SELECTIVE PHASE FORMATION AND TAILORED MORPHOLOGY OF OXIDE FILMS DEPOSITED BY PULSED REACTIVE MAGNETRON SPUTTERING

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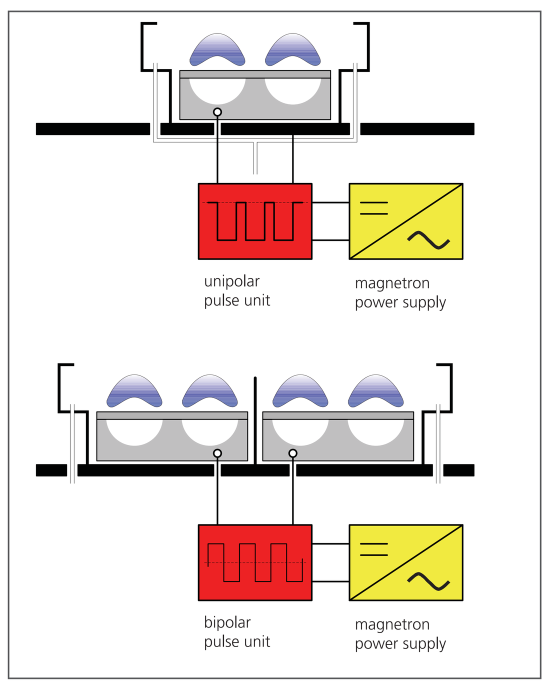
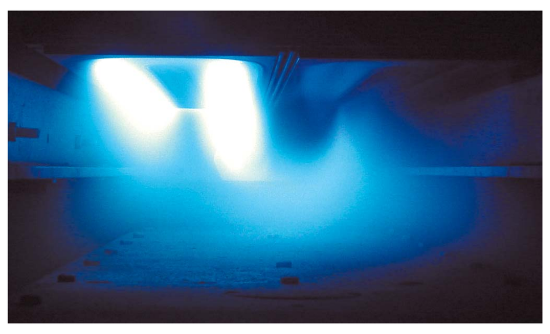
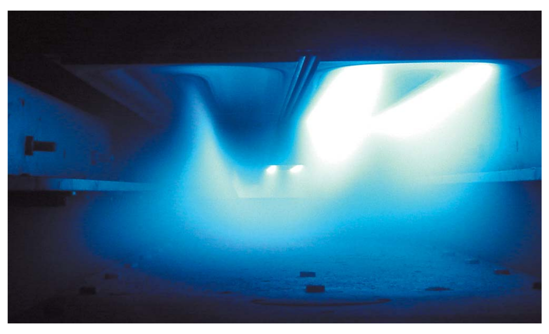
PULSE MAGNETRON SPUTTERING

Reactive Pulse Magnetron Sputtering is a versatile technology for the deposition of compound films with a high deposition rate. Pulsed powering allows the application of a high power density during the pulse-on phase resulting in an enhanced excitation and ionisation of particles.

