MODIFICATION OF THE WETTABILITY OF TiO_2 SURFACES WITH ION BOMBARDMENT

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INTRODUCTION

WETTING PROPERTIES

SURFACE COMPOSITON

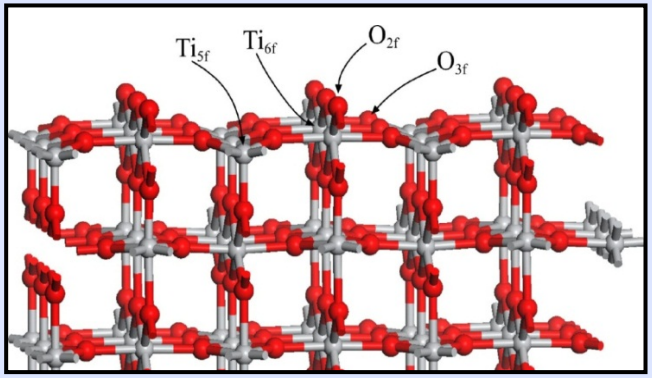
SURFACE ROUGHNESS

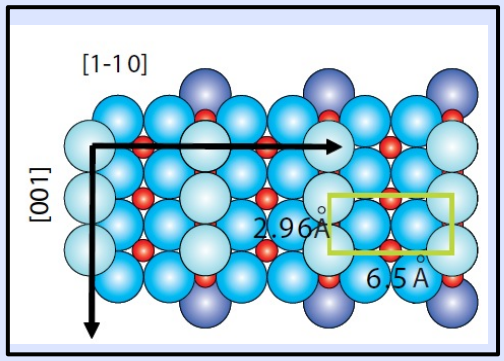
MICRON, Cassie, Wenzel, superhydrophobity…

NANOMETER, grains, texture...

ATOMIC SCALE, vacancies, surface steps...

