TECHNISCHE UNIVERSITÄT DRESDEN

Fraunhofer FEP

Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP

1st Thesis Advisory Committee Meeting, February 28th 2023
Maria Barrera

Development of coatings with an electrical insulating effect and hydrophilic surface for use in electrocaloric heat pumps

Outline

Introduction

- Electrocaloric heat pump

Motivation

- Surface functionalization of electrocaloric components

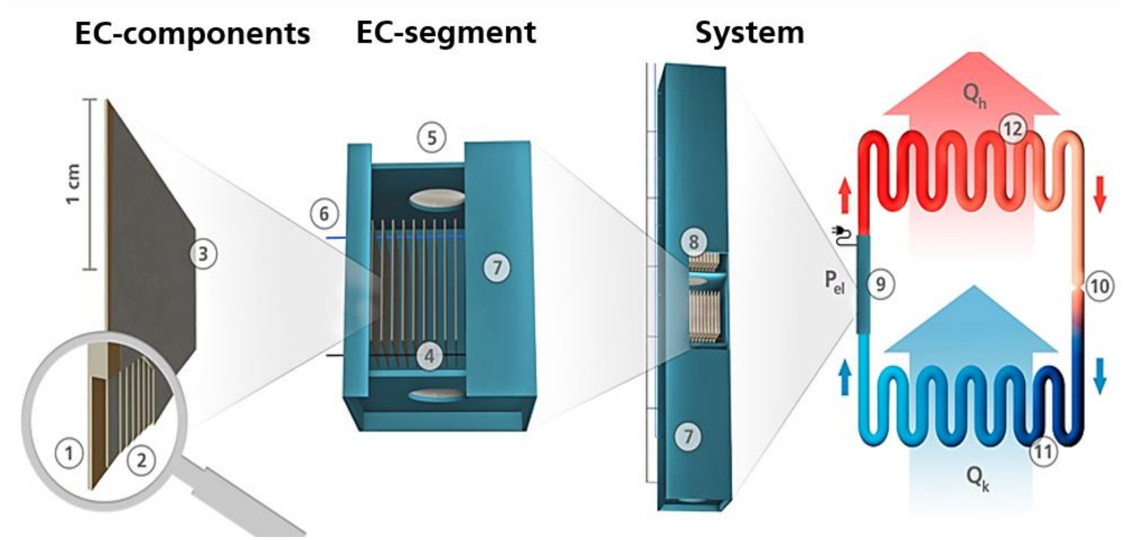
Experimental work

- Material system suitable for the application
- WO_3/W
- TiO_2-SiO_2
- TiO_2-$SiO_2/WO_3/W$
- Dynamic contact angle measurements
- Condensation/evaporation under heat pipe conditions

Summary and outlook

Electrocaloric heat pump

Introduction



Schematic representation of the electrocaloric heat pump. © 2019 Fraunhofer IPM.

(1)	EC materials	(7)	gas-proof housing
(2)	electrodes	(8)	EC segments
(3)	coatings	(9)	EC system
(4)	EC components	(10)	throttle
(5)	check valves	(11)	evaporator
(6)	electrical supply line	(12)	condenser

Heat transfer by means of **latent heat** when a fluid evaporates or condenses on the EC material

Surface functionalization of electrocaloric components

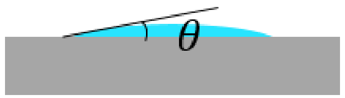
Motivation

Requirements

- Uniform wetting of the surface by the working fluid for heat transfer optimization

  → **(super)hydrophilic coatings**

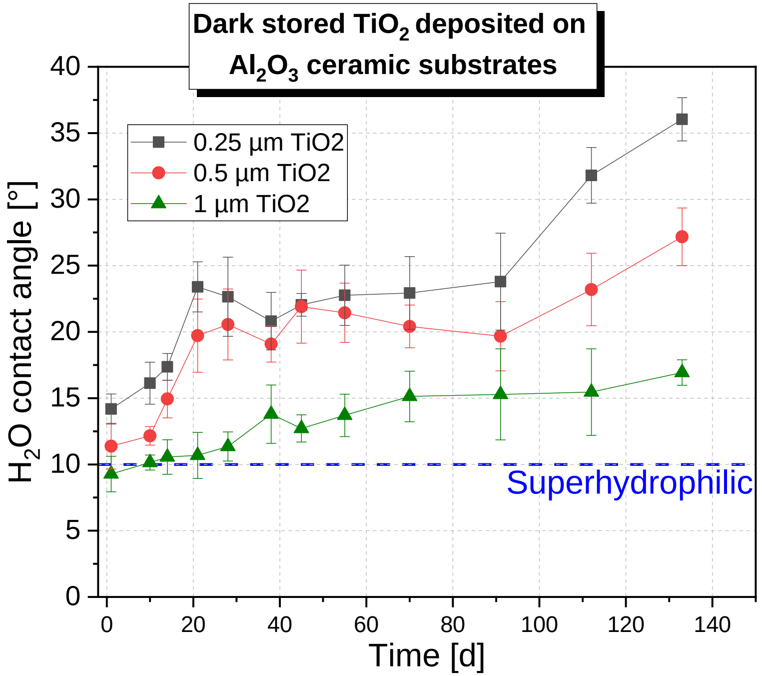
$$0^\circ < \theta < 10^\circ$$



- Optimal microstructure for suitable thermal, electrical and mechanical properties
- Preservation of electrocaloric properties

