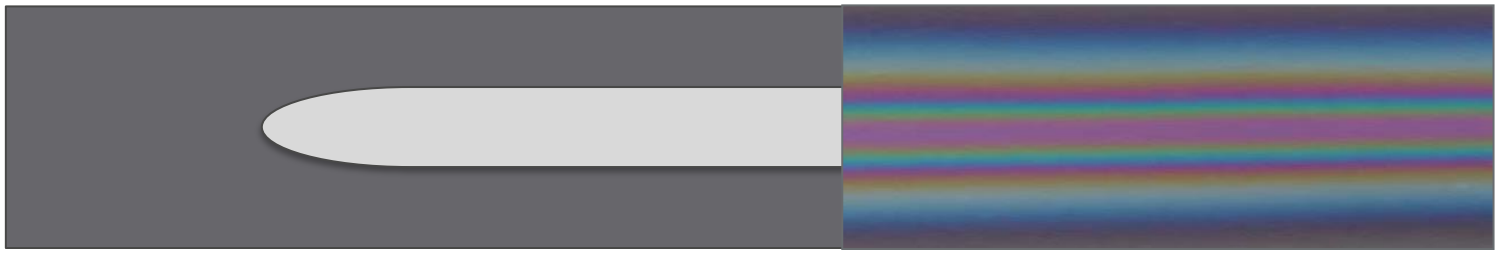




SiO_x films grown on stainless steel substrates
Thickness deposited : 150 nm
Deposition rate: 920 nm/s

Openair-Plasma® and PlasmaPlus® processes combination





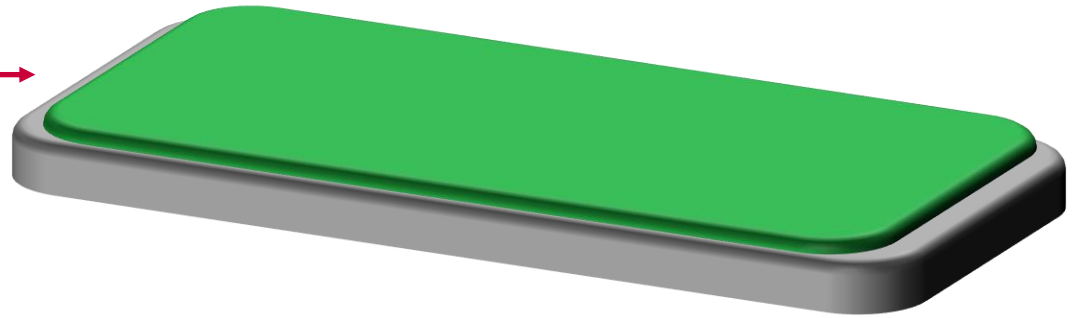
1. Step: Cleaning / Activation

2. Step: Coating

toward Plasma-based antimicrobial coatings...

Goal definition

Plasma deposited coatings



Substrate : Glass, Metal, Polymer, Ceramic…

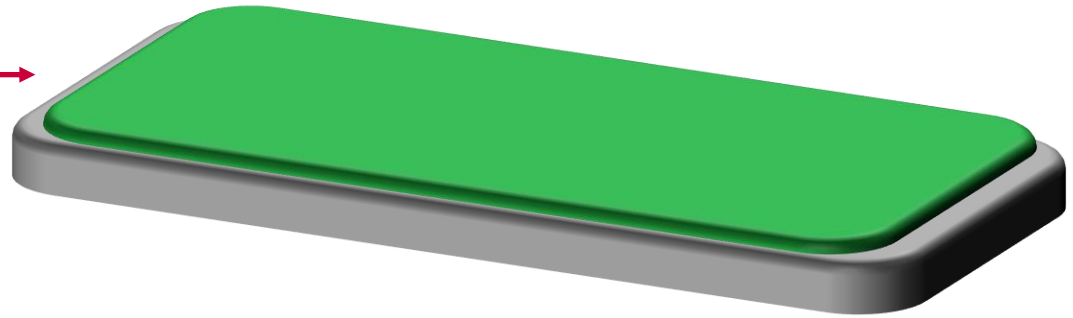
From Wfk Autoprotect presentation - 27.11.2017

Goal definition

Piezo-electric excitation
Pressure of <0,01 MPa
Contact pressure, wind, water

plasmatreat

Plasma deposited coatings



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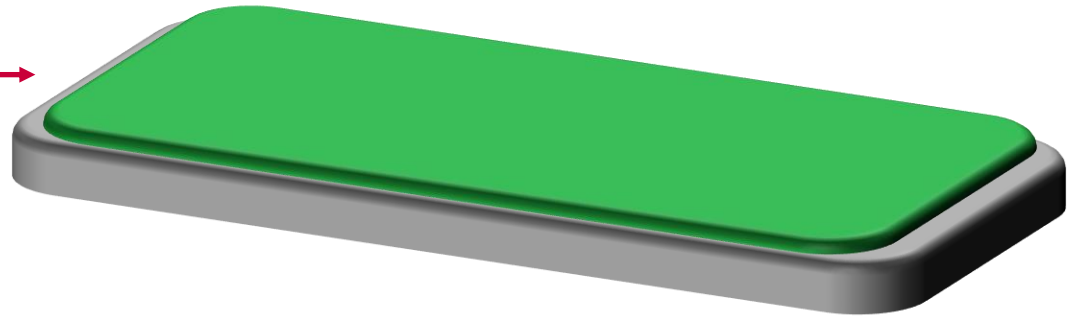
Pyro-electric excitation
Δ2-5 K
Heating, Cooling

Plasma deposited coatings →



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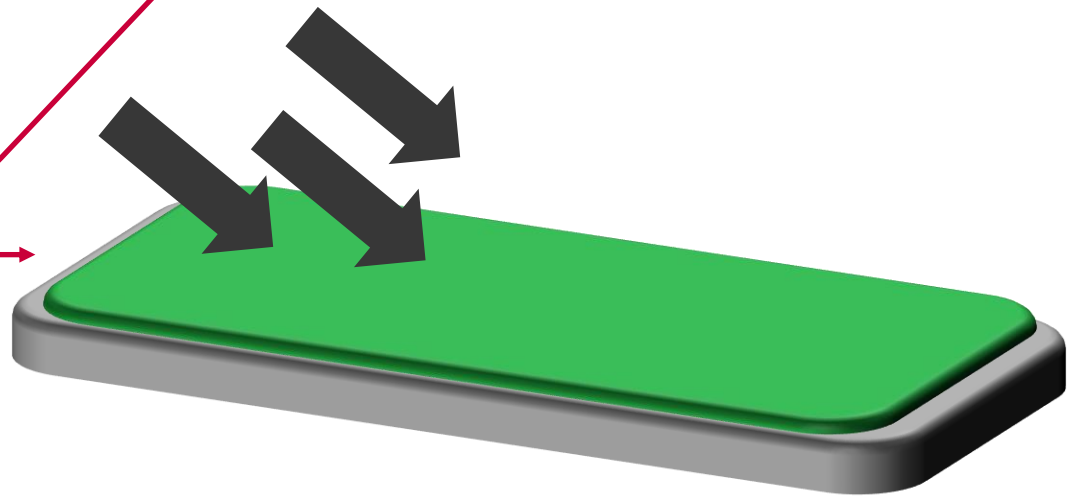
Δ2-5 K
Heating, Cooling

Photo-catalytic excitation
Light excitation 200-550 nm
Day light, artificial illumination

Plasma deposited coatings



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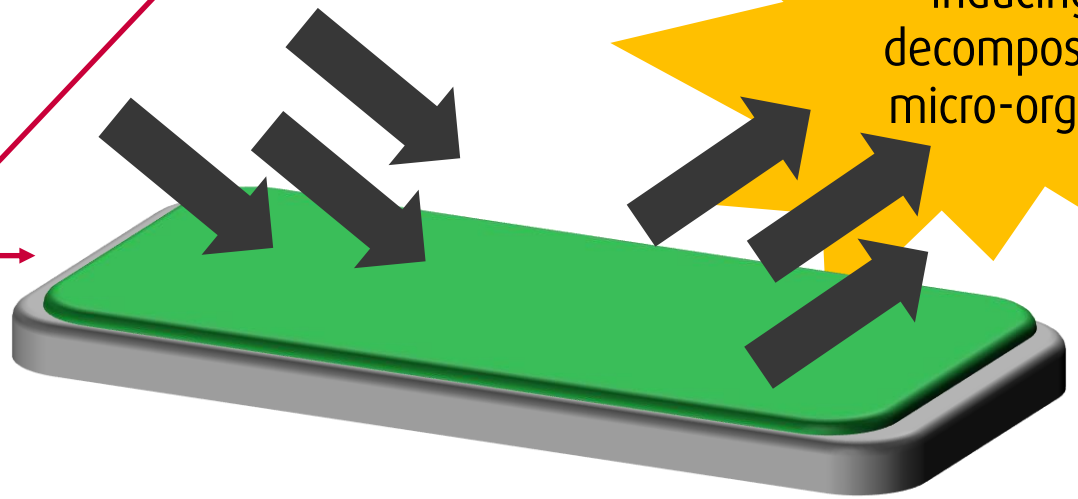

Hydroxyl radicals generation inducing the decomposition of micro-organisms

Substrate : Glass, Metal, Polymer, Ceramic…

From Wfk Autoprotect presentation - 27.11.2017

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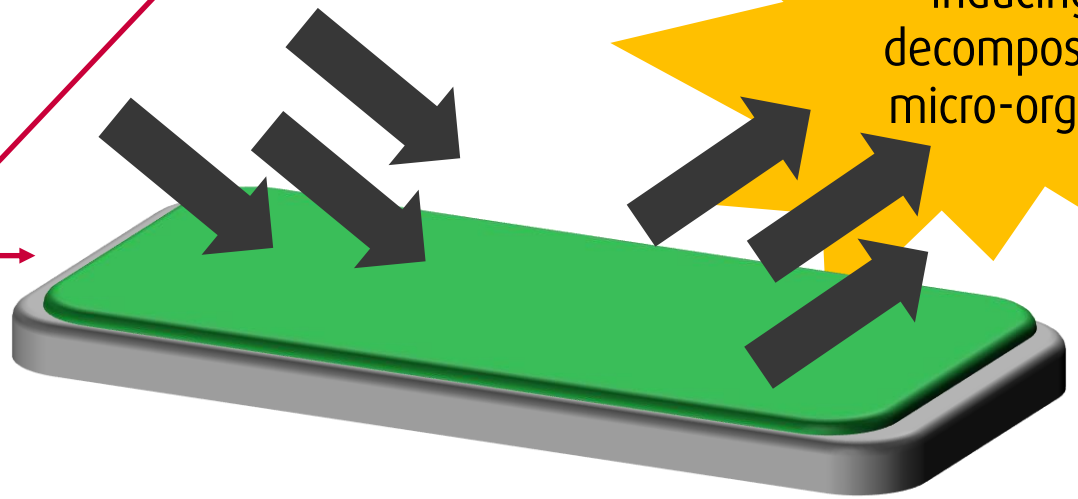

Hydroxyl radicals generation inducing the decomposition of micro-organisms

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Photocatalytic principle and coating definition

Light / Energy interacting with the material

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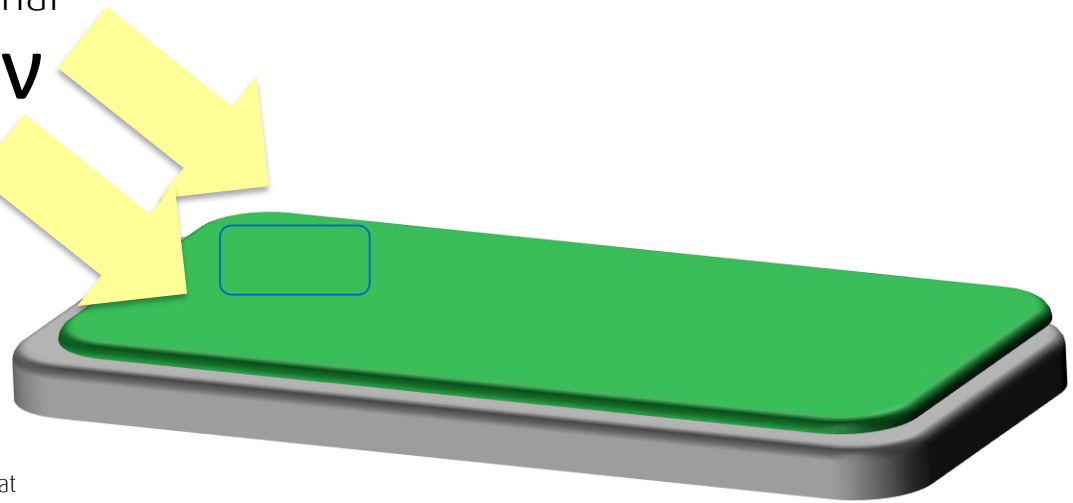
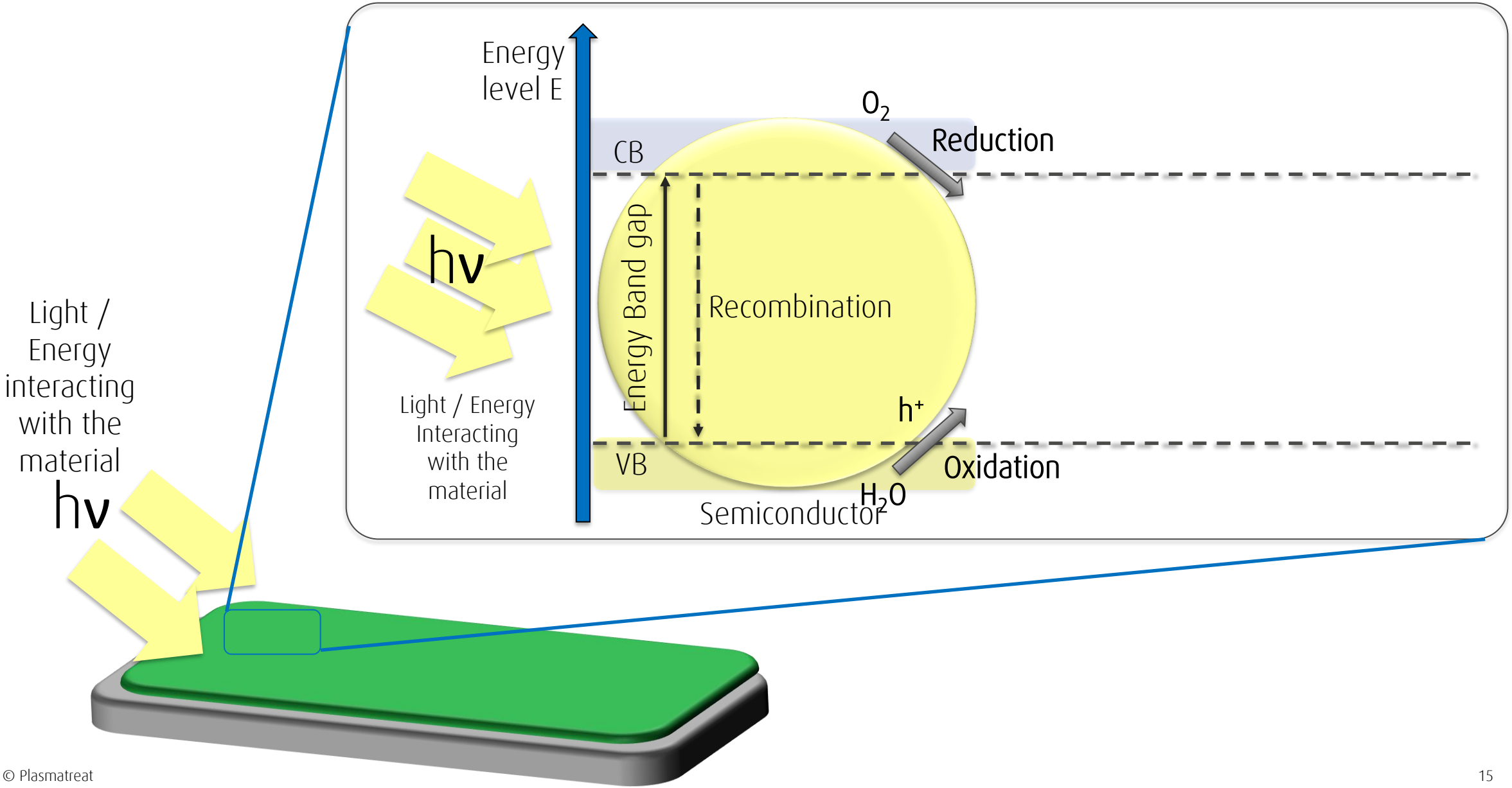