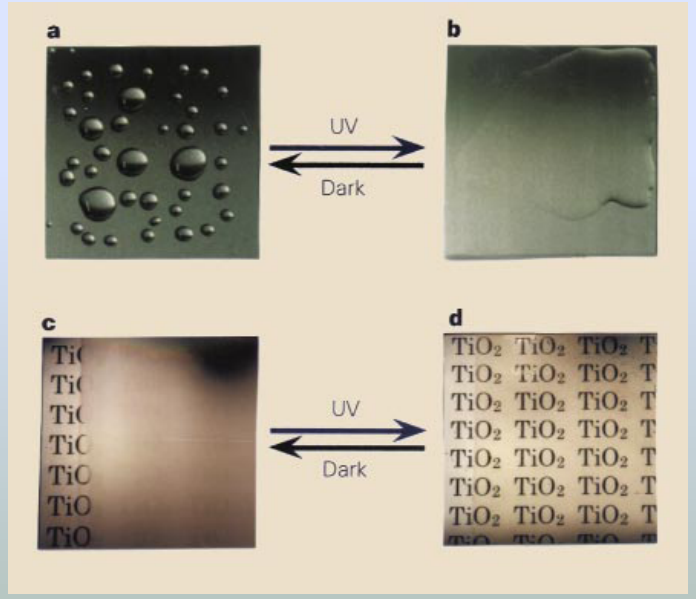
$TiO_2(110)$





- Easy to prepare
- Clean
- Stable
- Well known

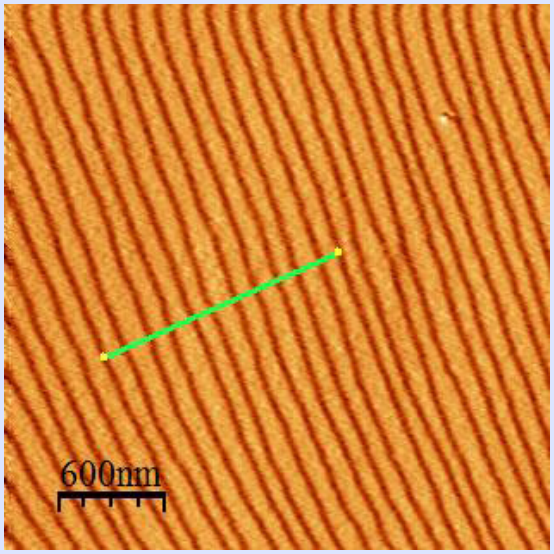
- photocatalytic
- self-cleaning

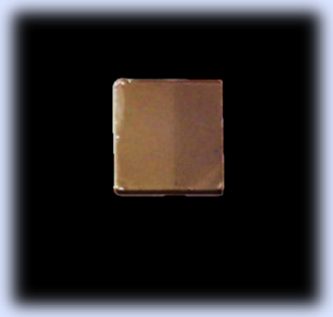


Wang *et al, Nature* **388**, 1997

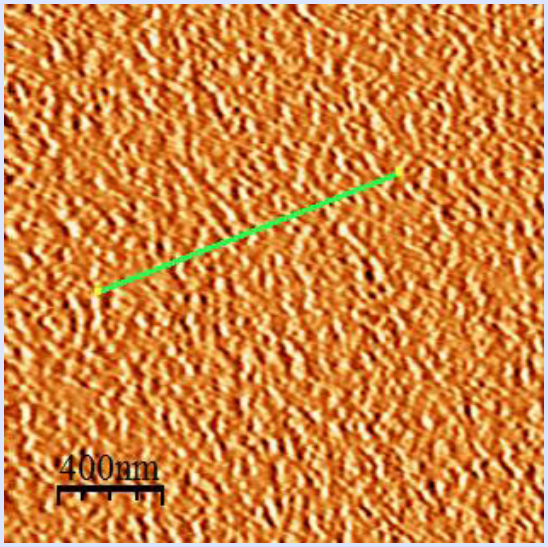
$TiO_2(110)$ - AFM

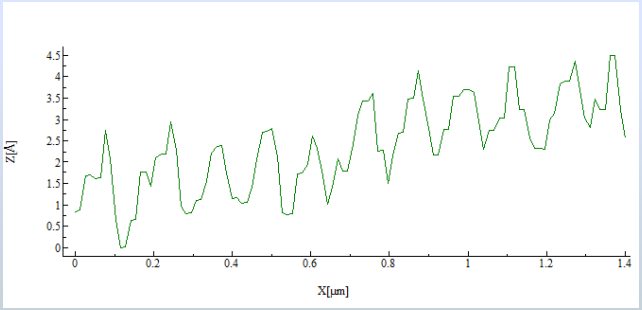
FLAT SURFACE

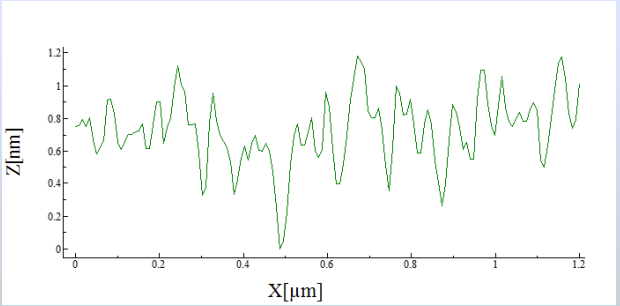




ION-BOMBARDED SURFACE







CLEANING PROCEDURE:

Immersed in HF
800 ºC in air for 2h
+
Low E ion bombardment
High T annealing in 10^{-7} mbar O_2

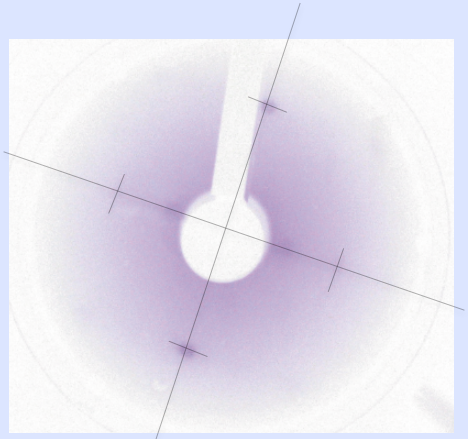
ION BOMBARDMENT:

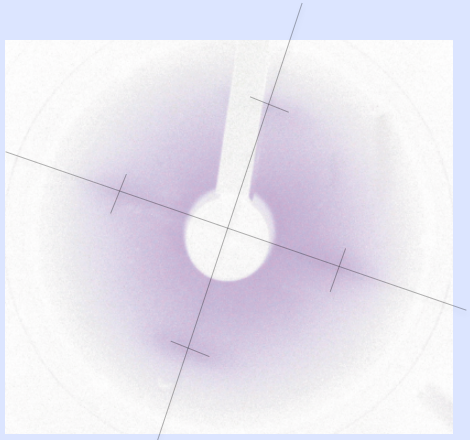
E = 3 keV @ RT for 1h
Dose = 10^{17} ions/cm^2

modified $TiO_2(110)$ – LEED

FLAT SURFACE

ION-BOMBARDED SURFACE





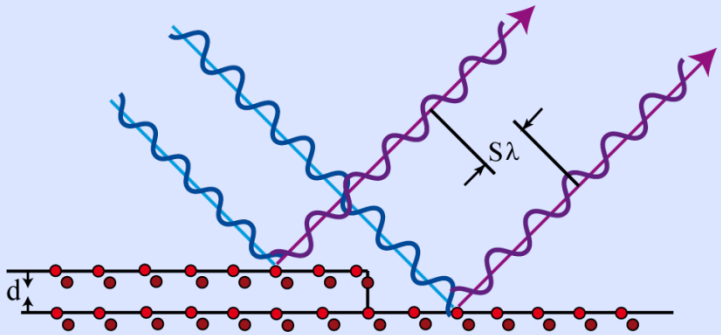
E=63 eV

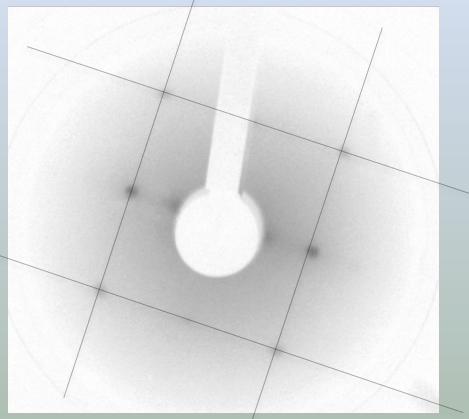
spot (2,0):
S=4.02

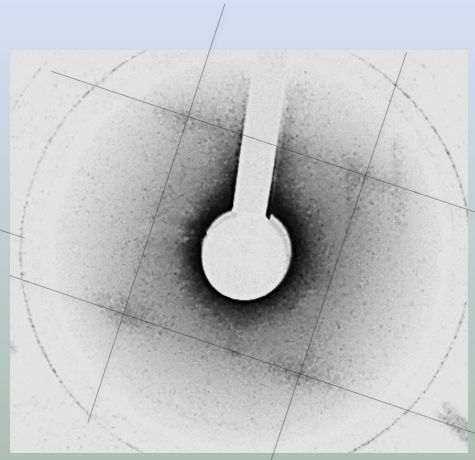
spot (0,1):
S=3.96

Scattering phase:

$S = k\downarrow\perp d/2\pi$

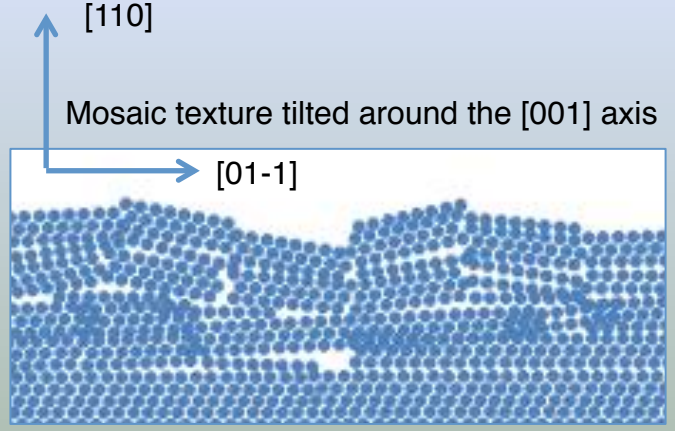




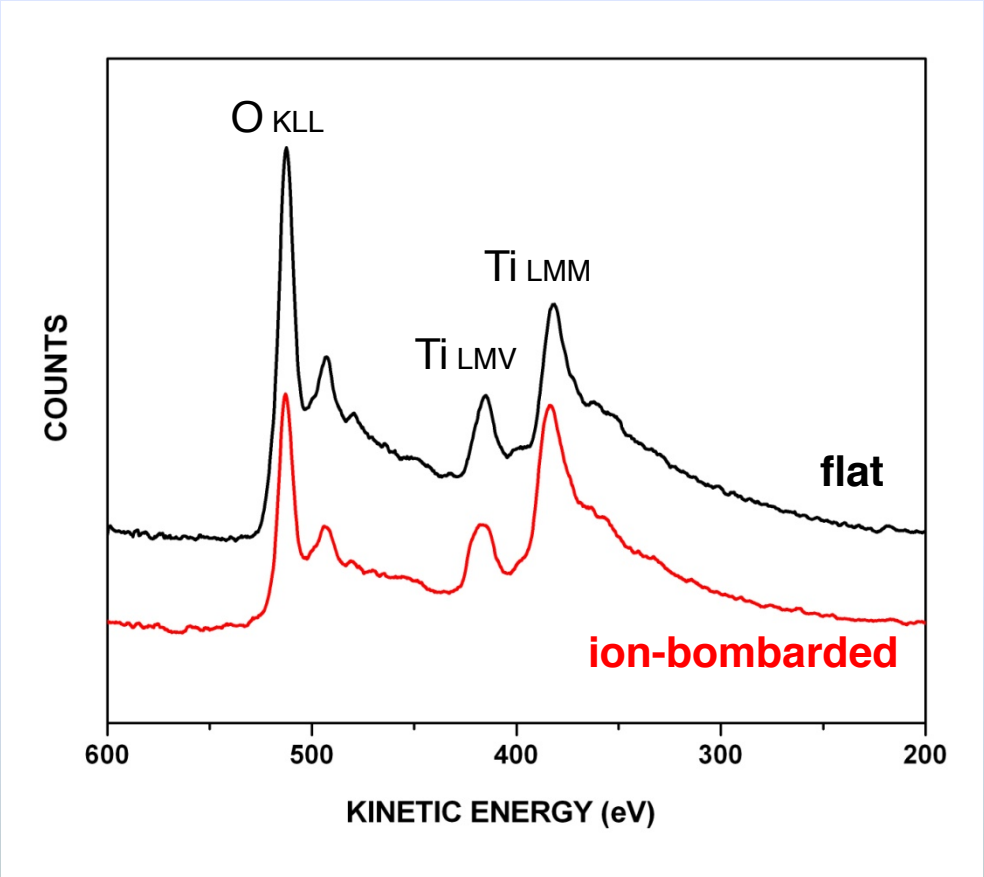