Challenge

Development of (super)hydrophilic coatings that do not require to be activated by periodical UV exposure



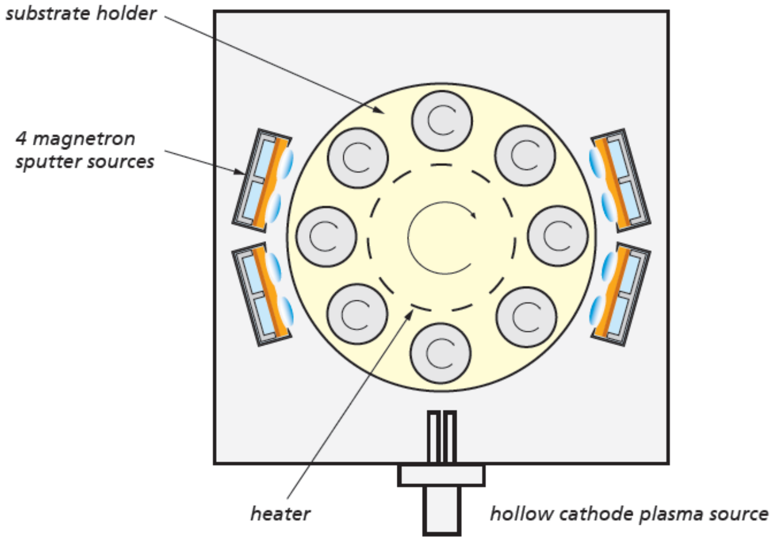
Material system suitable for the application

Approach

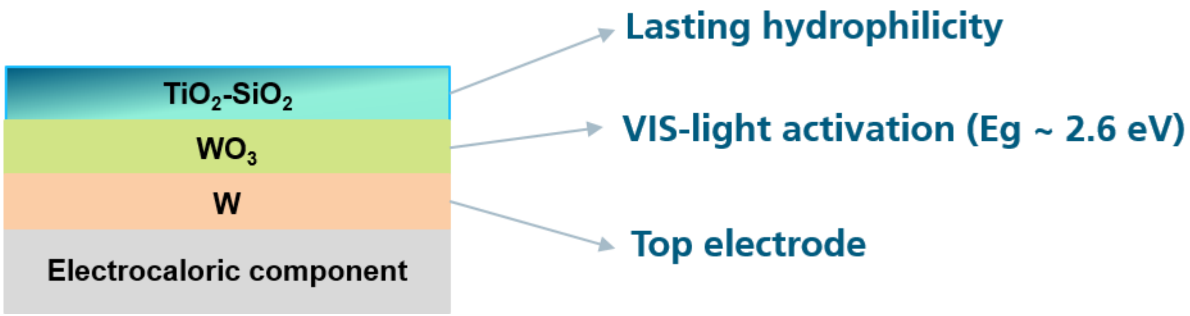
Development of long-lasting superhydrophilic thin films by means of pulsed magnetron sputtering.

Variation of deposition parameters:

- substrate temperature → crystal structure and morphology
- film thickness
- pulse frequency and duty cycle



Batch plant for coating 3D substrates

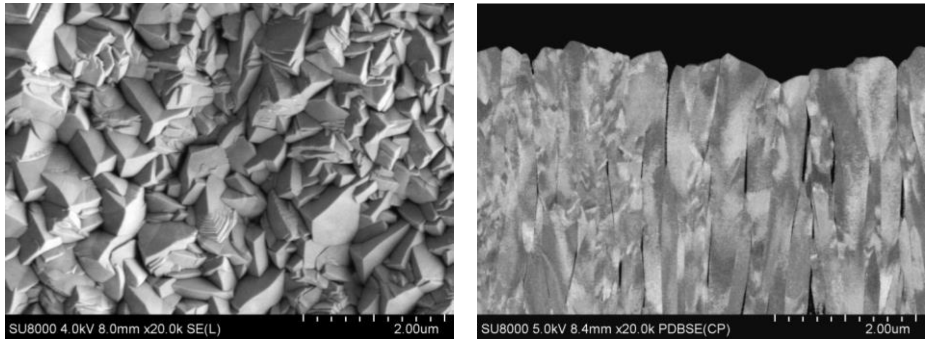


WO_3/W

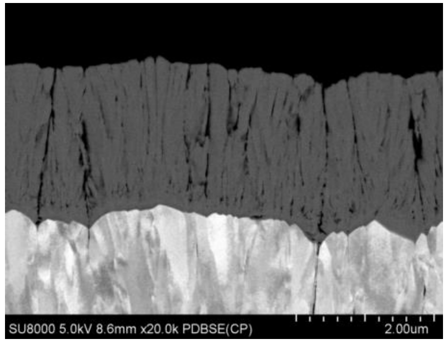
Optimization of coatings

Sputtered tungsten top electrodes:

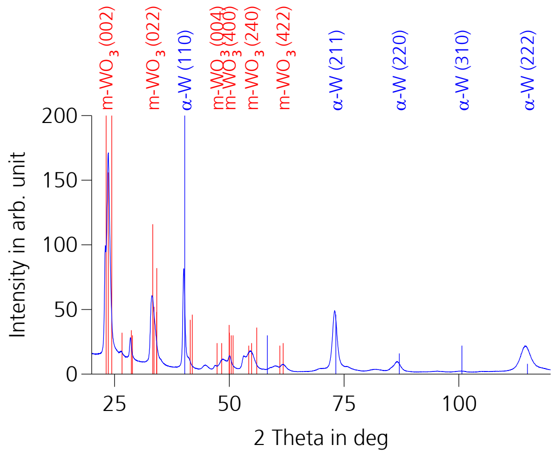
- highest thermal (bulk:164 $Wm^{-1}K^{-1}$) and electrical conductivity (bulk: 18.5 MS/m) of all non-noble metals.
- chemically and mechanically stable → better bonding of WO_3 layer.



5 µm W deposited at 500 °C on Al_2O_3 ceramic



5 µm W + 2 µm WO_3



- columnar crystallites
- electrical conductivity: 4 MS/m

- nanocrystalline structure
- high porosity
- XRD: α-W (bcc), monoclinic-WO_3

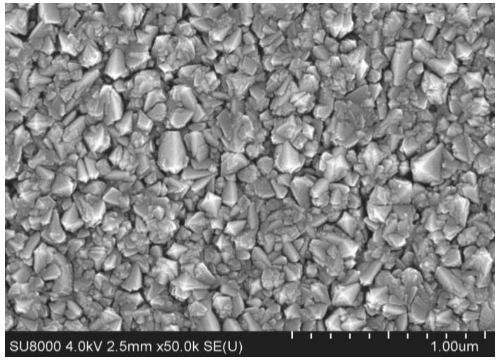
TiO_2-SiO_2

Optimization of coatings

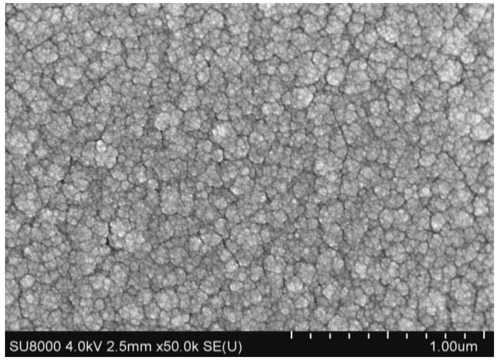
- Pulsed magnetron sputtering in double magnetron arrangement
- Variation of composition by different pulse lengths
- Optimum composition: 36 - 65 at.% Si.

Ti target – Si target

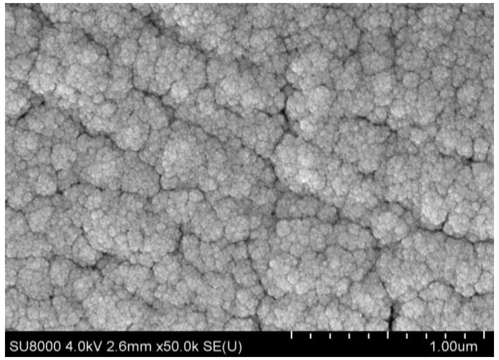
Crystallite size decreases with decreasing Ti content:



16:10:5:10 µs, $Ti_{0.96}Si_{0.04}O_2$



16:10:6:10 µs, $Ti_{0.76}Si_{0.24}O_2$



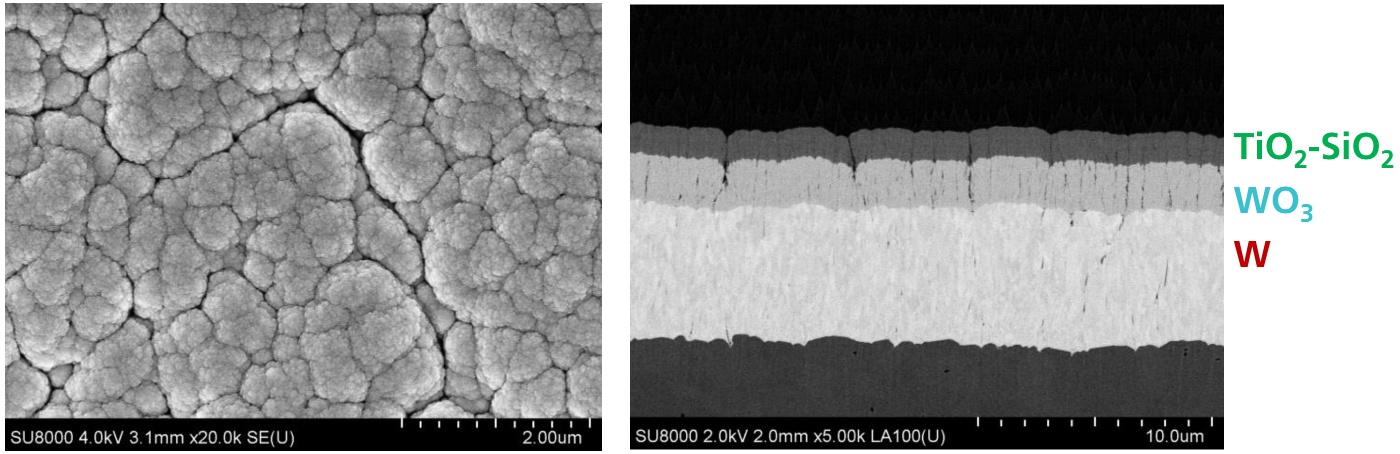
16:10:8:10 µs, $Ti_{0.50}Si_{0.50}O_2$

1 µm, deposited at 250 °C on Al_2O_3 ceramic

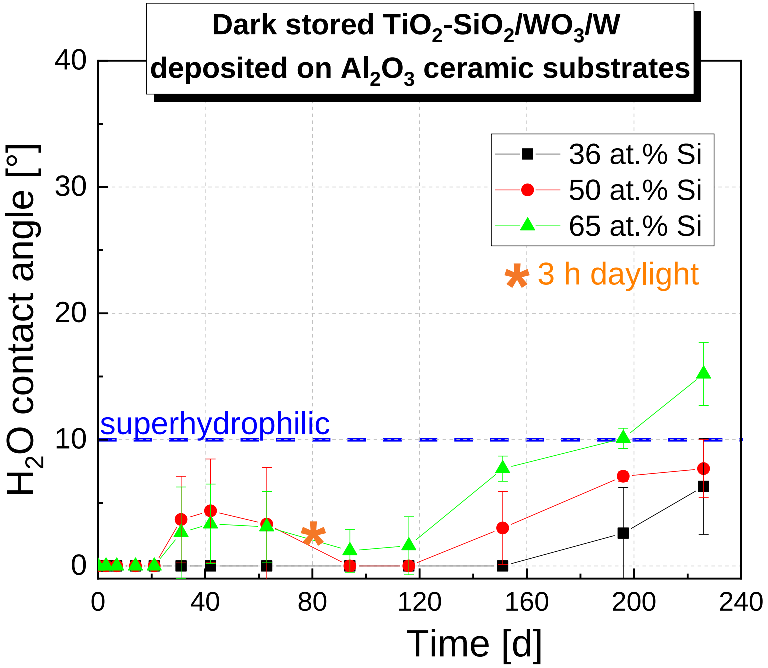
Long-lasting superhydrophilic TiO_2-SiO_2/WO_3/W

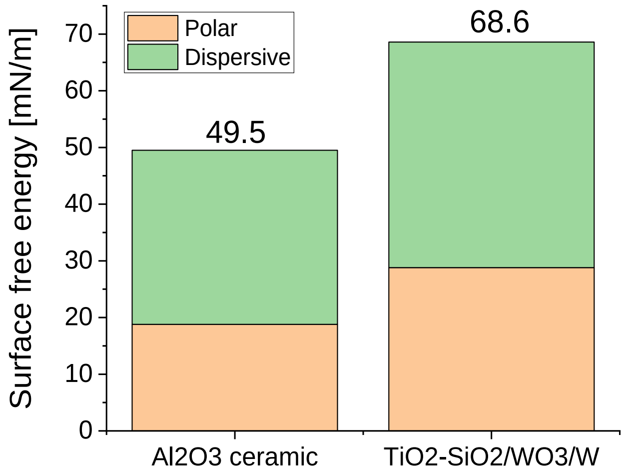
Suitable material system

- Lasting hydrophilicity for **more than 7 months** of **dark storage**.
- Complete wetting recovery (WCA = 0°) after exposure to 3 hours of daylight.
- Surface energy modification