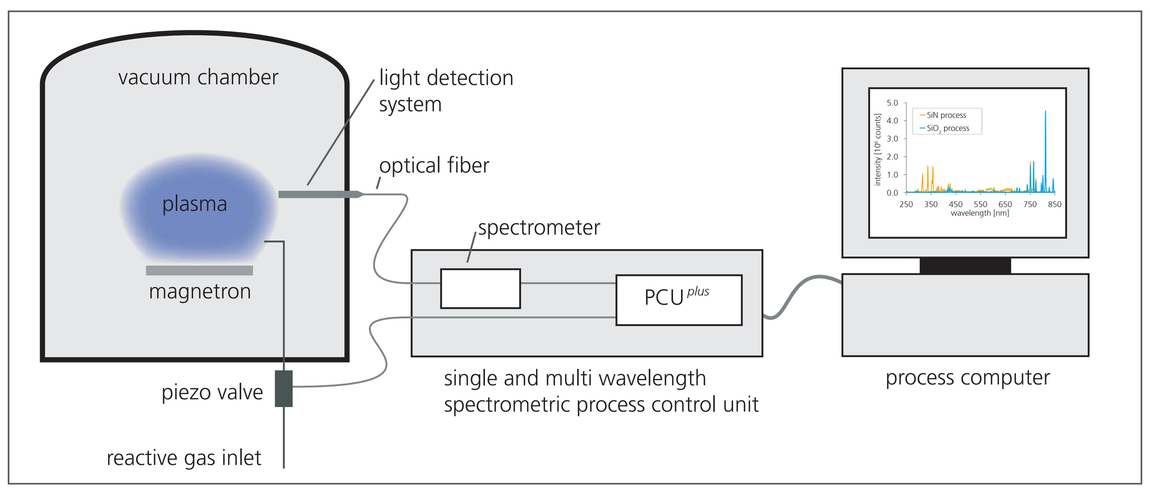


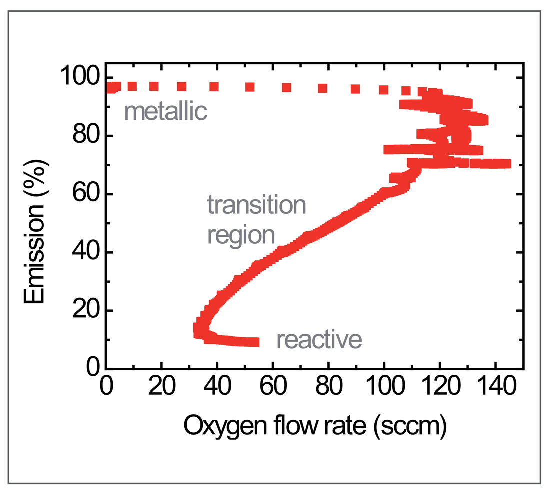
The appropriate choice of pulse mode, frequency, and duty cycle, on the one hand, deposition conditions and working point in controlled reactive sputter processes, on the other hand, allows the deposition of films of a wide range of compositions and properties.



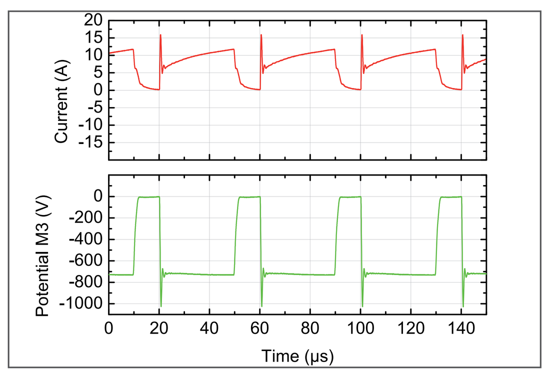


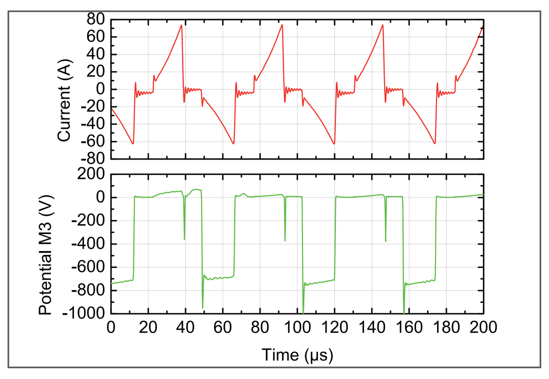
A feedback process control unit (PCU^{plus}) allows stabilization of working points throughout the whole characteristic curve.

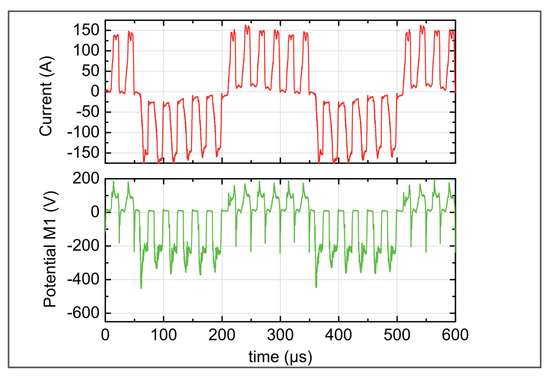




unipolar mode (metallic) | **bipolar mode (reactive)** | **pulse package mode (reactive)**







ALUMINUM OXIDE

Aluminum oxide as a chemically stable ceramic material is interesting for many coating applications like

- low refractive index layer in optical layer stacks
- passivation and conversion coating on metallic substrates
- permeation barrier coating on polymer substrates
- wear resistant coating on high speed cutting tools

Alumina coatings can be deposited by pulsed reactive magnetron sputtering processes from metallic aluminum targets in Ar-O_2-atmosphere.
A feedback control ensures stable operation in transition mode with relatively high deposition rates of 25 … 100 nm/min on moving substrates, depending on the deposition conditions and on the structure of the growing film.