Photocatalytic principle and coating definition



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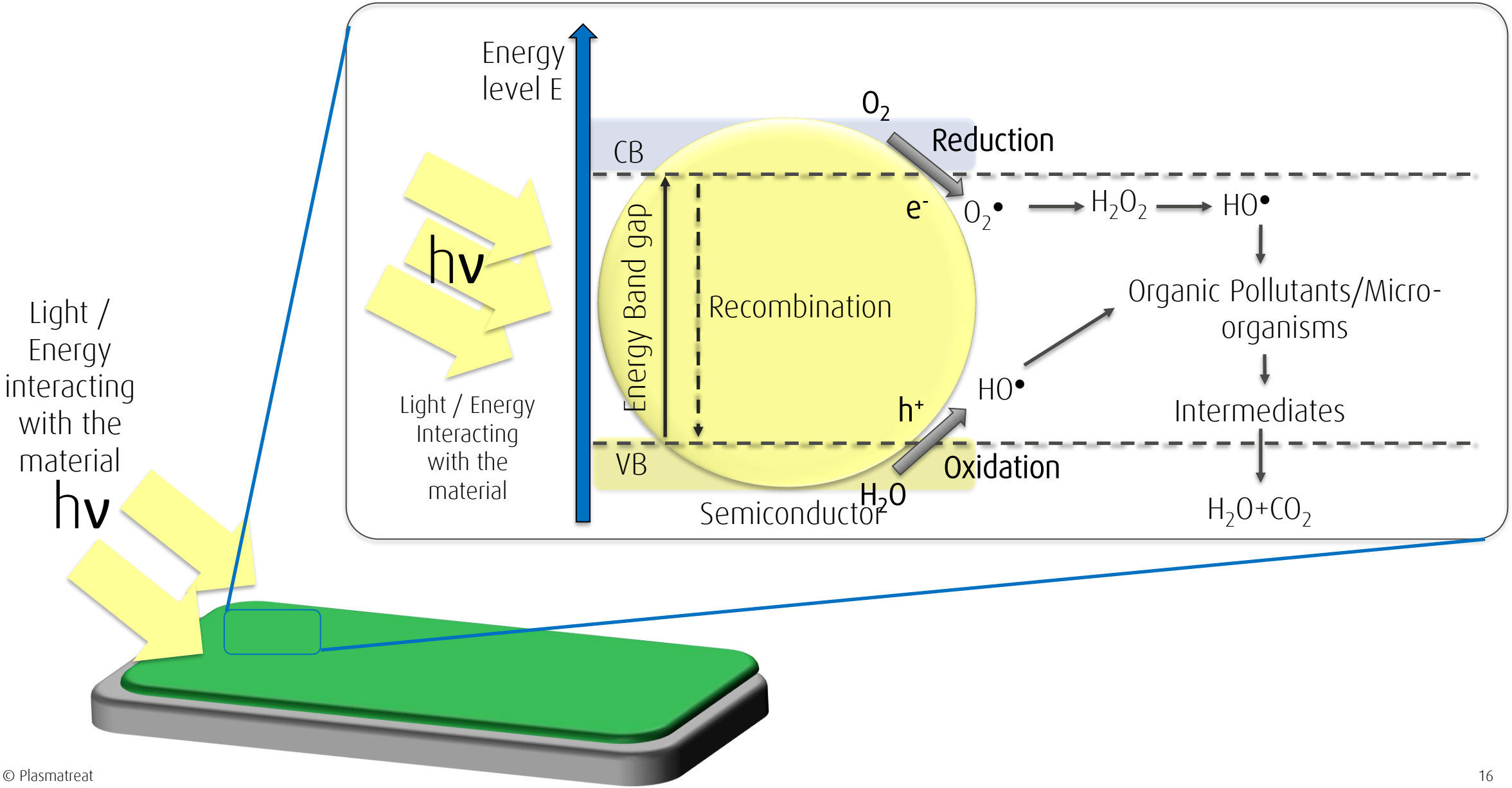

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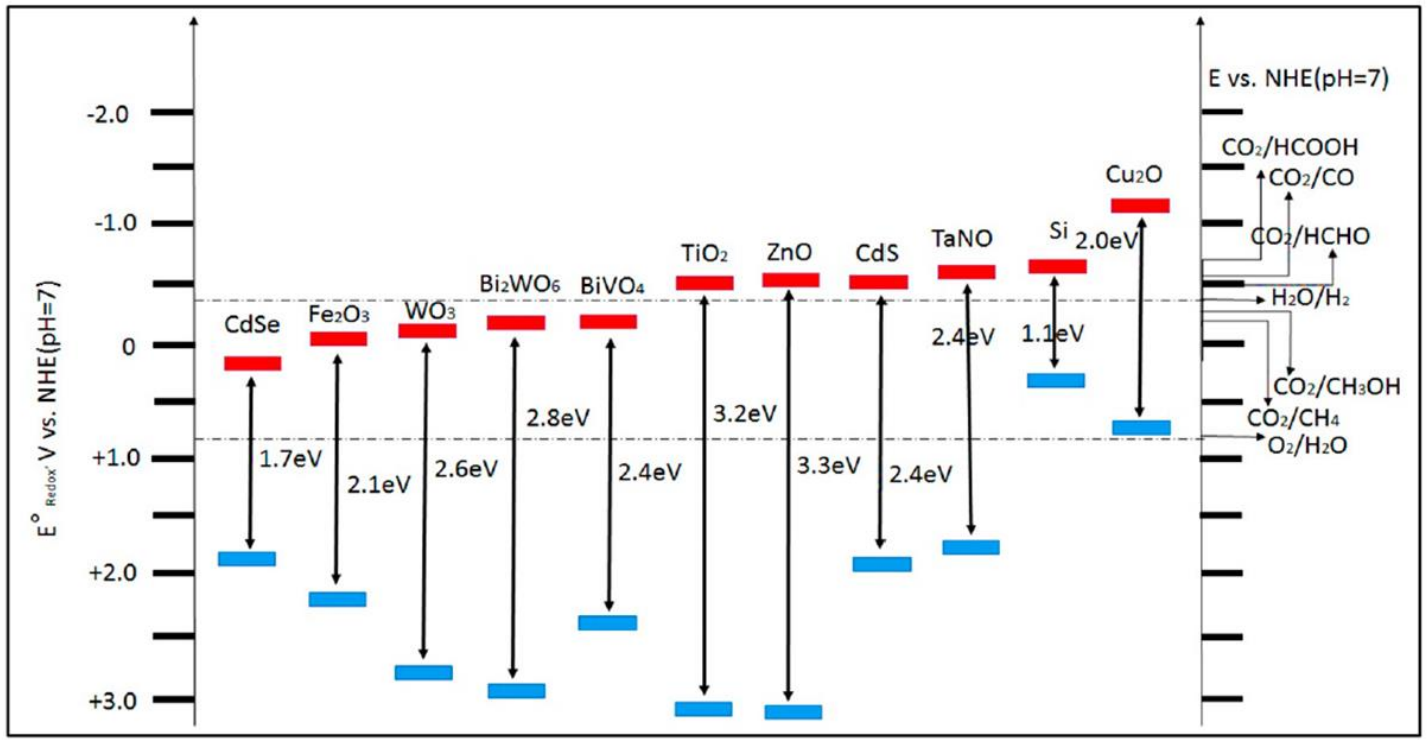
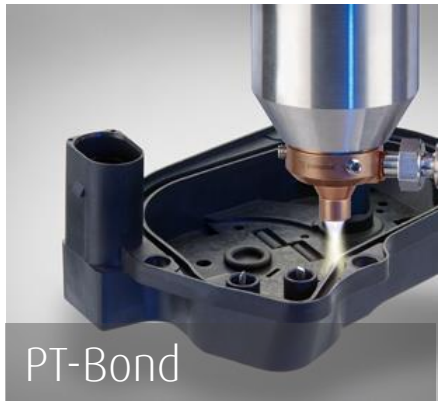


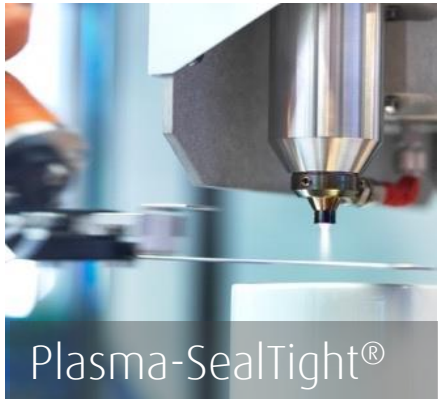
Photocatalyst	Band gap (eV)	Spectral region
ZnS	3.8	UV (326 nm)
SnO_2	3.8	UV (326 nm)
TiO_2 (anatase)	3.24	UV (383 nm)
$SrTiO_2$	3.2	UV (387 nm)
ZnO	3.2	UV (387 nm)
Degussa P25	3.14	UV (395 nm)
TiO_2 (rutile)	3.02	Visible (411 nm)
WO_3	2.8	Visible (443 nm)
CdS	2.4	Visible (517 nm)
Fe_2O_3	2.3	Visible (539 nm)
Cu_2O	2.2	Visible (564 nm)
MoS_2	1.8	Visible (689 nm)
CdSe	1.7	Visible (729 nm)

Source : Materials 2017, 10, 629; doi: 10,3390/ma10060629

Photocatalytic principle and coating definition
PlasmaPlus® Technology



PT-Bond is a plasma coating designed to promote the adhesion of adhesives and sealants

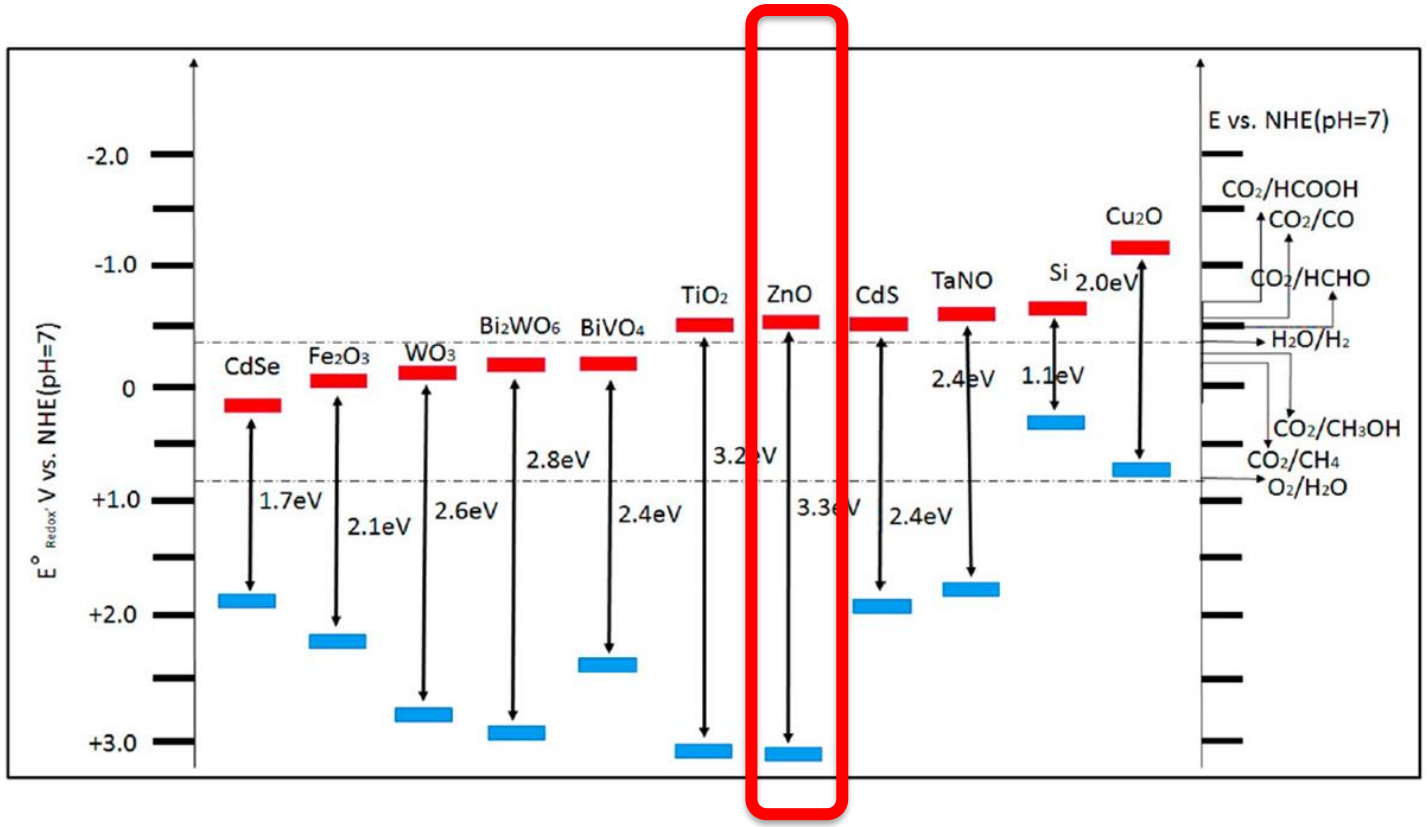


Plasma-SealTight® coating for a strong, covalent bond between component parts

A high-performance barrier coating which provides an inline and active corrosion protection

PT-Print enables a one-step digital printing process which significantly improves the adhesion and moisture resistance of UV inks on hard materials

Photocatalytic principle and coating definition
PlasmaPlus® towards innovative coatings