1.2 µm TiO_2-SiO_2 / 2 µm WO_3 / 5 µm W on Al_2O_3 ceramic





Long-lasting superhydrophilic TiO_2-SiO_2/WO_3/W

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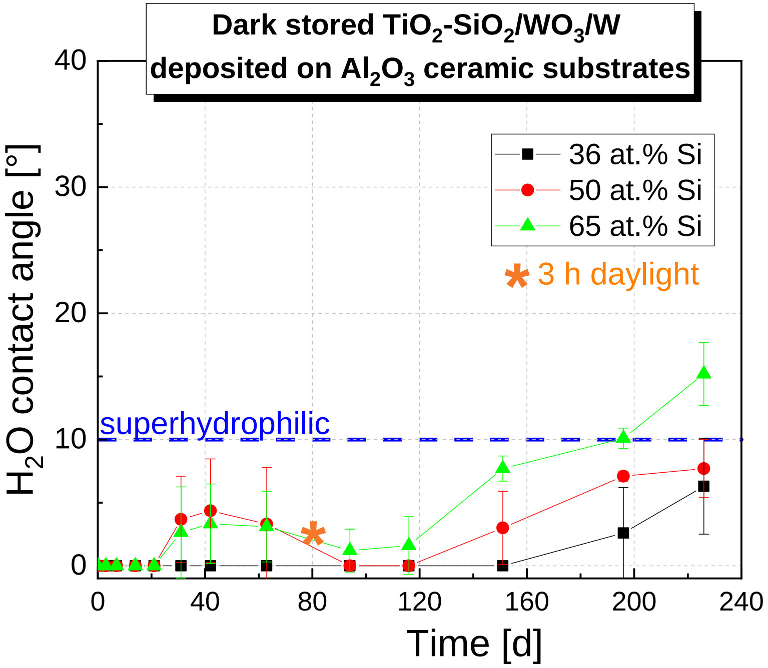
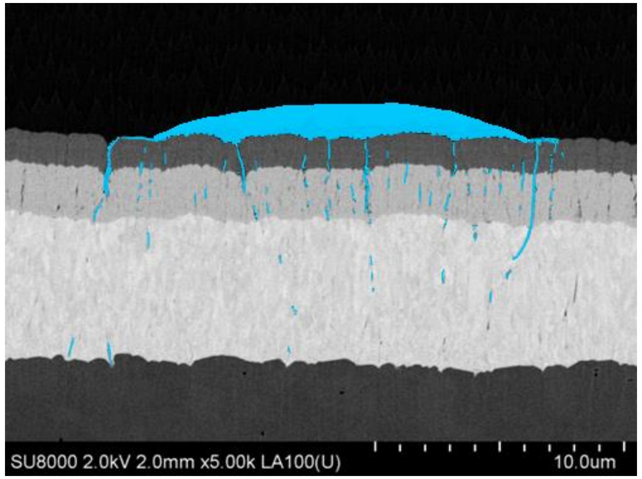
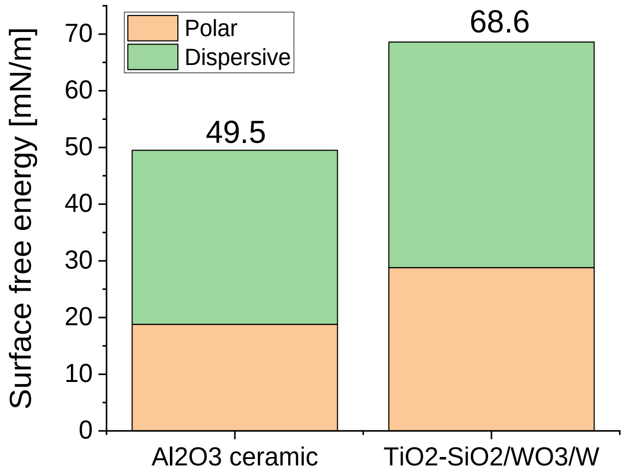