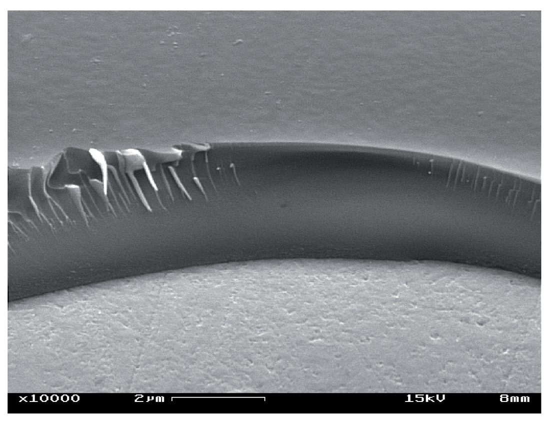
Depending on temperature, the following phases are observed under equilibrium conditions:

T < 500°C	amorphous, low hardness (13 GPa)
T = 500°C … 1000°C	metastable phases γ, δ, θ, hard (>20 GPa)
T > 1000°C	thermodynamically stable α-phase and metastable κ-phase, hard (α bulk hardness 22 GPa)

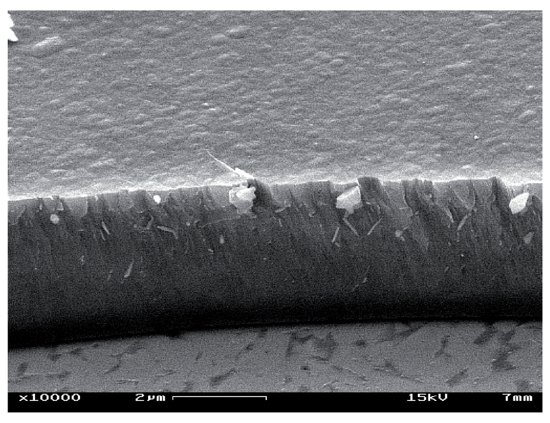
Temperature is therefore also a key parameter for the growth of crystalline films under non-equilibrium conditions.

The challenge is to deposit hard, wear resistant crystalline coatings at as low temperature as possible on a variety of substrate materials. For high temperature cutting applications, the thermodynamically stable α-phase is aimed to achieve.