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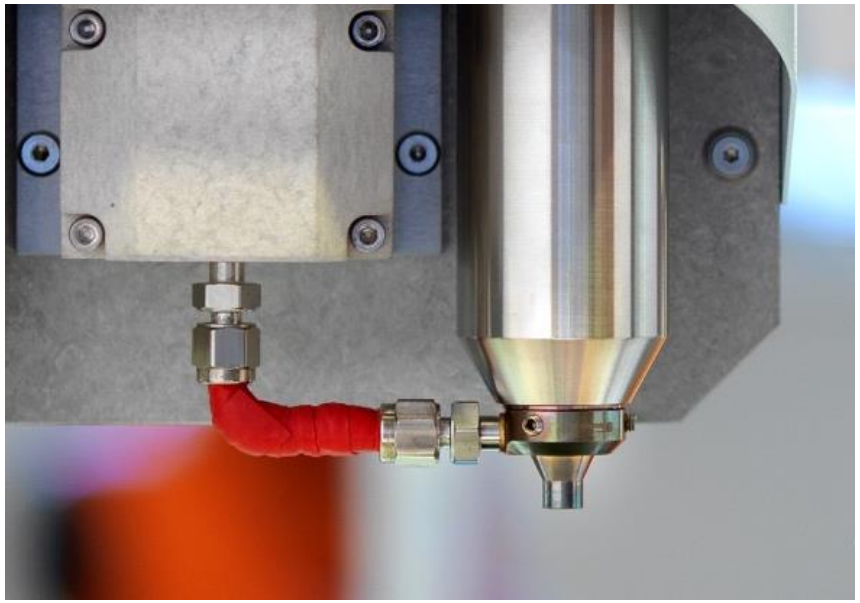
This presentation will be focused on presenting the latest results obtained depositing ZnO/SiO mixed oxide films by plasma

Source : Materials 2017, 10, 629; doi: 10,3390/ma10060629

Results and characterization

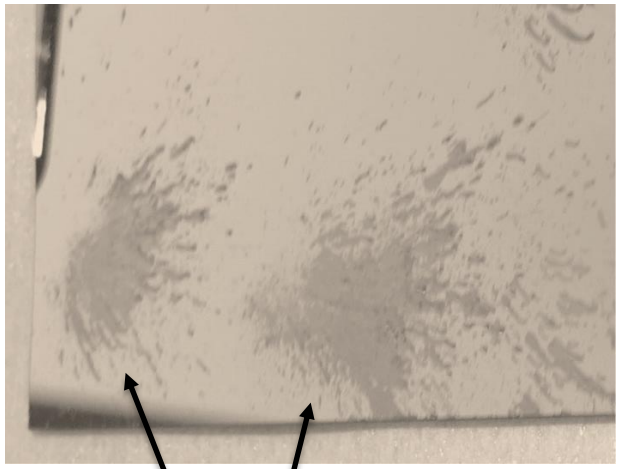
PlasmaPlus® process



Formulation and optimization of SiOx/ZnOx precursor.

Coating goal is to obtain ZnOx embedded in the SiOx matrix

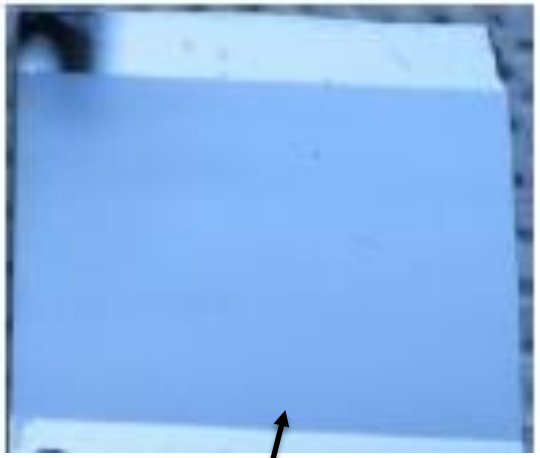
Crystallized precursor observed in the plasma nozzle head



Inhomogeneous coating observed during deposition on Si Wafer

Results and characterization

PlasmaPlus® process optimization



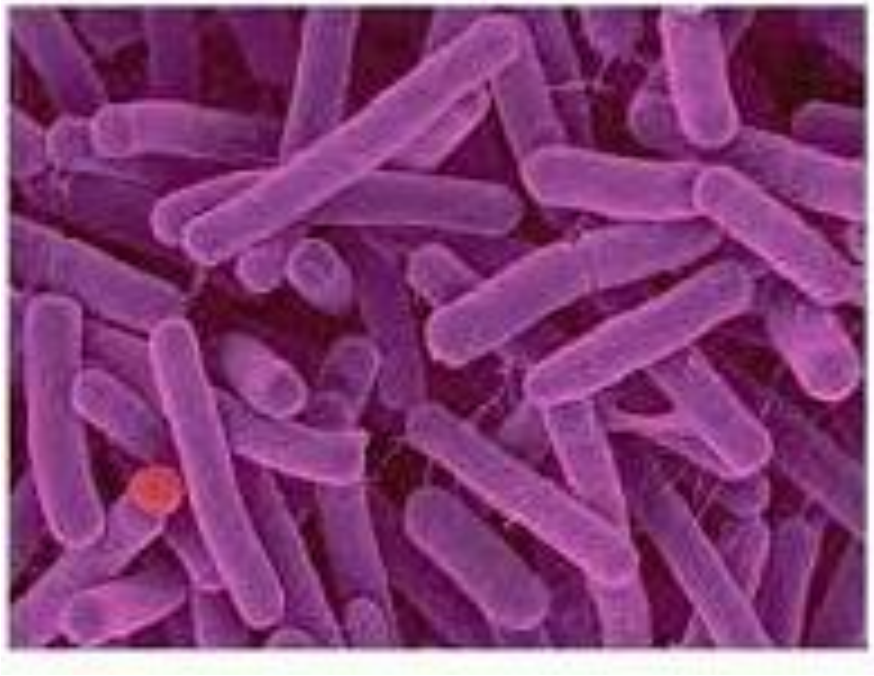
Homogeneous coating
observed during
deposition on Si Wafer

More homogeneous coating obtained using the external precursor introduction – Validation of the deposition process

Results and characterization

Methodology used for Antibacterial surface property evaluation:

- Test germ: Bacillus atrophaeus 2277 in LB Solution
- Incubation: 20°C, rf. ca 90%, 2h
- Samples : Polycarbonate samples 1x1 cm
  5 samples per coating parameter



Source :
https://www.sciencephoto.com/media/798576/view/bacillus-atrophaeus-bioindicator-bacterium-sem

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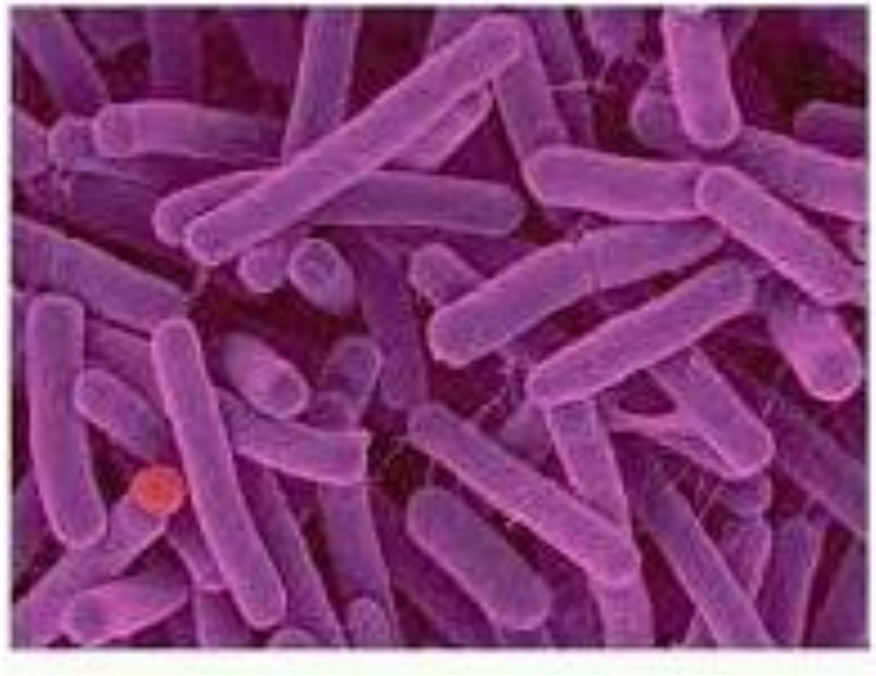

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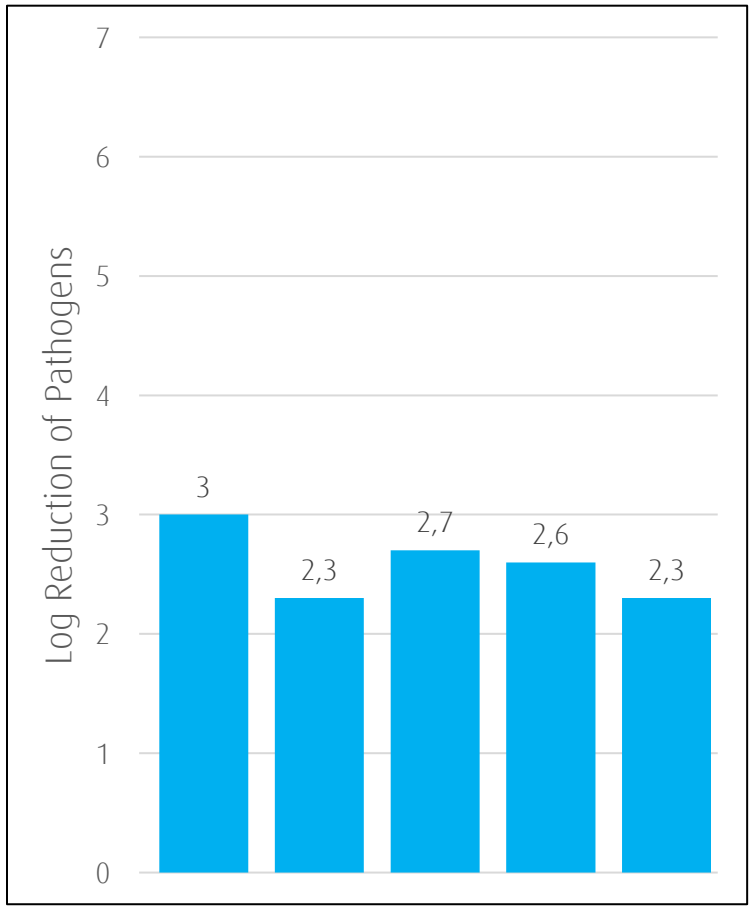
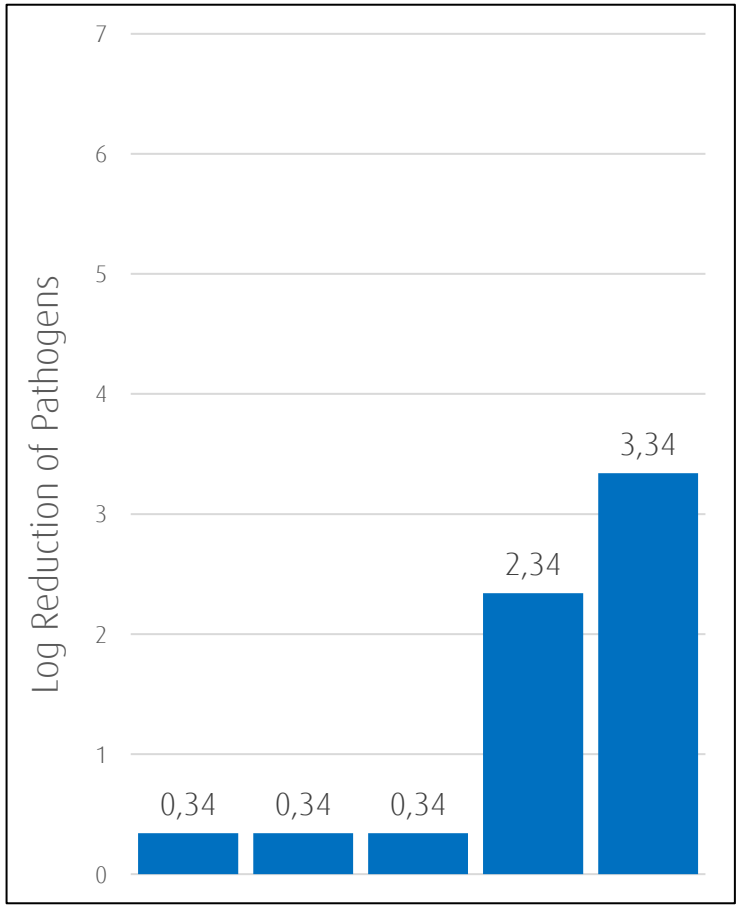
Results and characterization