E=95 eV

spot (2,1):
S=4.76



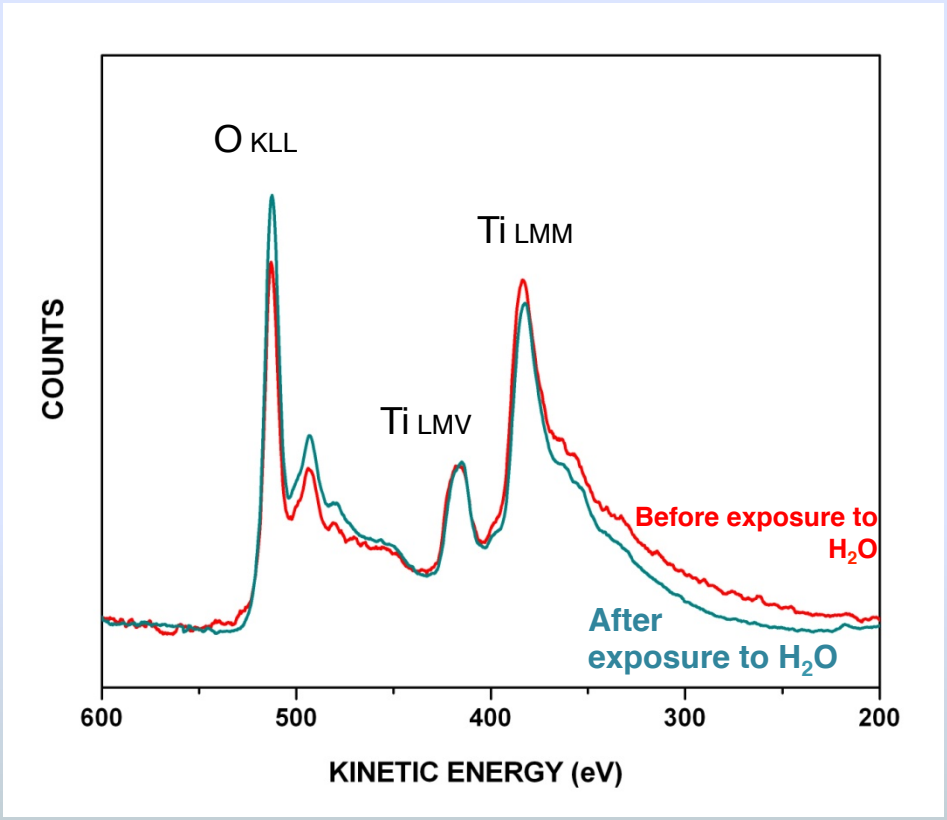
modified TiO_2(110) - Auger Electron Spectroscopy