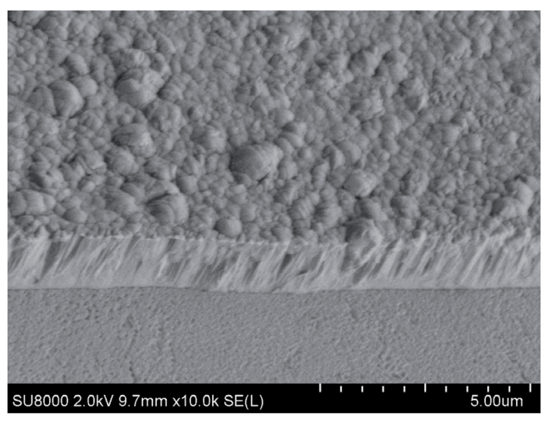
Amorphous
H = 13 GPa



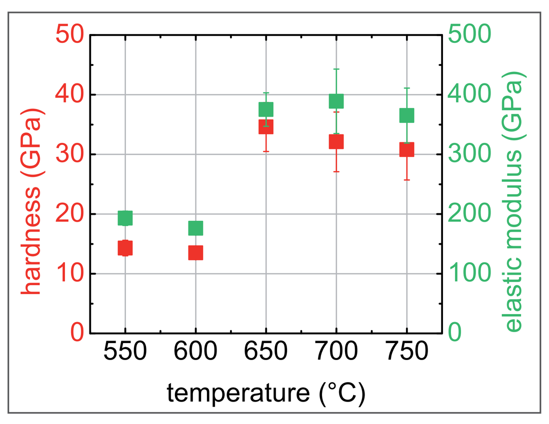
γ-crystalline
H = 32 GPa



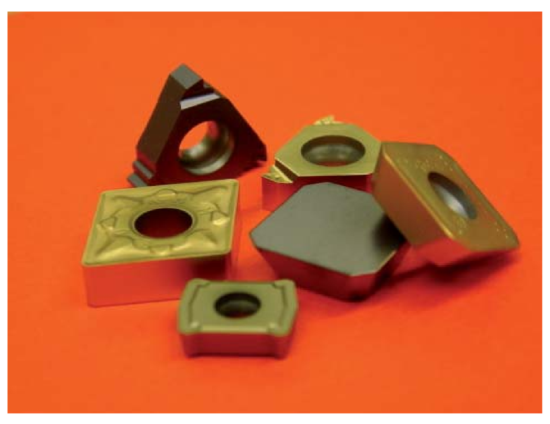
mixed γ- and α-crystalline
H = 30 GPa



Optical coatings, passivation and scratch resistant layers



Wear resistant coatings e.g. for cutting tools



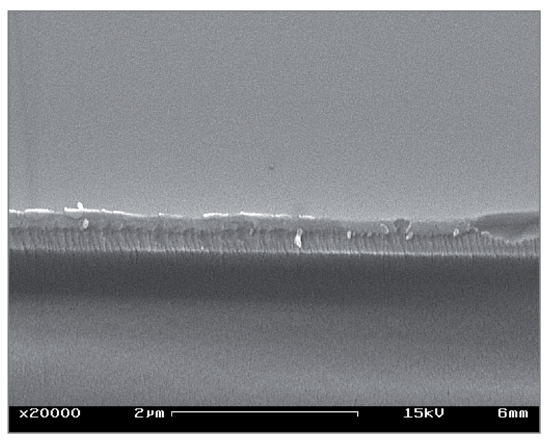
TITANIUM OXIDE

TiO_2 is well established as a high refractive index coating for optical applications. TiO_2 films deposited under low temperature conditions and with low energy input from the process are amorphous, TiO_2 films deposited at higher temperature and/or high energy input are crystalline.
Two different crystalline phases are observed in thin films deposited with PVD techniques: Anatase and rutile.
Anatase exhibits pronounced photosensitive properties under UV-irradiation:

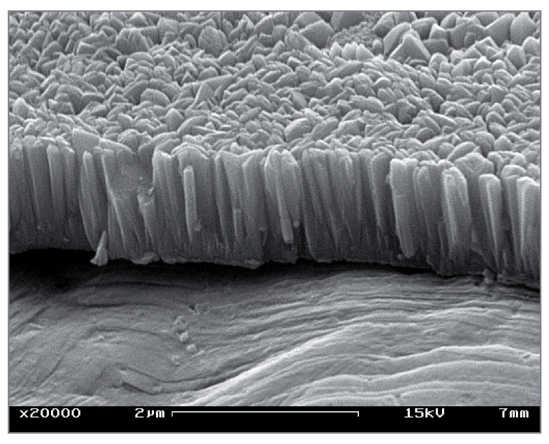
- photoinduced superhydrophilicity (polar binding of OH-groups at the surface)
- photocatalytic properties (oxidation and reduction reactions at the surface) which are both a consequence of the generation of electron-hole-pairs by the UV light.

Key parameters for the generation of the different phases are the substrate temperature and the energy of the film forming particles. The latter depends on the deposition technology and is influenced by the total gas pressure.

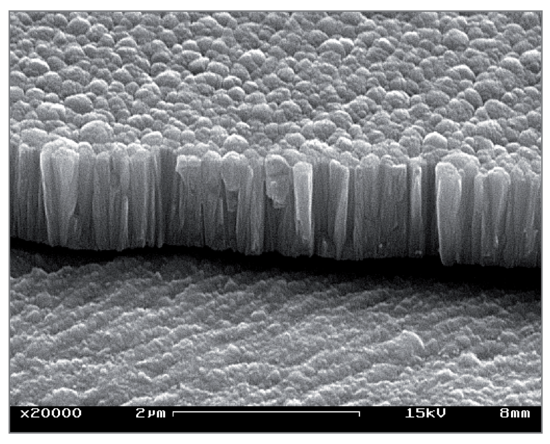
Amorphous
n@550nm = 2.1 … 2.4, H = 4 … 6 GPa