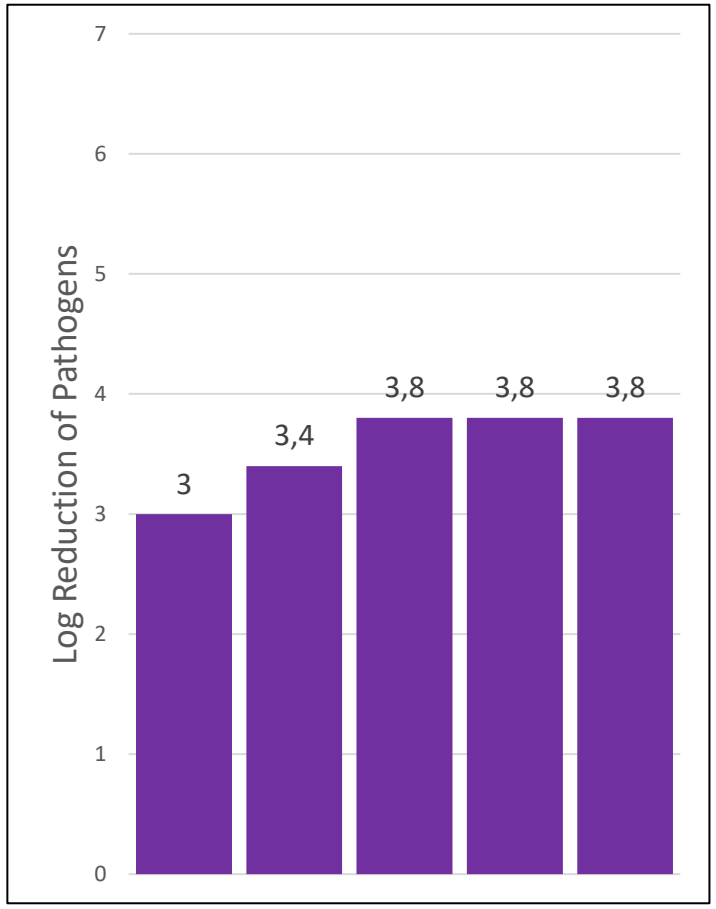
Influence of film composition



ZnO coatings Air-Plasma



SiO_x/ZnO Air-Plasma



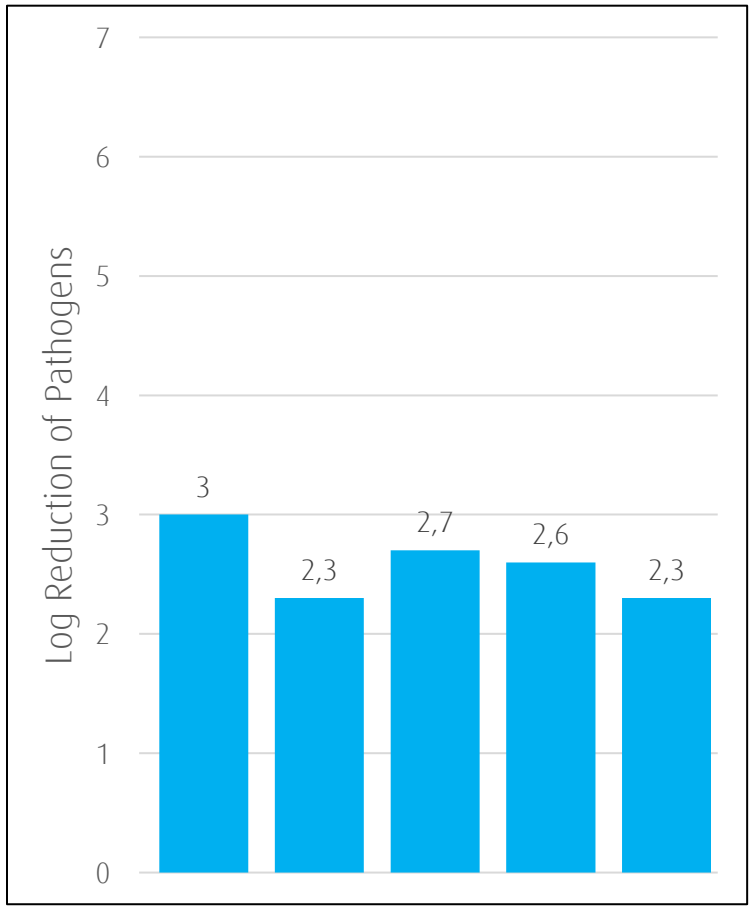
SiO_x/ZnO Nitogen-Plasma

Good antimicrobial properties of ZnO based coating

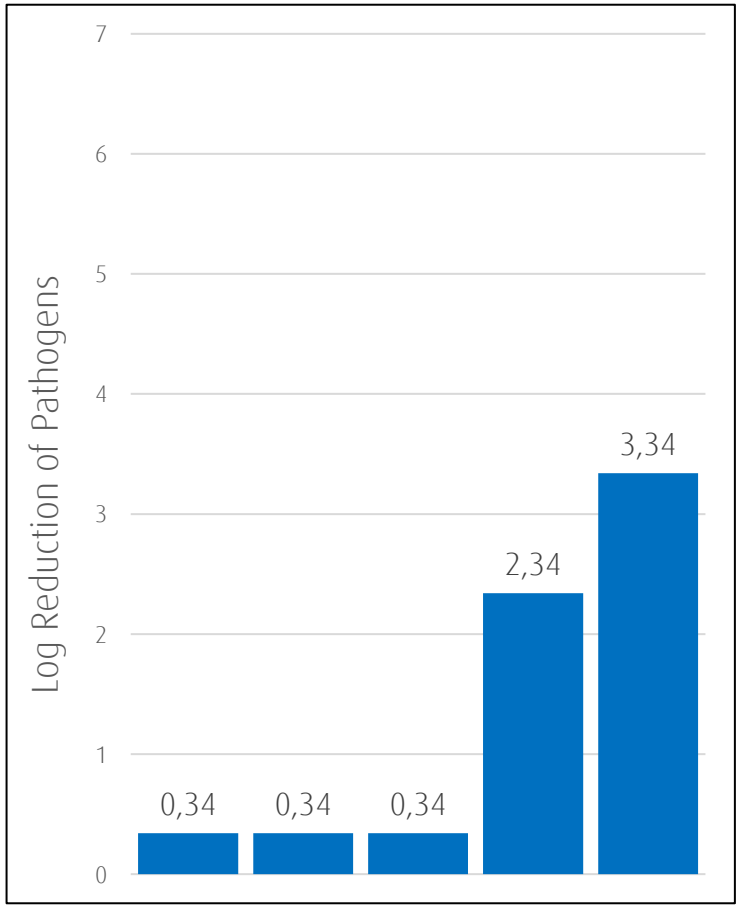
Improvement of the antimicrobial properties observed for SiO/ZnO based coating
However additional efforts required to improve the mechanical stability

Results and characterization

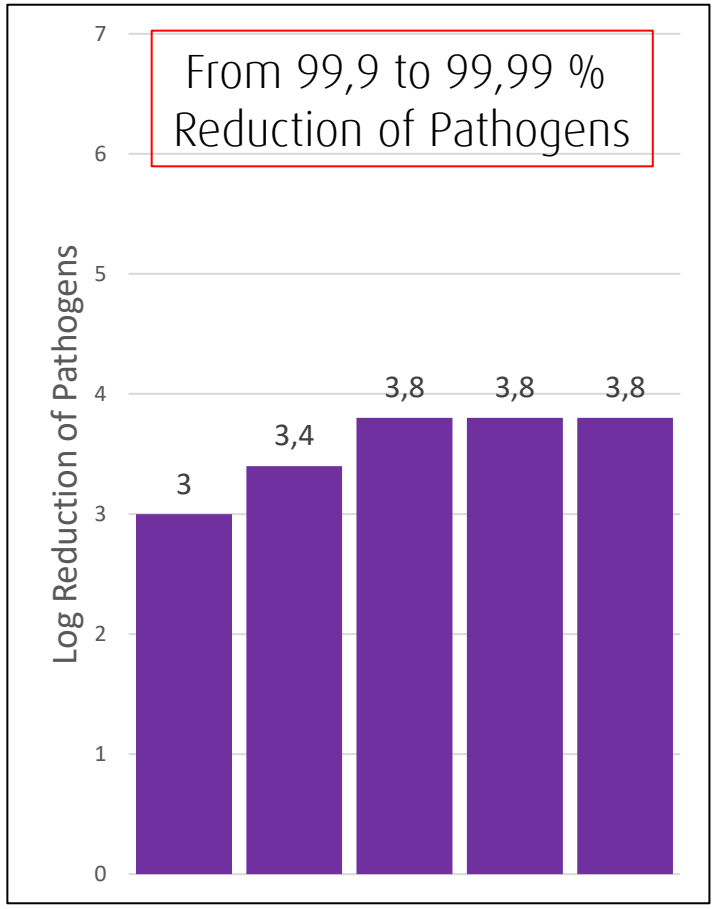
Influence of film composition



ZnO coatings Air-Plasma



SiO_x/ZnO Air-Plasma



SiO_x/ZnO Nitogen-Plasma

Good antimicrobial properties of ZnO based coating

Improvement of the antimicrobial properties observed for SiO/ZnO based coating
However additional efforts required to improve the mechanical stability

Results and characterization

Through changes in deposition parameters mechanically stable coatings could be achieved

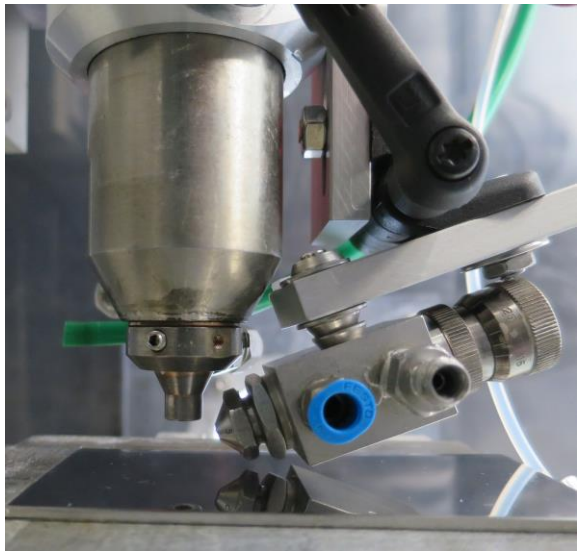
Stability on Substrates:

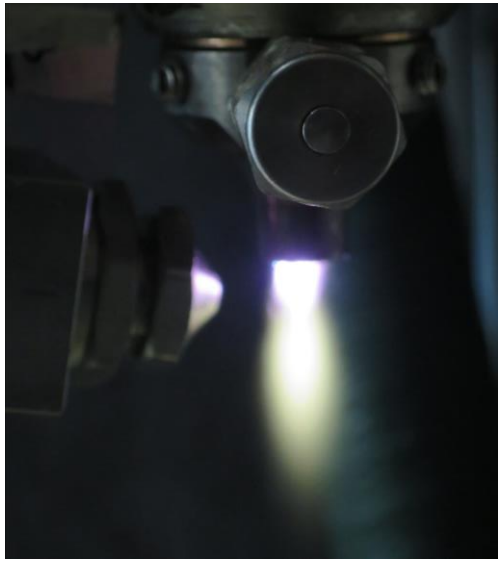
Tested by tape-test in reference to Din EN ISO 2409

As well as crosscut test as described in Din EN ISO 2409

2. Optimized Spray configuration

Substrate	Tape test	Crosscut -Test
Si Wafer	No detachment	Value 0 - OK
Aluminium	No detachment	Value 0 - OK
Polycarbonate	No detachment	Value 0 - OK

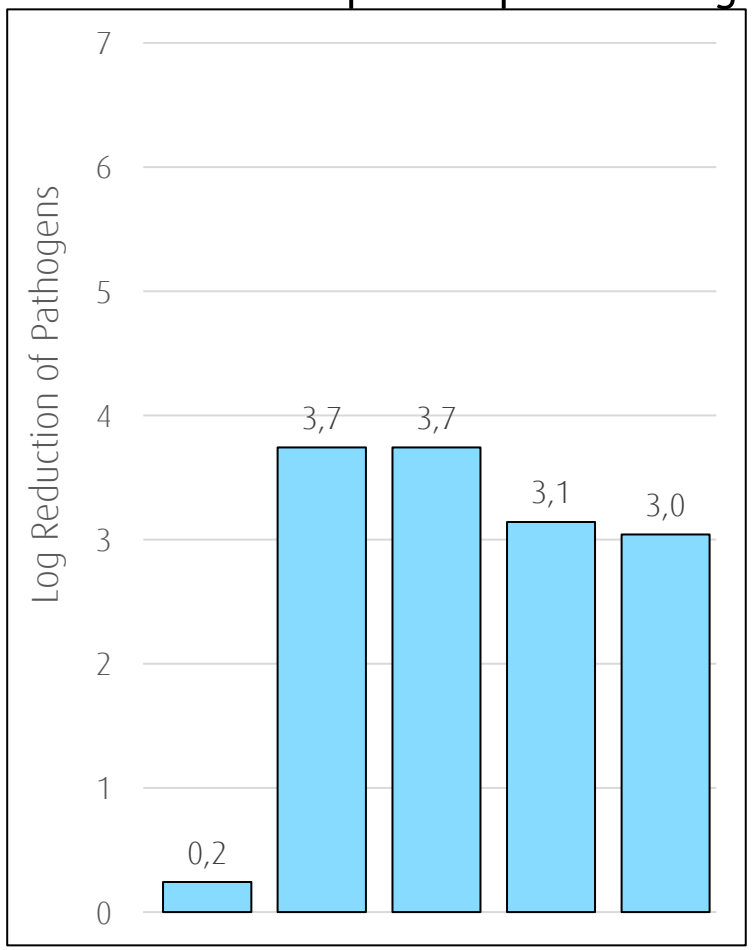




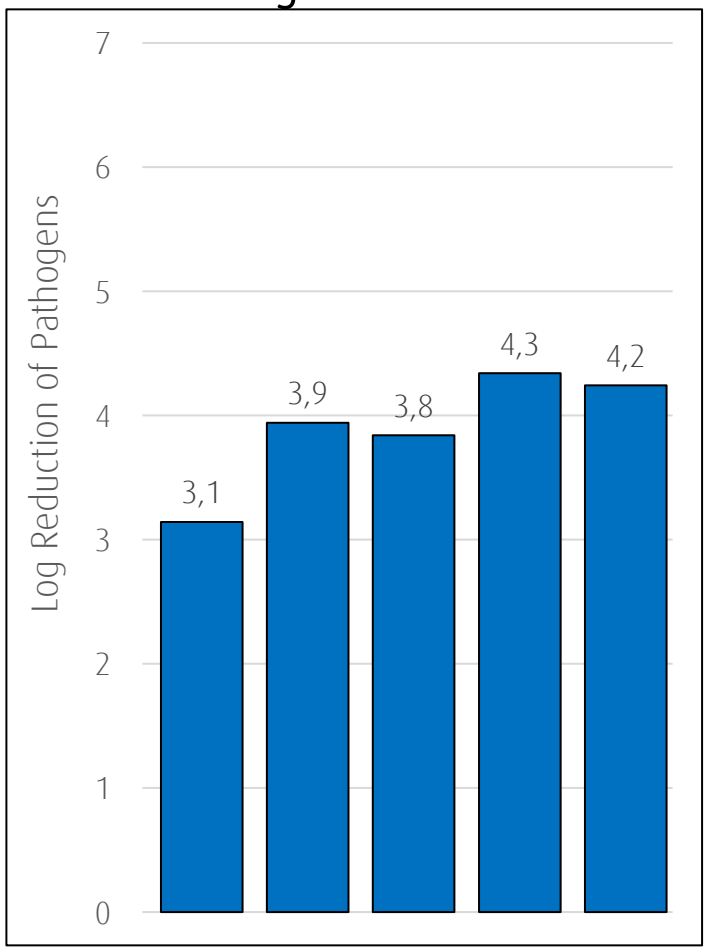
Optimization in deposition parameters :
Spray fixtures
Spray parameters
Angle of injection

Results and characterization

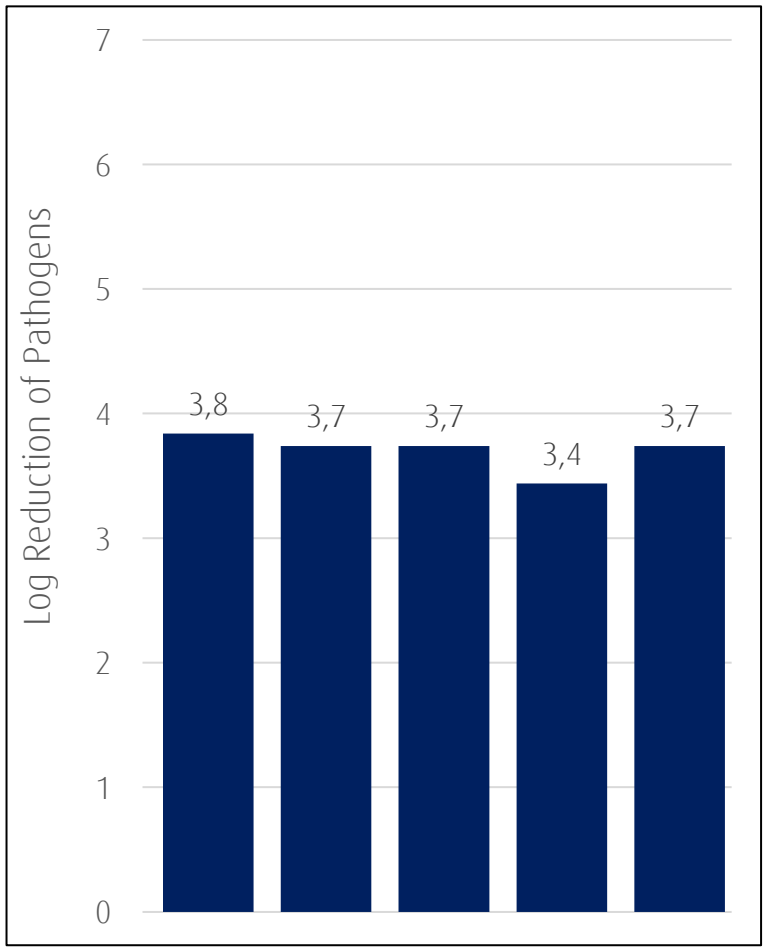
Influence of the plasma power using Air as ionization gas