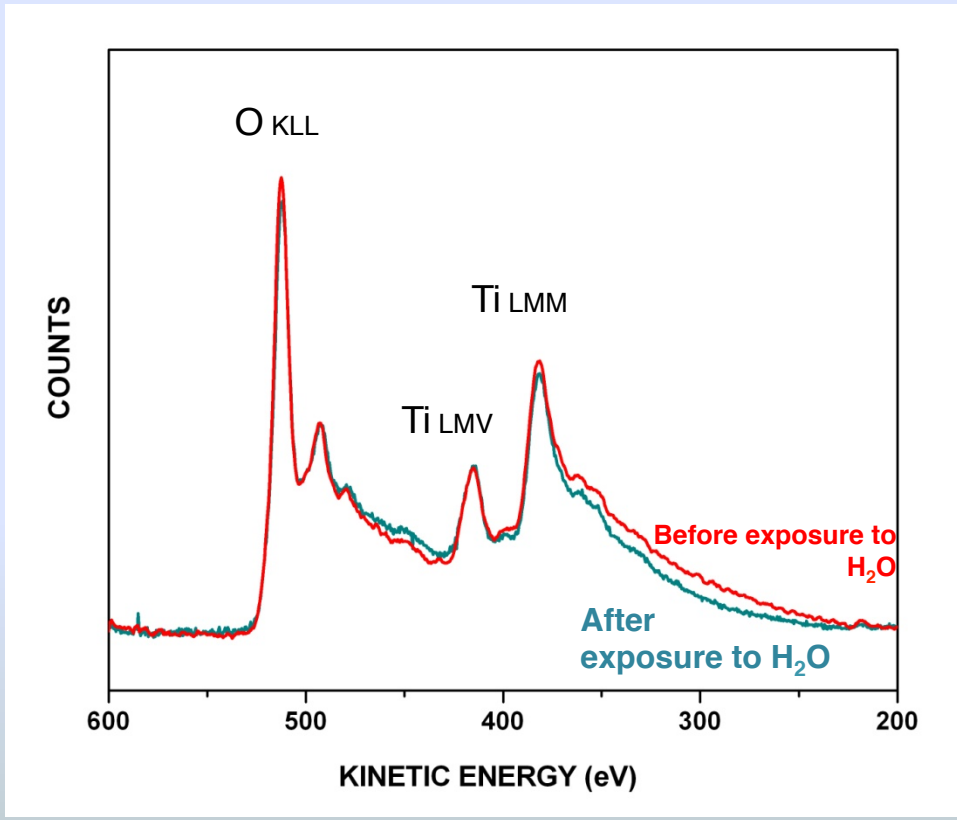
PREFERENTIAL SPUTTERING OF OXYGEN AND REDUCTION OF THE Ti CATIONS

modified TiO_2(110) - Auger Electron Spectroscopy

ION-BOMBARDED SURFACE