Anatase
n@550nm = 2.5, H = 4 … 5 GPa



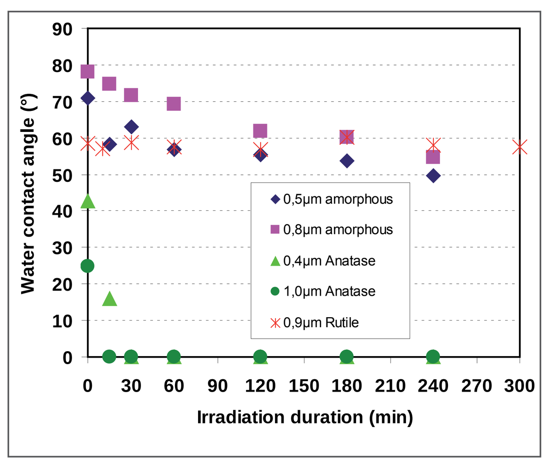
Rutile
n@550nm = 2.7, H = 15 … 17 GPa



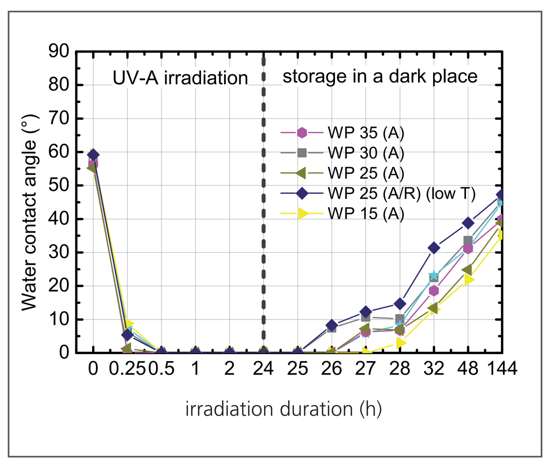
PHOTOINDUCED SUPERHYDROPHILICITY

Films containing anatase phase TiO_2 (pure or mixed phases) exhibit photoinduced superhydrophilicity. The hydrophilic property persists for several days after activation. The decay length, microscopically, depends on crystallite size and imperfections, macroscopically, on the overall layer structure (sublayer, initial film growth, gradient). Above a certain threshold thickness, superhydrophilic behaviour is independent of film thickness.