SiO/ZnO coatings
Air-Plasma Low Power



SiO/ZnO coatings
Air-Plasma Medium Power

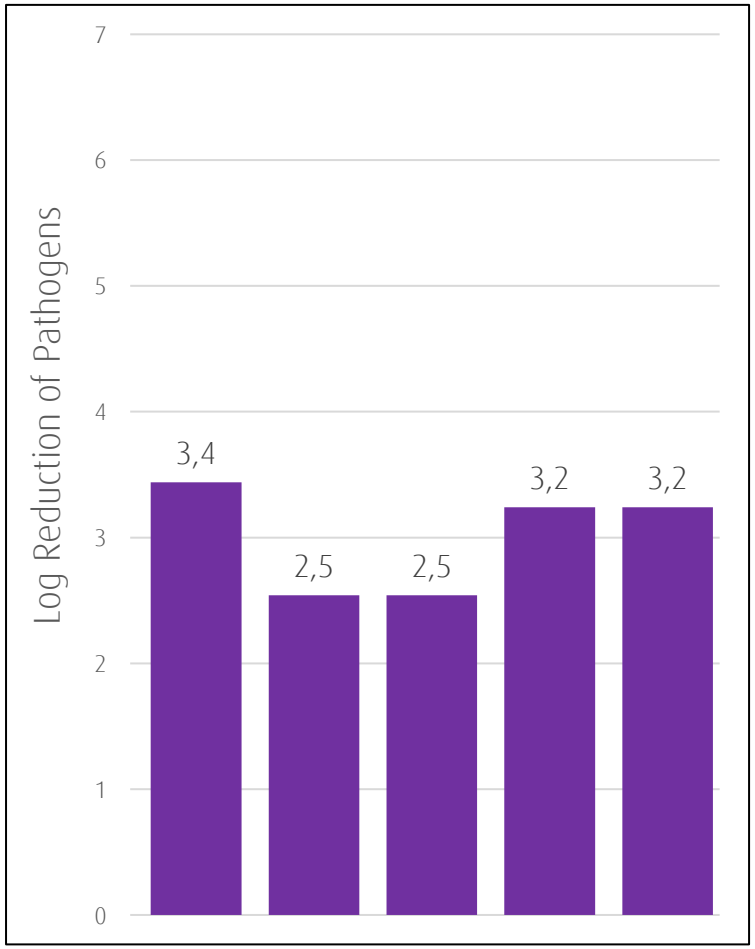


SiO/ZnO coatings
Air-Plasma High Power

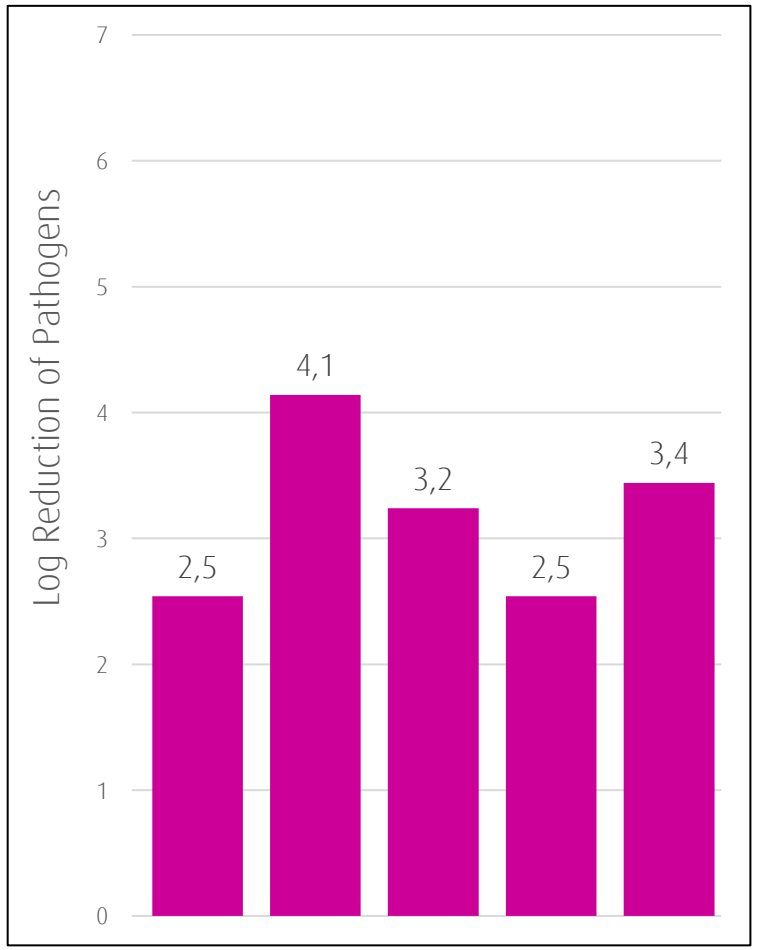
Plasma Power shows little influence on antibacterial properties, but slightly increased mechanical stability.

Results and characterization

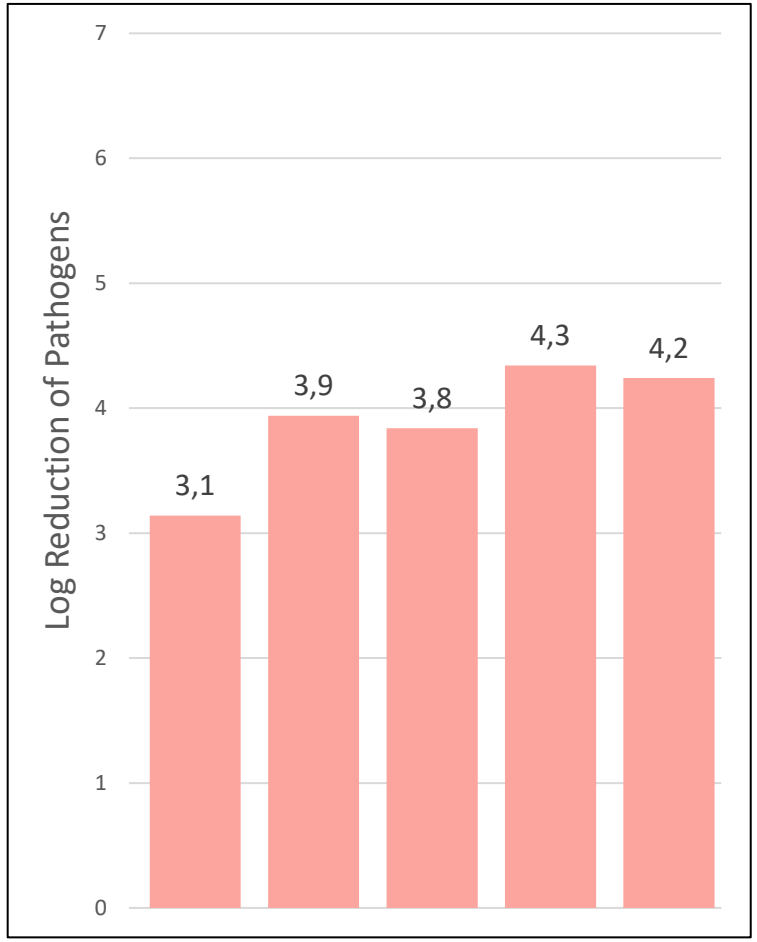
Influence of the plasma power using Nitrogen as ionization gas



SiO/ZnO coatings Nitrogen Plasma High Power



SiO/ZnO coatings Nitrogen Plasma Medium Power

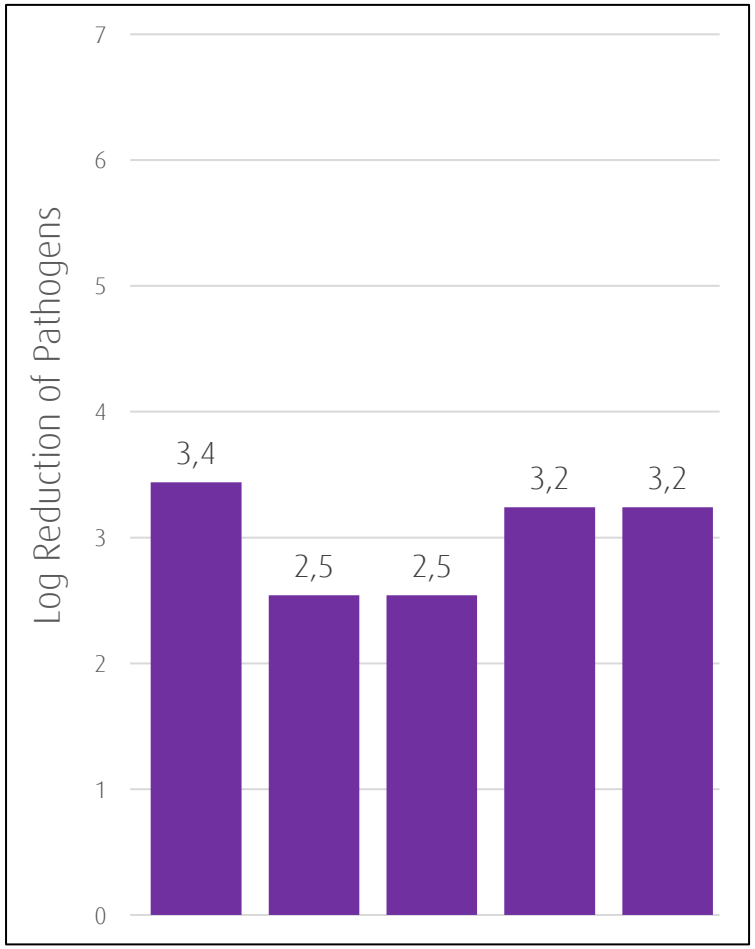


SiO/ZnO coatings Nitrogen Plasma Low Power

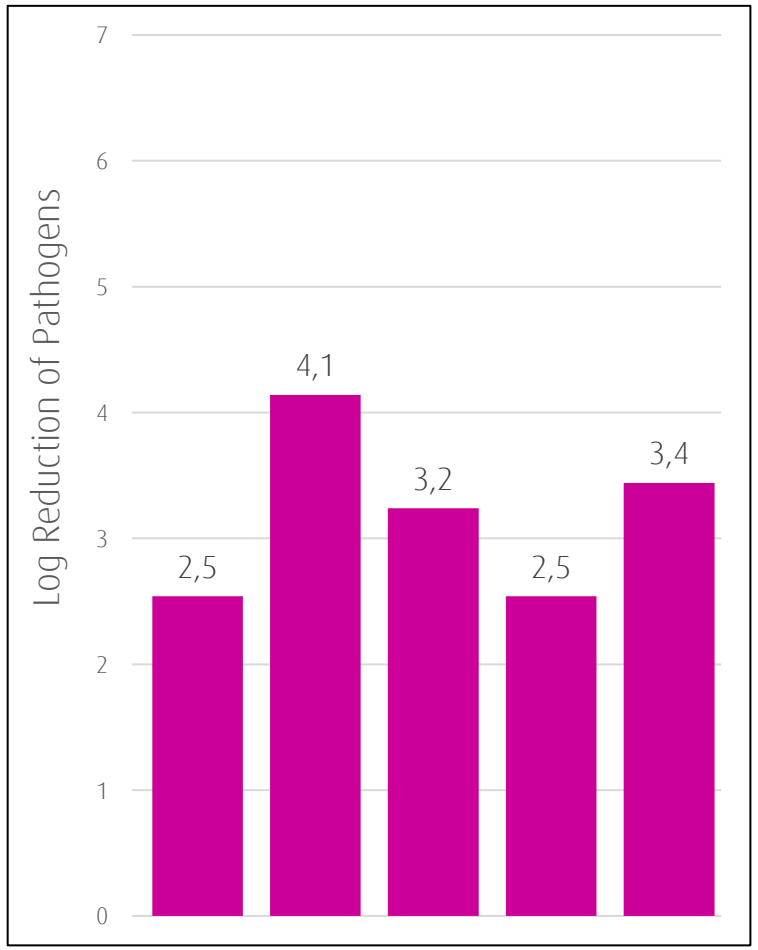
Plasma Power shows little influence on antibacterial properties, but slightly increased mechanical stability.

Results and characterization

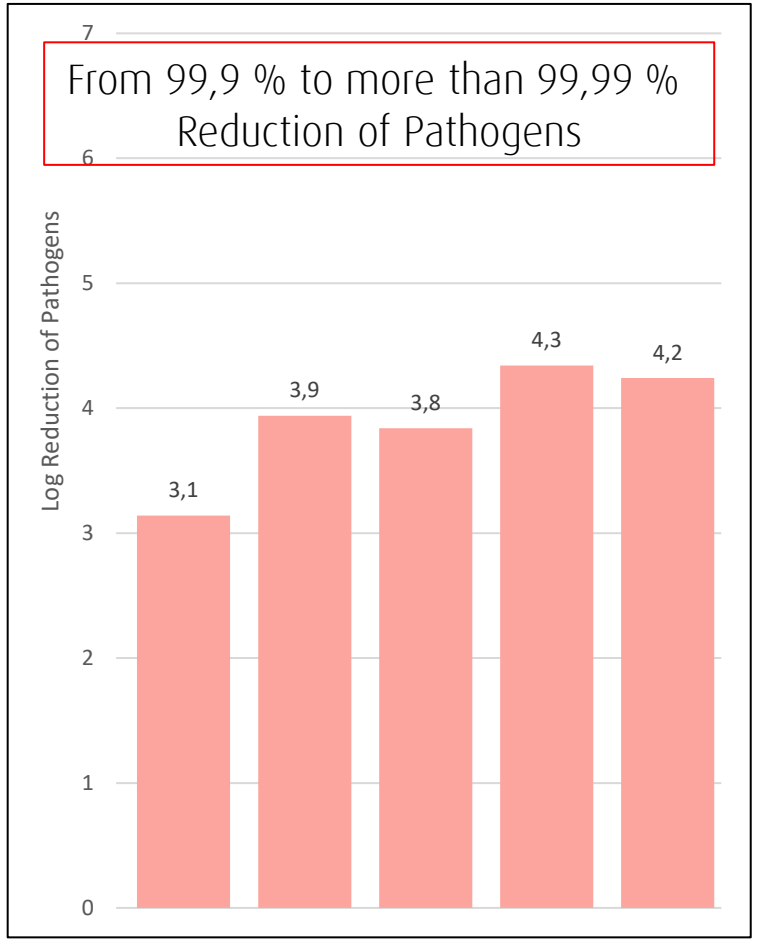
Influence of the plasma power using Nitrogen as ionization gas