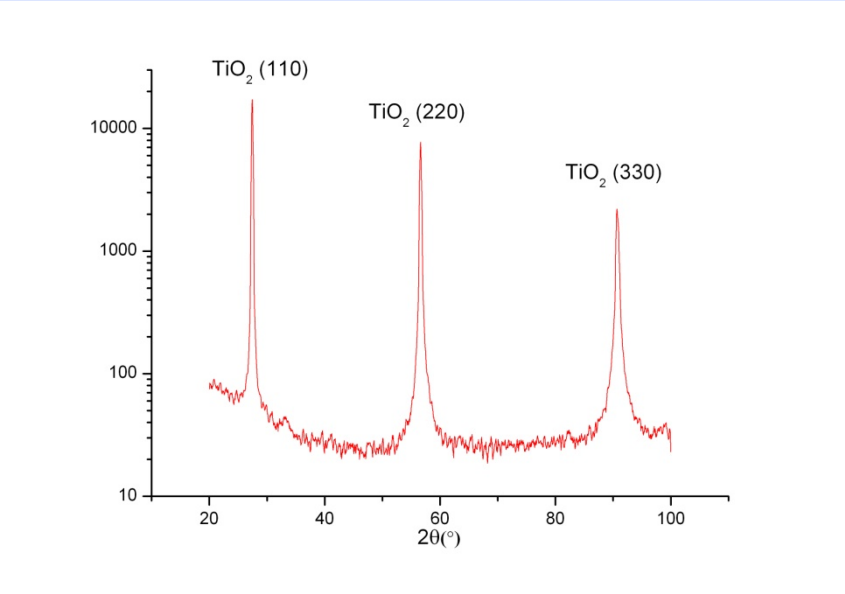
FLAT SURFACE



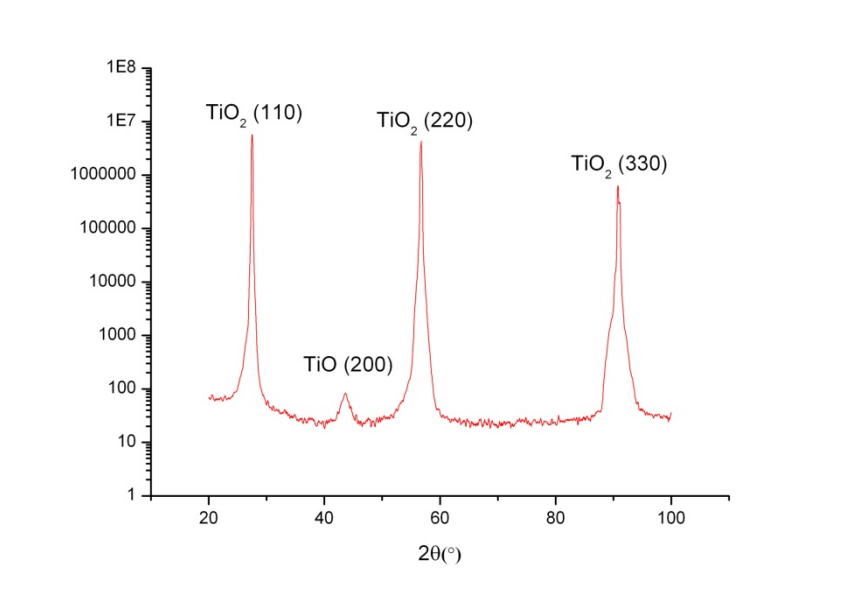
PARTIAL REOXIDATION (HYDROXYLATION) OF THE UPPER LAYER AFTER WATER EXPOSURE

modified TiO_2(110) – X Ray Diffraction