Wenzel's equation:
$\cos\theta^* = r\ \cos\theta$

Capillary effect:
spreading + wicking



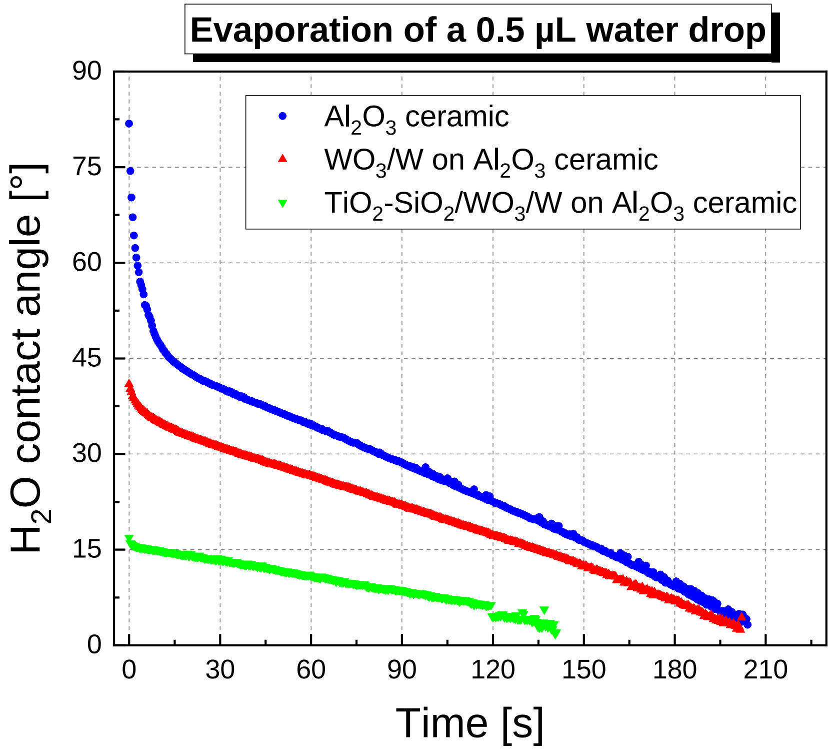
TiO_2-SiO_2
WO_3
W

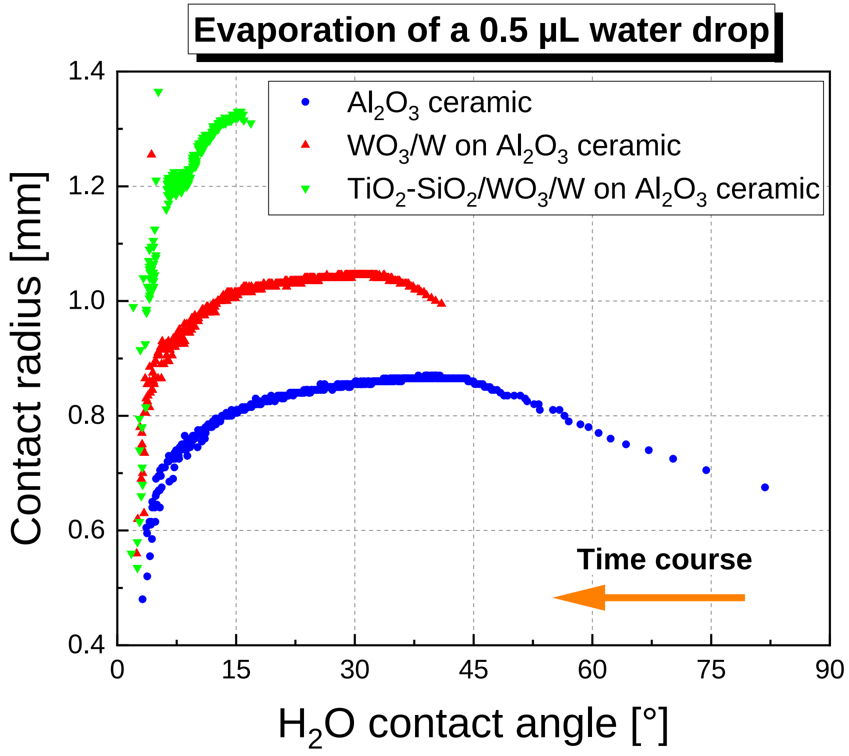


Dynamic contact angle measurements

Evaporation of a 0.5 µL water drop

- Faster evaporation of a water drop on the multilayer TiO_2-SiO_2/WO_3/W.
- Bigger contact radius on the multilayer TiO_2-SiO_2/WO_3/W → a larger surface area is wetted.