SiO/ZnO coatings Nitrogen Plasma High Power



SiO/ZnO coatings Nitrogen Plasma Medium Power

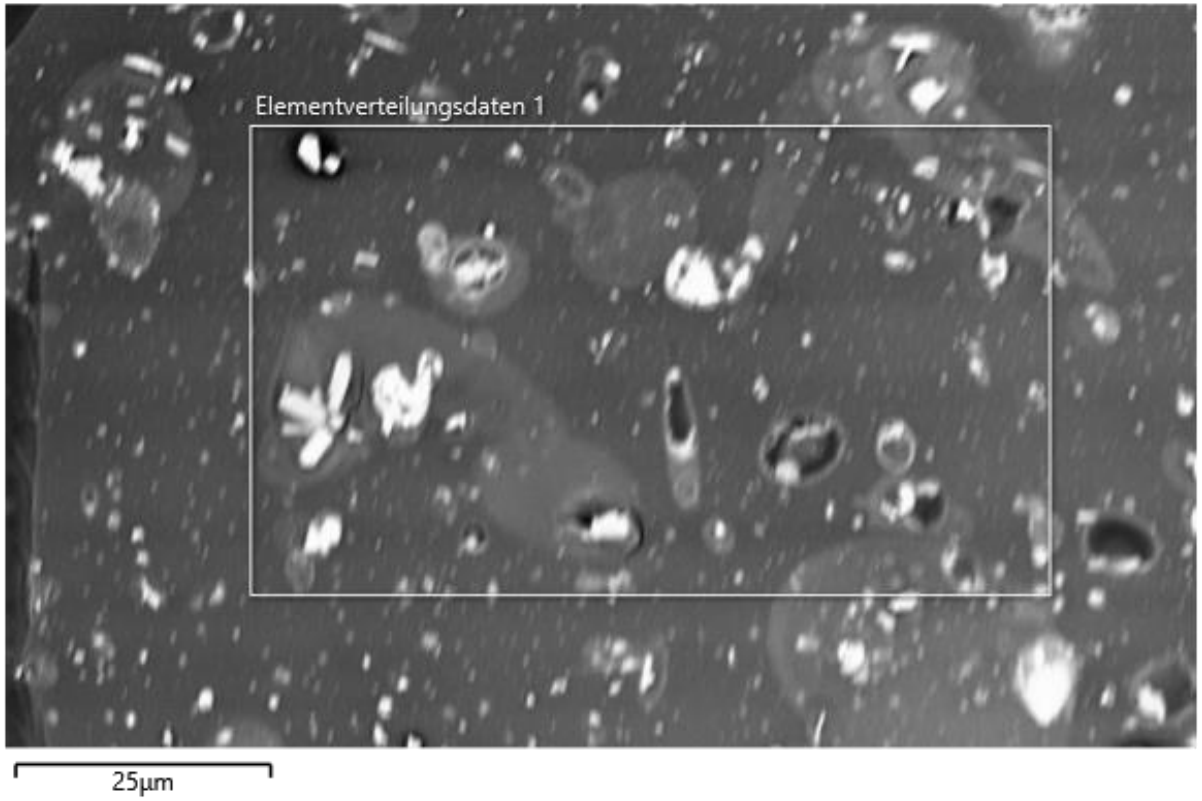


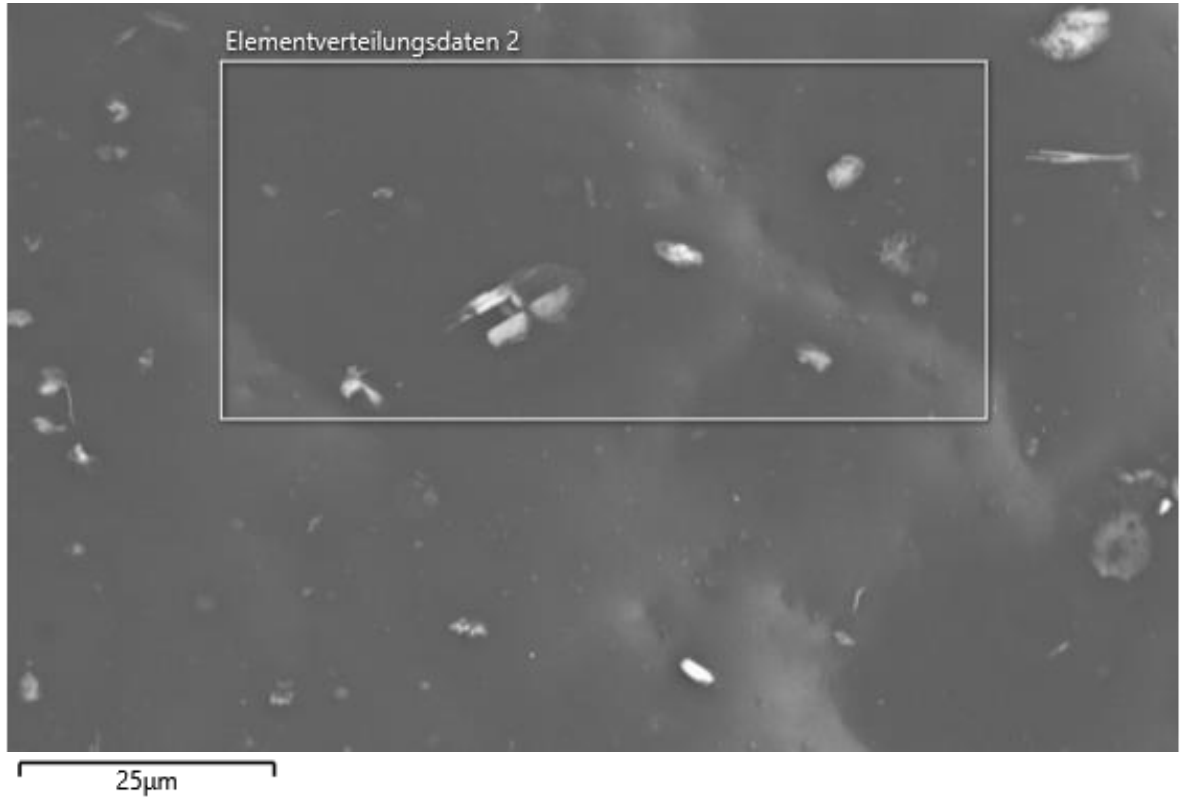
SiO/ZnO coatings Nitrogen Plasma Low Power

Plasma Power shows little influence on antibacterial properties, but slightly increased mechanical stability.

Results and characterization

Scanning Electron Microscopy observations before and after cleaning

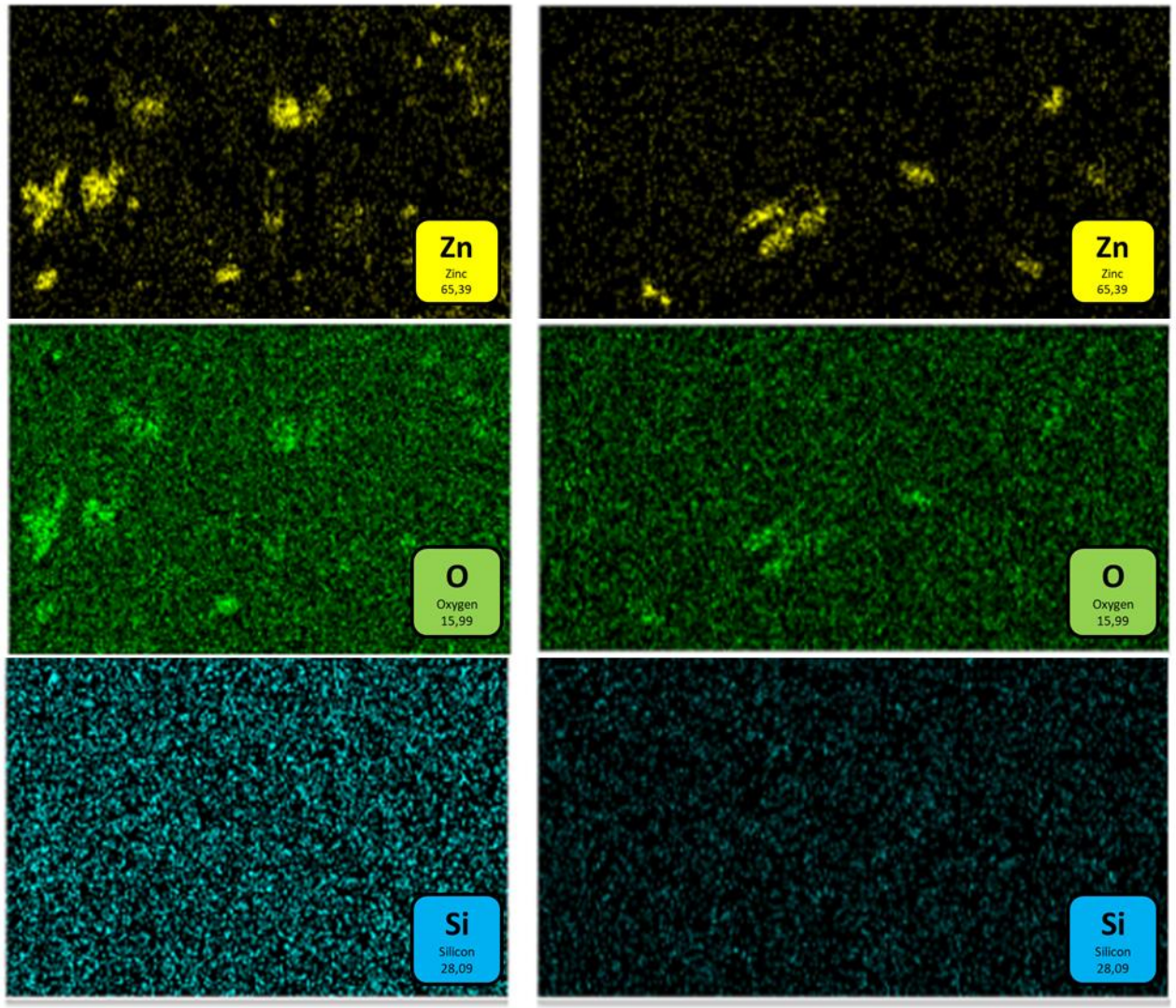




Electron micrographs at 1000 times magnification of the SiOx ZnO coatings on polycarbonate before a) and after 5 cleaning cycles b). The frame shown represents the area of element analysis examined in the EDX.

Results and characterization

Scanning Electron Microscopy observations before and after cleaning - EDX



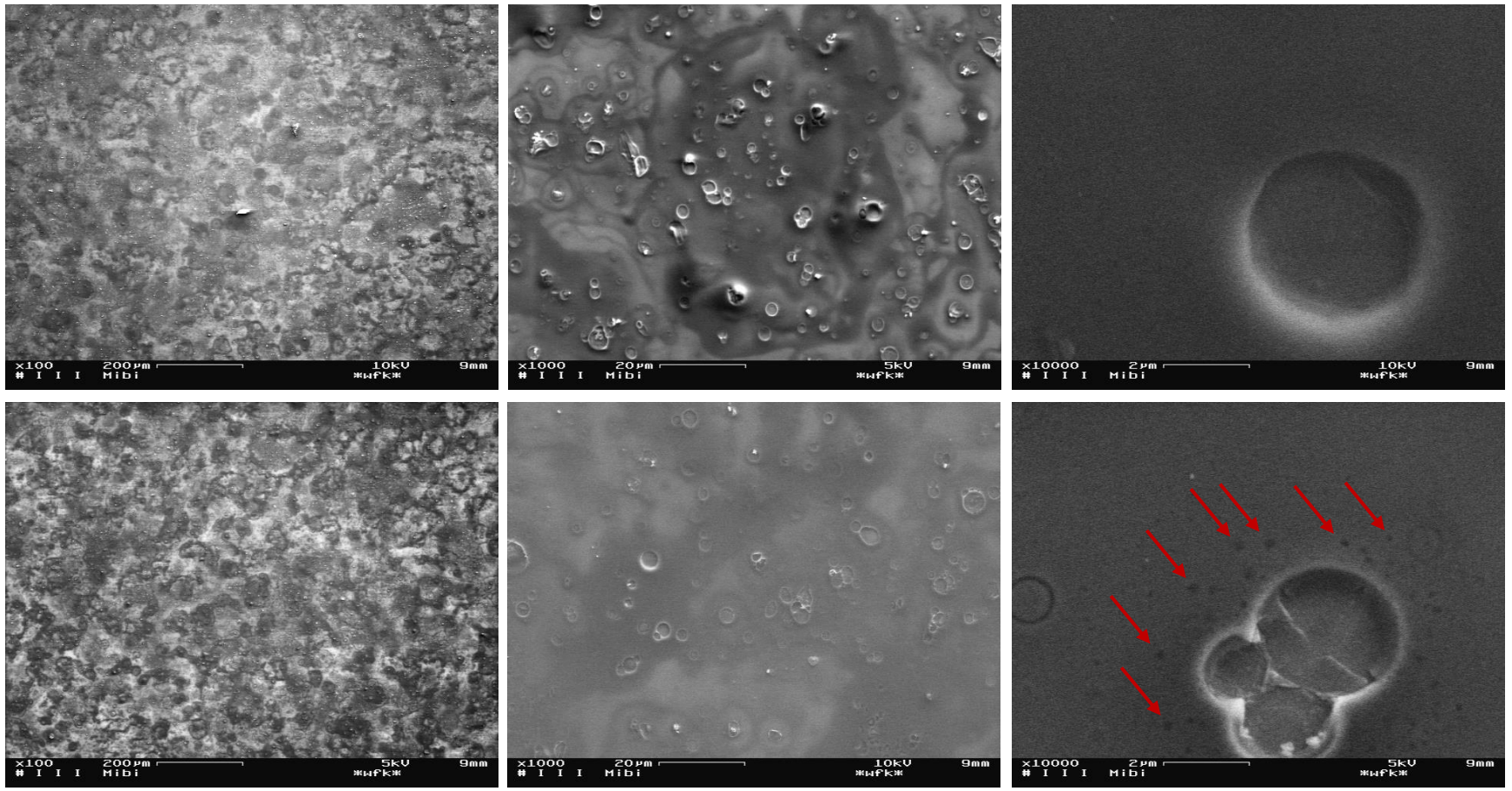
EDX – Elemental analysis highlighting
Zn , Si and Oxygen elements
before a) and after 5 cleaning cycles b)

Following the coating, Zn / Si / O are clearly present on the surface however following the cleaning it can be observed that Zn particles are removed from the surface but also Oxygen content.