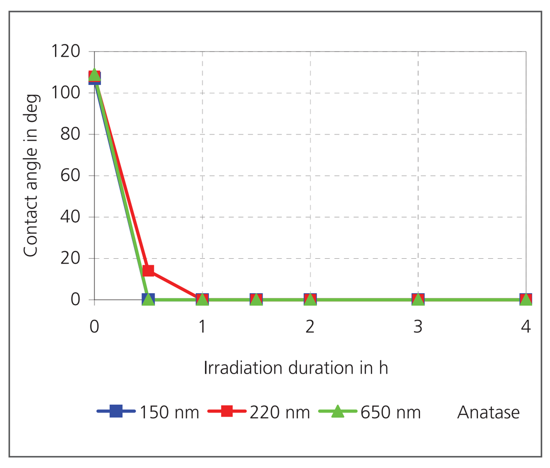
Influence of phase composition



Decay of activity

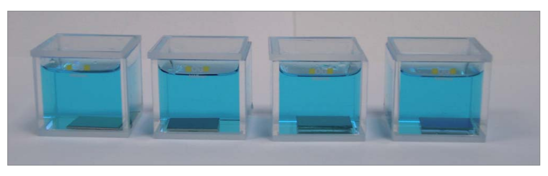


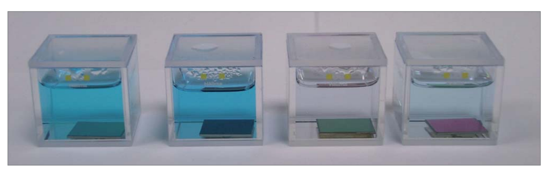
Influence of film thickness



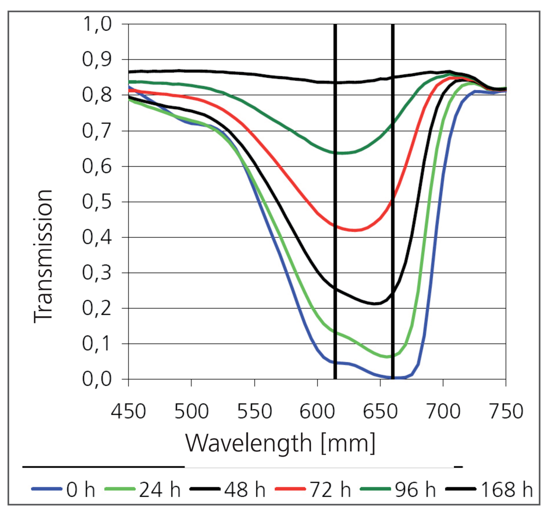
PHOTOCATALYTIC ACTIVITY

Characterization method: Decomposition of methylene blue

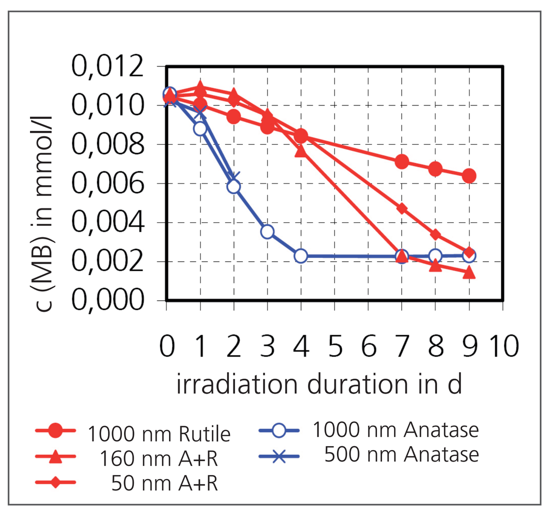




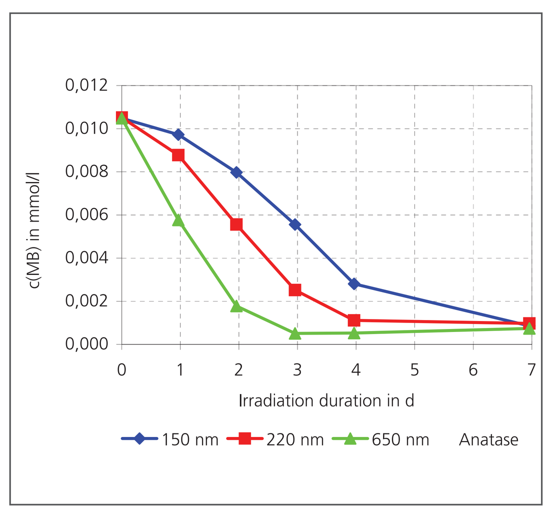
- Sample irradiation for 72 h
- Decomposition of 20 ml aqueous solution of MB (0.01 mmol/l) under UV-A irradiation
- Radiation power density 1 mW/cm² ~ insolation on a sunny day
- Photometric determination of concentration every 24 h
- Exclusion of artefacts: Measurement of samples stored in a dark place, Measurement of uncoated sample, exclusion of reversible conversion MB → LMB (colourless) (dark storage + O_2)
- Duration of a whole measurement cycle: 7 days



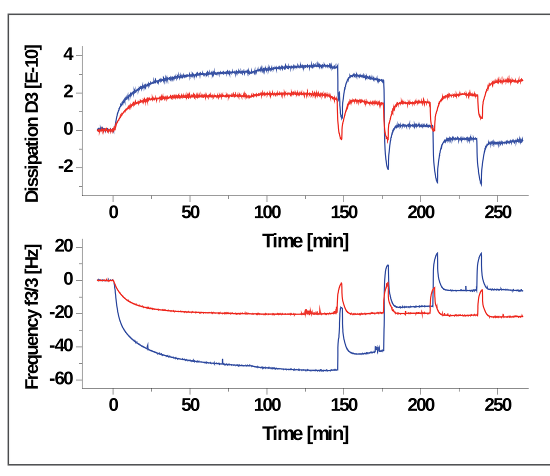
Influence of phase composition



Influence of film thickness



PROTEIN ADSORPTION AND DECOMPOSITION



uncoated Ti-QC

anatase coated Ti-QC

t<0:	buffer PBS
t=0…90:	HSA solution
t > 90:	buffer

t=145, 180, 210, …
consecutive UV-irradiation under PBS-flow (3 min each)

Protein adsorption is a first step in biofilm formation on surfaces. Quarz Crystal Microbalance measurements with Dissipation (QCM-D) have been carried out in a flow cell reactor with human serum albumin.
They show that decomposition of the protein film at the surface-biofilm interface under in situ-UV-irradiation effectively supports biofilm removal.

CONTACT

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