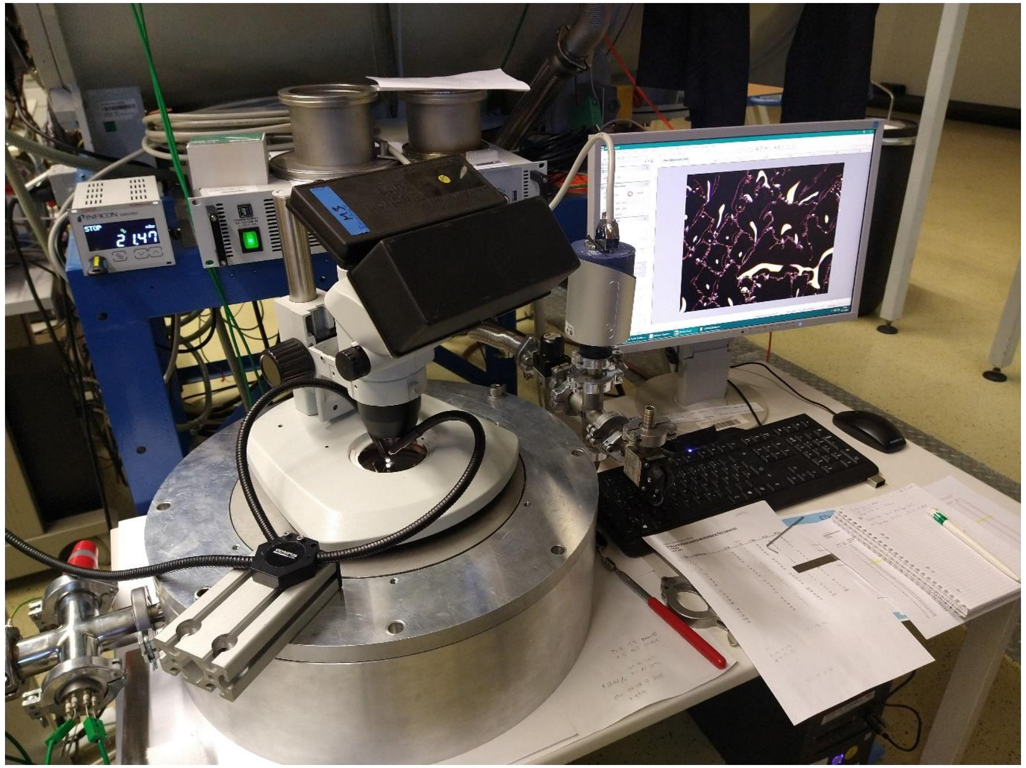


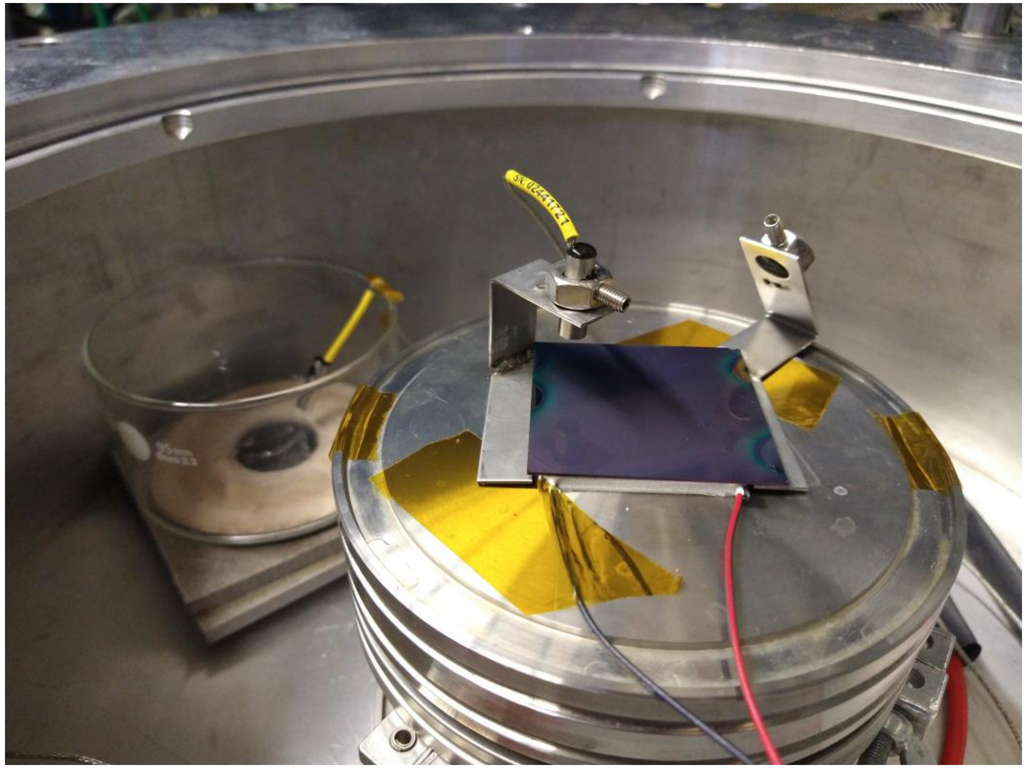


Condensation/evaporation experiments

Dynamic wetting under heat pipe conditions

Time-dependent condensation and re-evaporation processes on surfaces with different wettability:



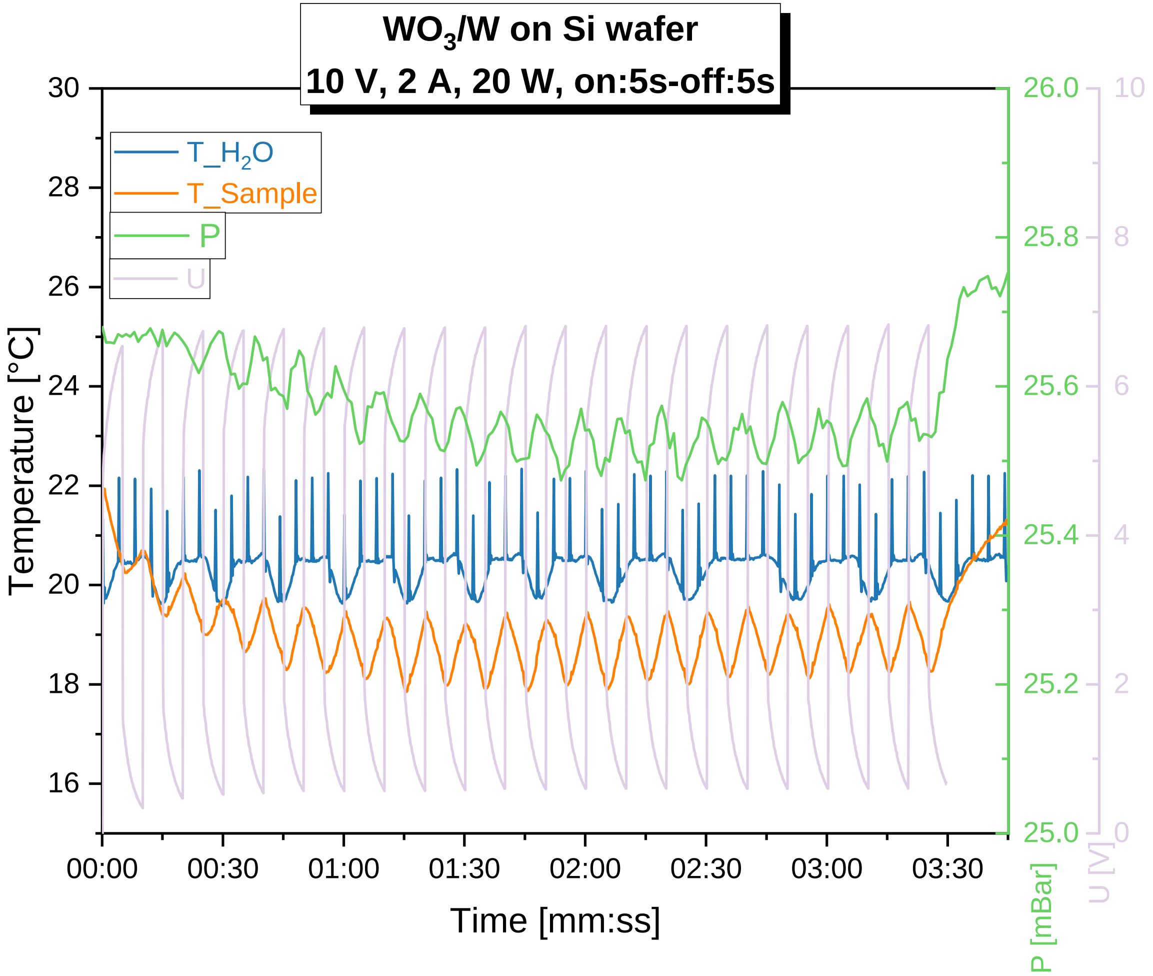


Condensation/evaporation experiments

Dynamic wetting under heat pipe conditions

Periodic process WO_3/W on Si wafer:

- Recipient is evacuated to approx. 25 mbar (H_2O vapor pressure at 21.5°C)
- Amount of water is adapted to chamber volume
- Water is evaporated
- Temperature of sample is controlled by Peltier device
- Pulses: 5 s on, 5 s off



Condensation/evaporation experiments

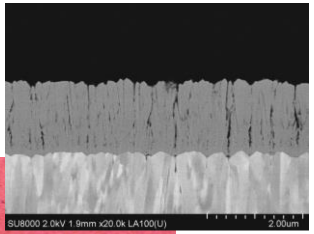
Dynamic wetting under heat pipe conditions

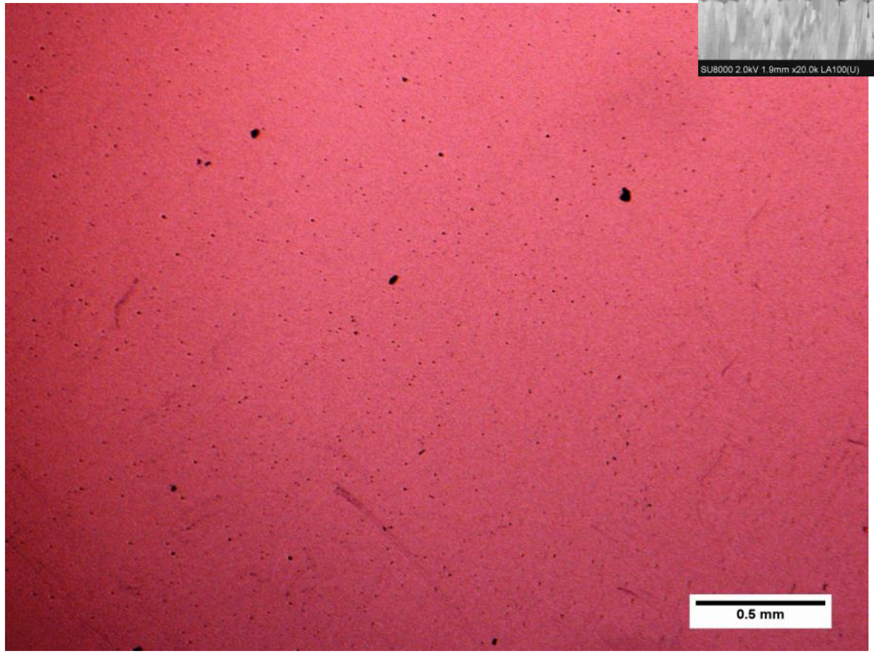
Uncoated Si wafer (ideal smooth surface):

0.5 mm

- Nanodroplets → microdroplets
- Spherical cap shape, separated by dry areas
- Contraction of microdroplets (Constant contact angle mode)

WO_3/W on Si wafer:





- Precursor film → nanodroplets
- Flat, irregularly-shaped (capillary effect)
- Flattening of microdroplets (Constant contact radius mode)

Summary and outlook

- Long-lasting superhydrophilic TiO_2-SiO_2/WO_3/W multilayers have been developed by pulsed magnetron sputtering.
- Chemical properties + porous microstructure → capillarity → super-hydrophilicity (water contact angle < 10°), even after 7 months of dark storage.
- No need of periodical UV exposure.

- Improvement of condensation/evaporation experiments under reduced pressure conditions for heat transfer evaluation → (ESEM?)
- Surface functionalization of polymer electrocaloric materials taking into account their thermal stability.

Thank you for your attention