For the Si content, it seems that the Si is stable and no visual modification following the cleaning step on the concentration of the particles (only loss in the intensity)

Results and characterization

Scanning Electron microscopy characterization

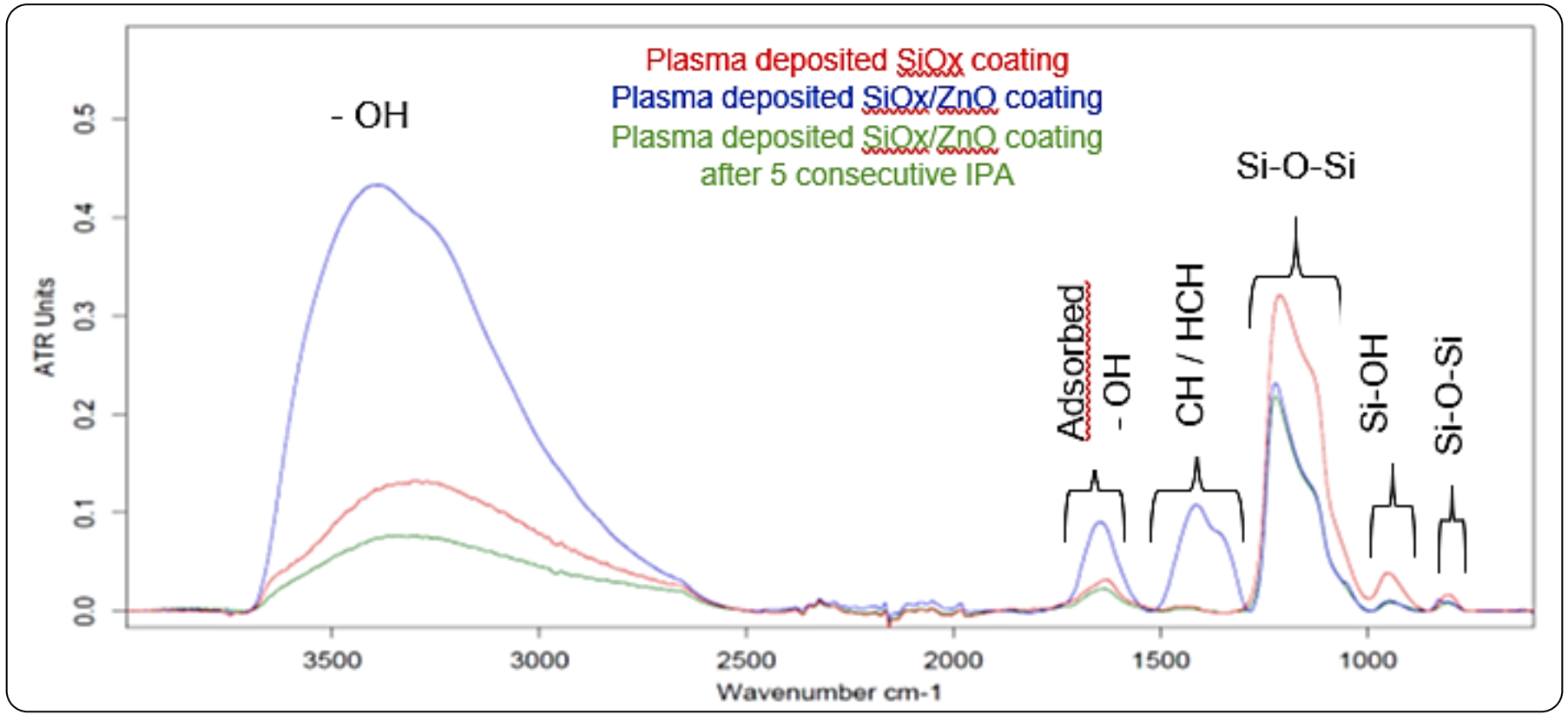


SEM images of a ZnO-coated silicium carrier (Au/Pd-sputtered, 15.09.2020)

Source : WFK – SEM characterization of Plasma deposited Coating

Results and characterization

FTIR characterization in ATR Mode

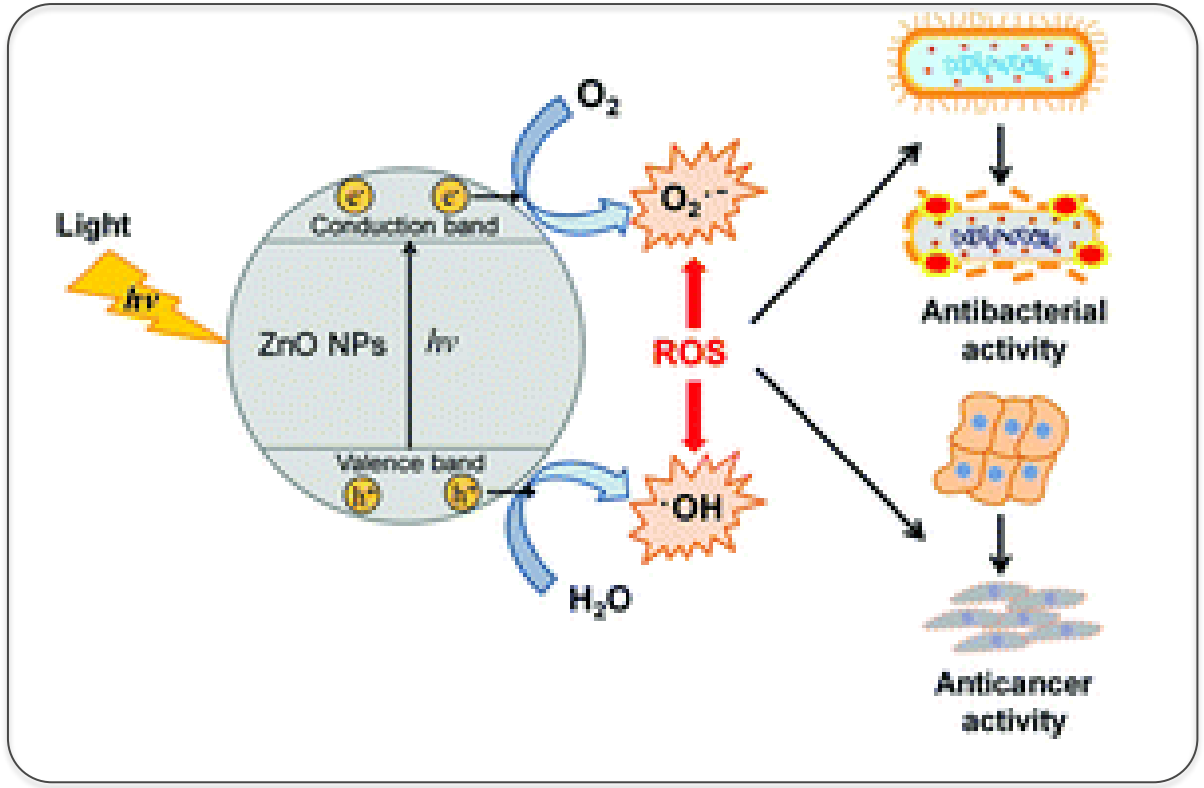


Chemical composition of the SiOx/ZnO plasma deposited coating films :

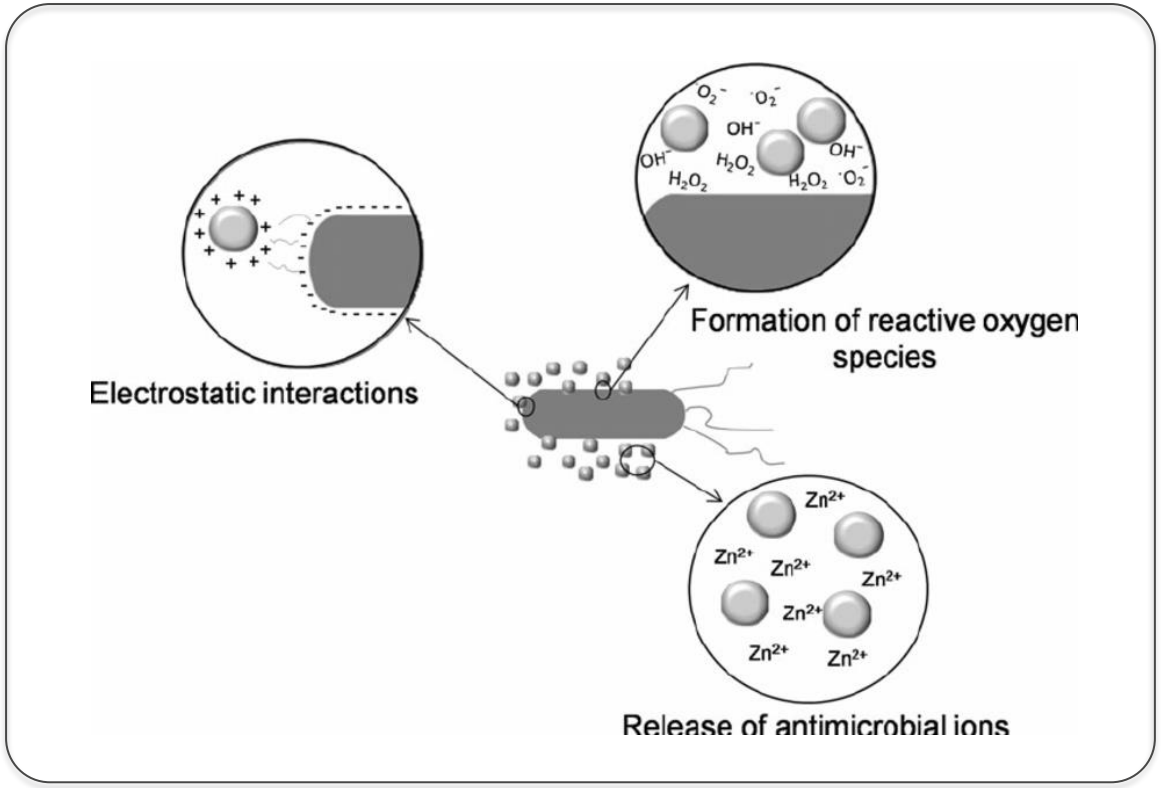
- SiOx Plasma deposited Coating
- SiOx/ZnO plasma deposited coating composition similar to the composition of SiOx/ZnO even following 5 cleaning cycles

The loss in absorbance may be attributed to a thinner coating.

Proposed mechanisms for antibacterial activity



Release of ROS (Reactive Oxygen Species) under Light excitation



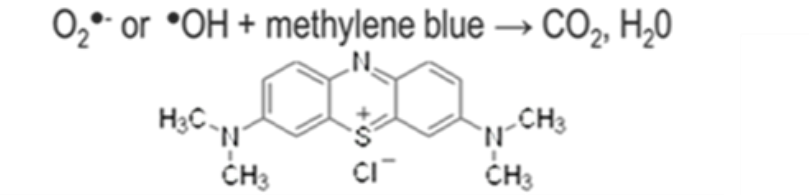
Release of Zn^{2+} antimicrobial ions

Sivakumar et al., Photo-triggered antibacterial and anticancer activities of zinc oxide nanoparticles, *J. Mater. Chem. B*, 2018,6, 4852-4871 (2018) https://doi.org/10.1039/C8TB00948A

Espitia *et al.* Zinc Oxide Nanoparticles: Synthesis, Antimicrobial Activity and Food Packaging Applications. *Food Bioprocess Technol* **5**, 1447–1464 (2012). https://doi.org/10.1007/s11947-012-0797-6

Evaluation through MB degradation and optimization in UV/Vis region

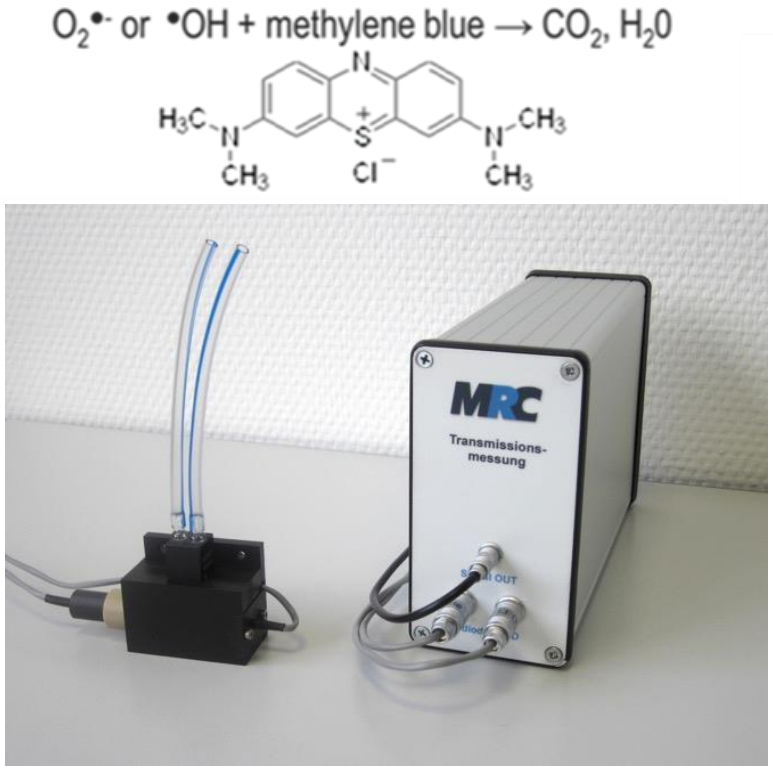
Photocatalytic evaluation according to **German Standard DIN 52980** with the degradation of methylene blue solution



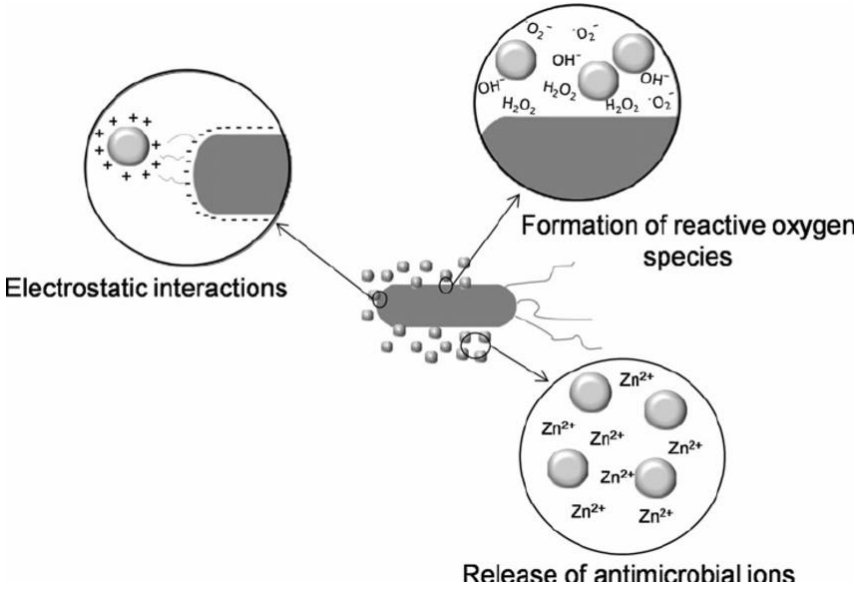
Source : https://www.mrc-systems.de/en/products/photo-activation

Evaluation through MB degradation and optimization in UV/Vis region

Photocatalytic evaluation according to **German Standard DIN 52980** with the degradation of methylene blue solution



The plasma deposited ZnO/SiO coating presented no photocatalytic activity following plasma deposition that indicates that the mechanism of antibacterial activity is associated to the release of Zn^{2+} ions in the medium.

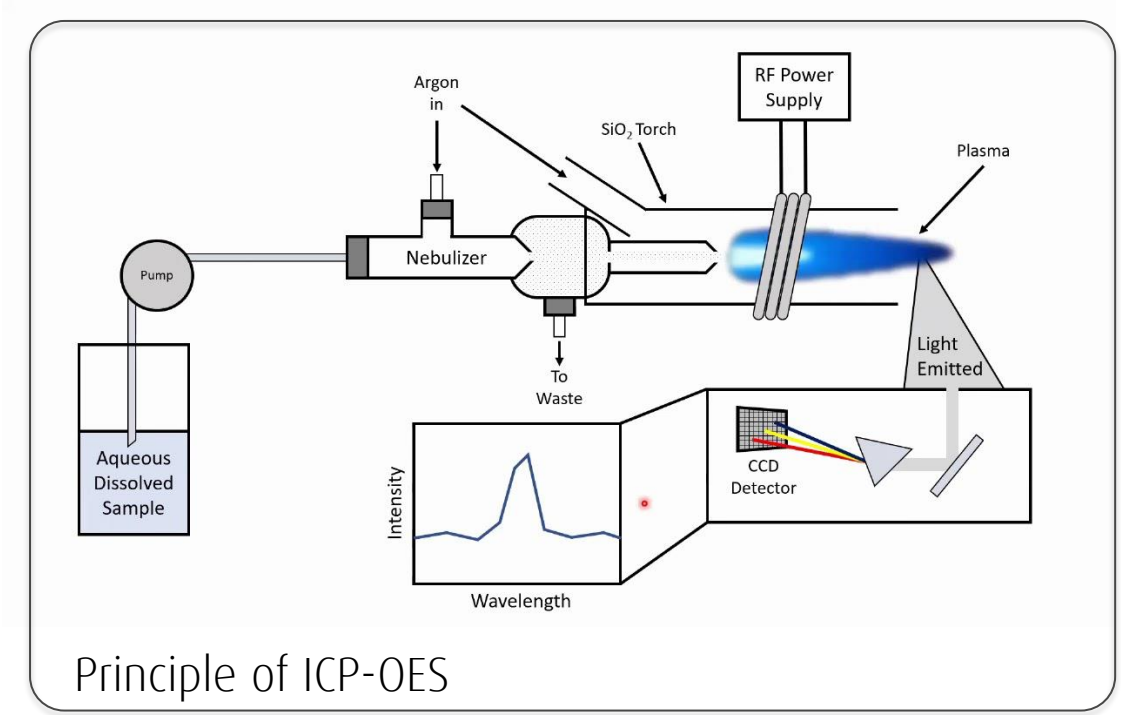


Source : https://www.mrc-systems.de/en/products/photo-activation

Results and characterization

Methodology used for ICP/OES:

- Plasma coated polycarbonate samples on approximately - 200 cm^2 are immersed in 100 mL of pure HPLC Water
- Samples are prepared for 12 / 24 and 48 h to maximize the release of ions in the solution
- Zinc ion concentration are then evaluated in comparison with Zn calibration done prior measurement



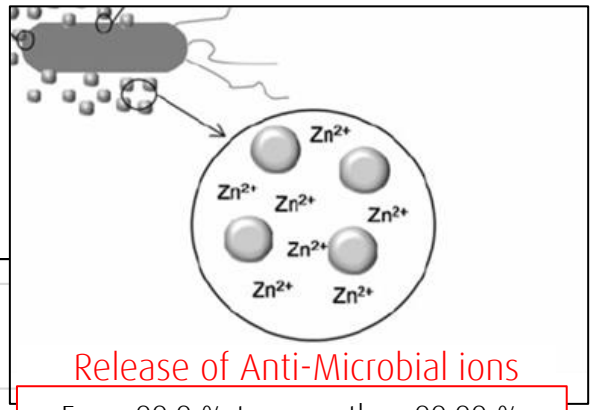
Principle of ICP-OES

Time [h]	12	24	48
Calculated concentration [mg / l]	7.3	4.52	5.62

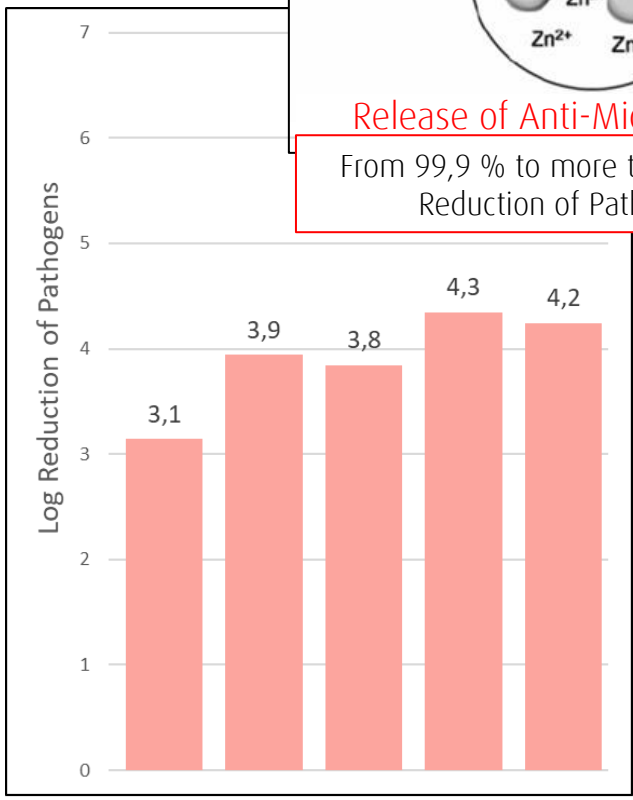
ICP-OES measurement results of the coatings produced based on a 200 cm^2 coating area per 100 ml of solution.

Conclusion

- It was possible to deposit an antibacterial coating using ZnO/SiO based precursor
- Idendification of the mechanism associated to the antibacterial activity due to the release of Zn^{2+} ions.



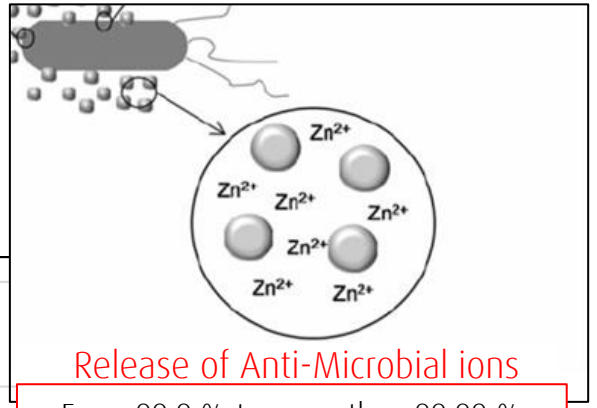
From 99,9 % to more than 99,99 % Reduction of Pathogens



SiO/ZnO coatings Nitrogen Plasma Low Power

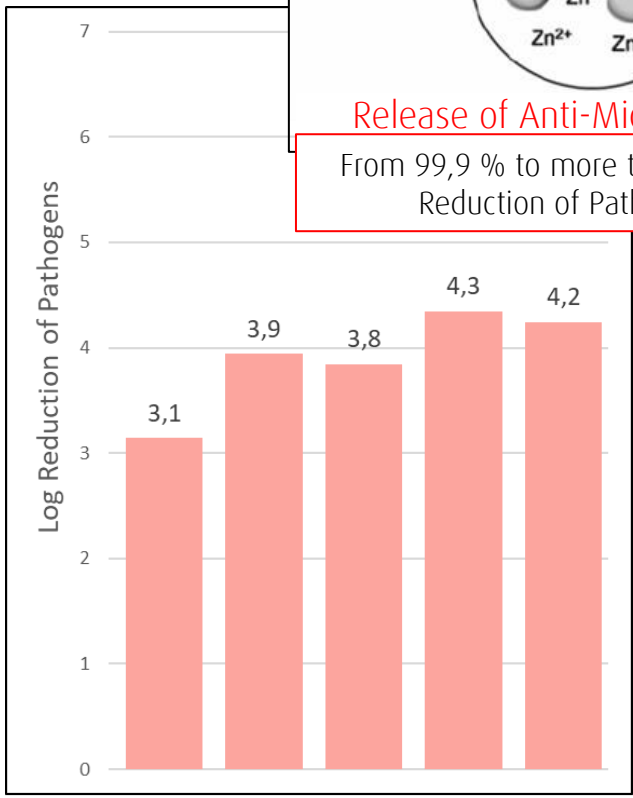
Conclusion

- It was possible to deposit an antibacterial coating using ZnO/SiO based precursor
- Idendification of the mechanism associated to the antibacterial activity due to the release of Zn^{2+} ions.
- Further work will be focused on improving the « photocatalytic » properties of the ZnO/SiO coatings and consider thermal post treatment procedure.
- Additional work will also be focused on the development on different Metal Oxide thin films coatings from other precursors
- Coatings will be deposited on Glass and Metal more suitable substrates for thermal post treatments



Release of Anti-Microbial ions

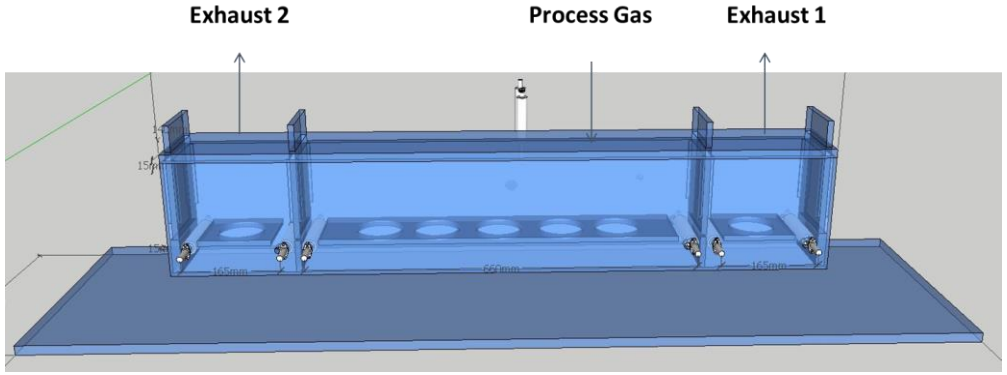
From 99,9 % to more than 99,99 % Reduction of Pathogens

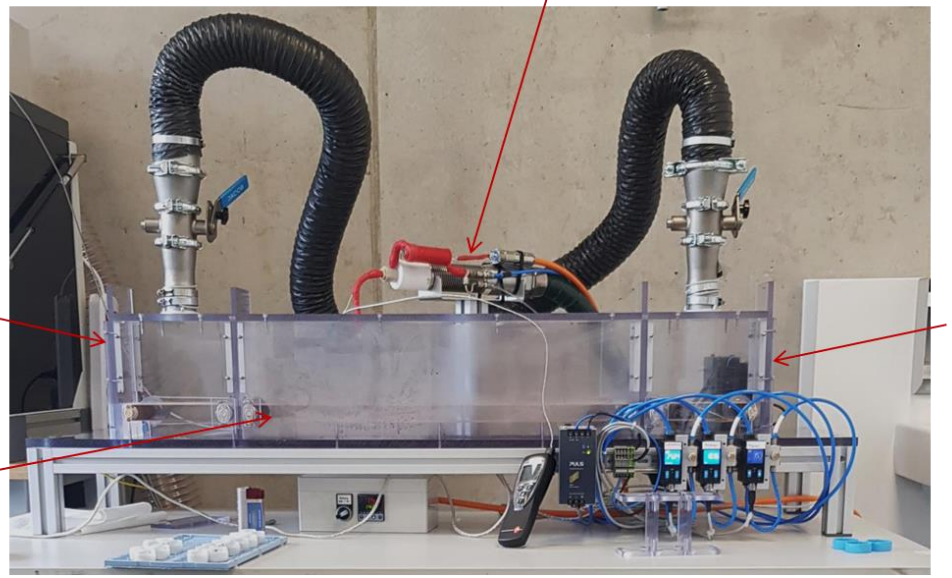


SiO/ZnO coatings Nitrogen Plasma Low Power

Further work

Regarding Decontamination and current situation





- Moving Belt in each chamber
- Process Gas is injected in the middle chamber

Further work

Regarding Decontamination and current situation

Plasmatreat Sterilization Cabinet (PTSC580)

Further work

Regarding Decontamination and current situation

Case study : Ventilation Tube Sterilization

Autoprotect – Project partners

plasmatreat

wfk

Beltech
Industrial Automation with Vision

omneo

Business APS
bedreven in bedrijven

causa

Chemelot
Innovation and
Learning Labs
NEW CONNECTIONS • NEW SOLUTIONS

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Robert Beckers
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Siemsa
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Niedersächsische Staatskanzlei

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provincie groningen

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provincie limburg

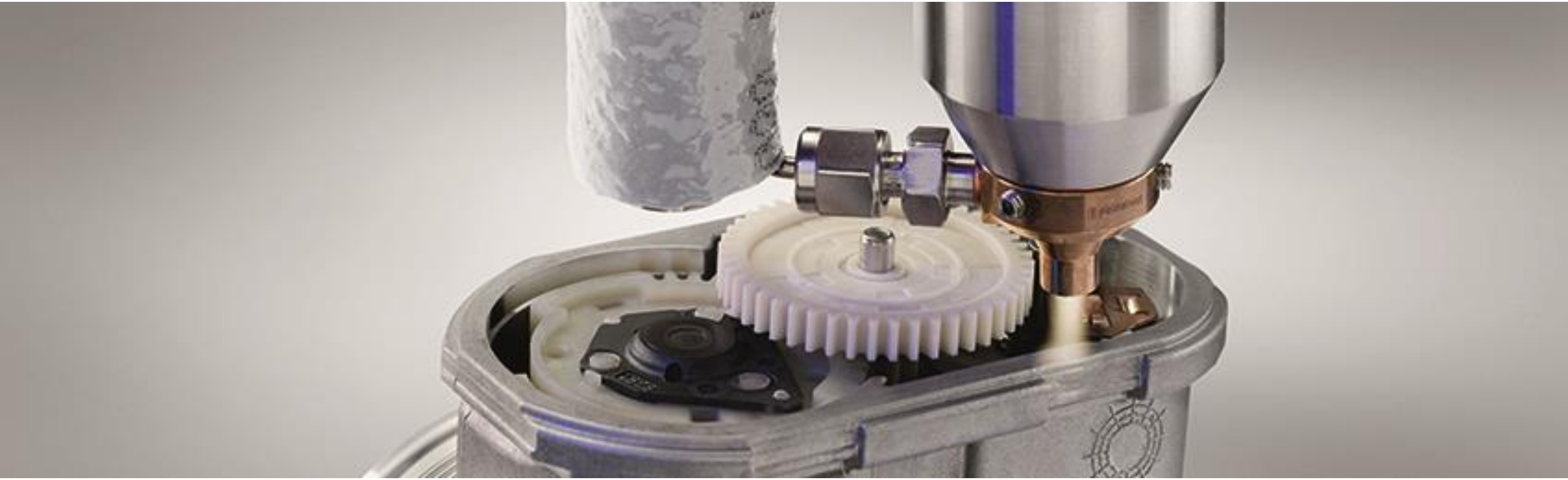
INTERREG Deutschland Nederland

Europäische Union
Europese Unie

Ministerium für Wirtschaft, Innovation, Digitalisierung und Energie des Landes Nordrhein-Westfalen

Ministerie van Economische Zaken en Klimaat

Thank you for your attention !



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