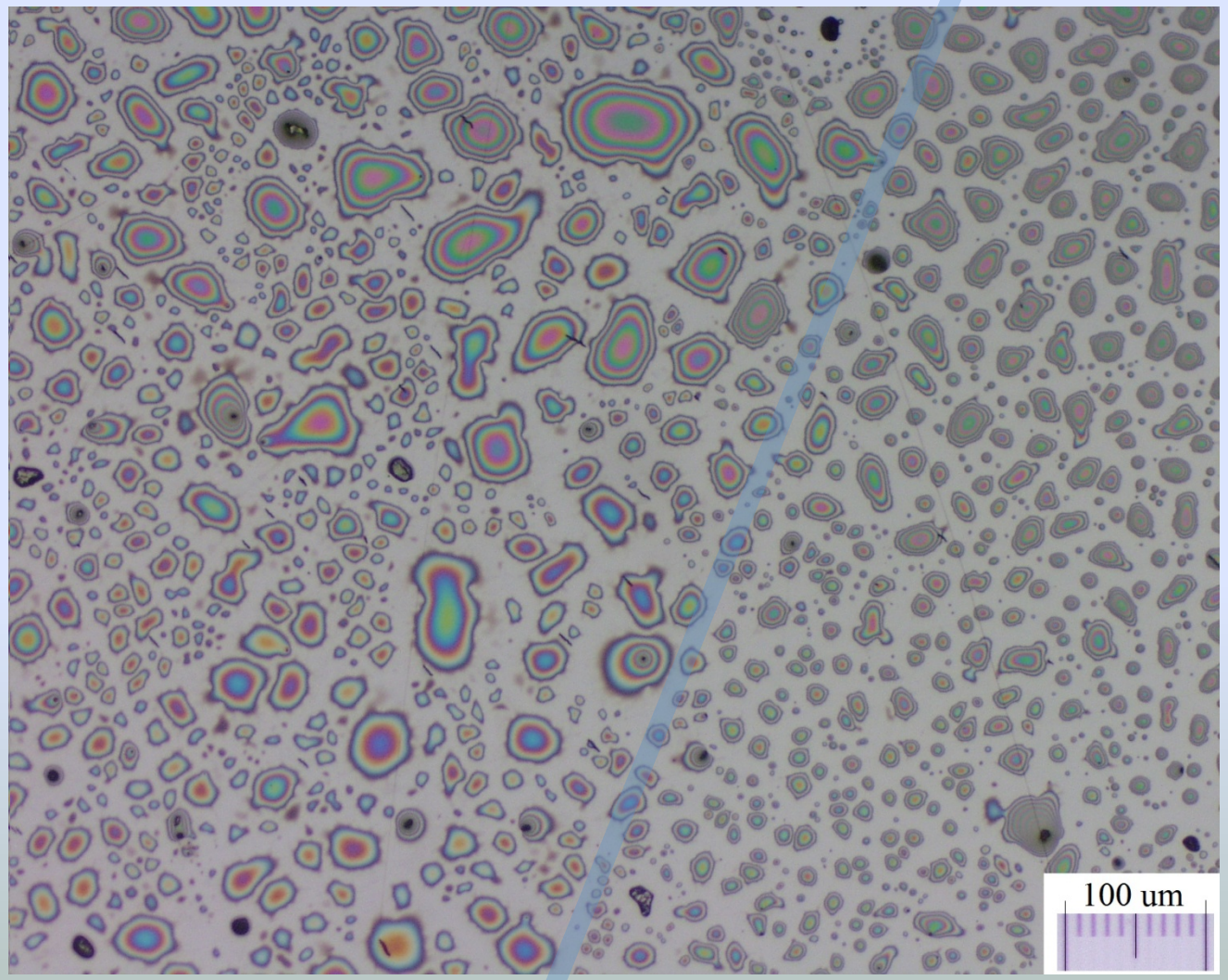
FLAT SURFACE



ION-BOMBARDED SURFACE



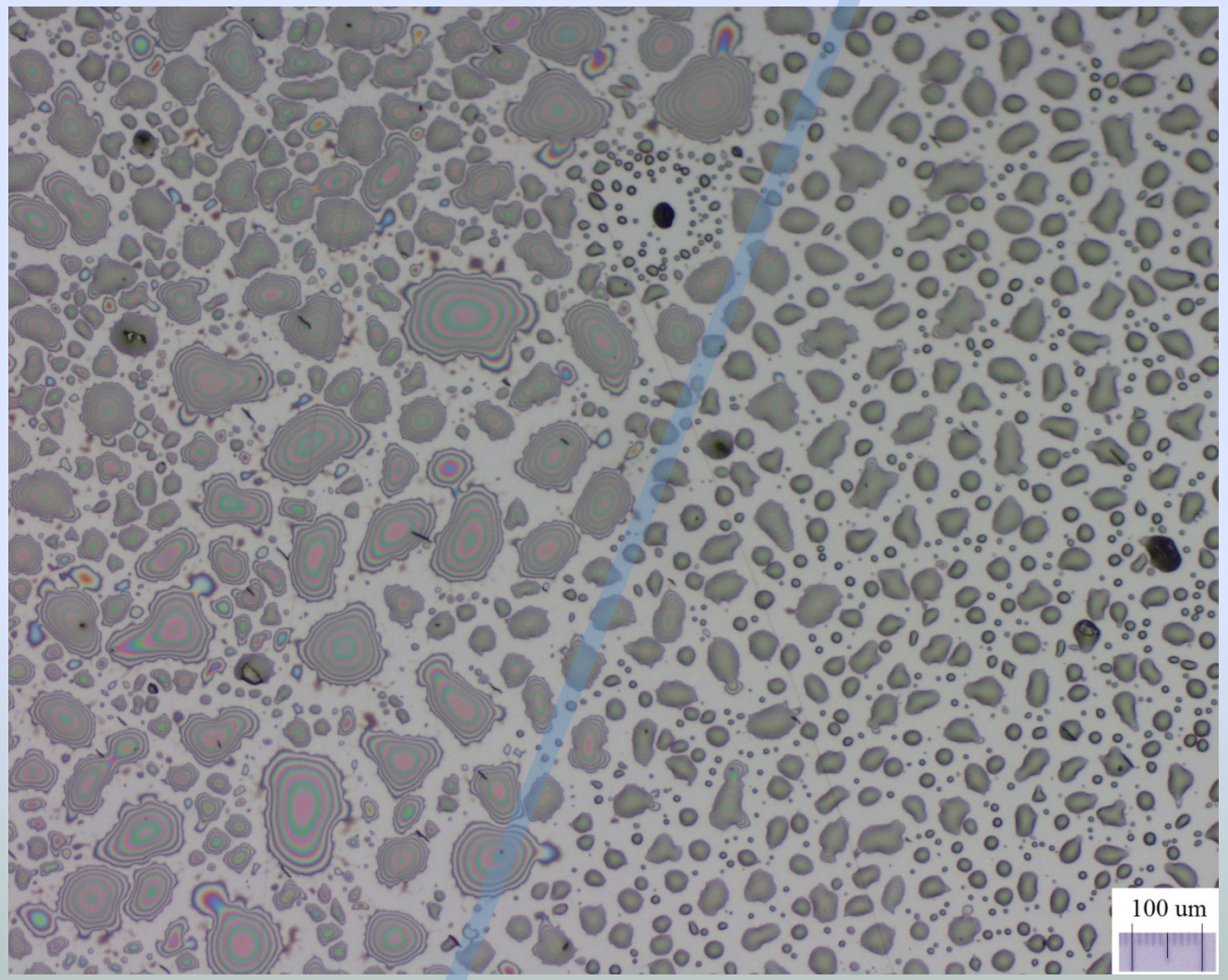
WATER CONDENSATION



Flat region

Ion bombarded region

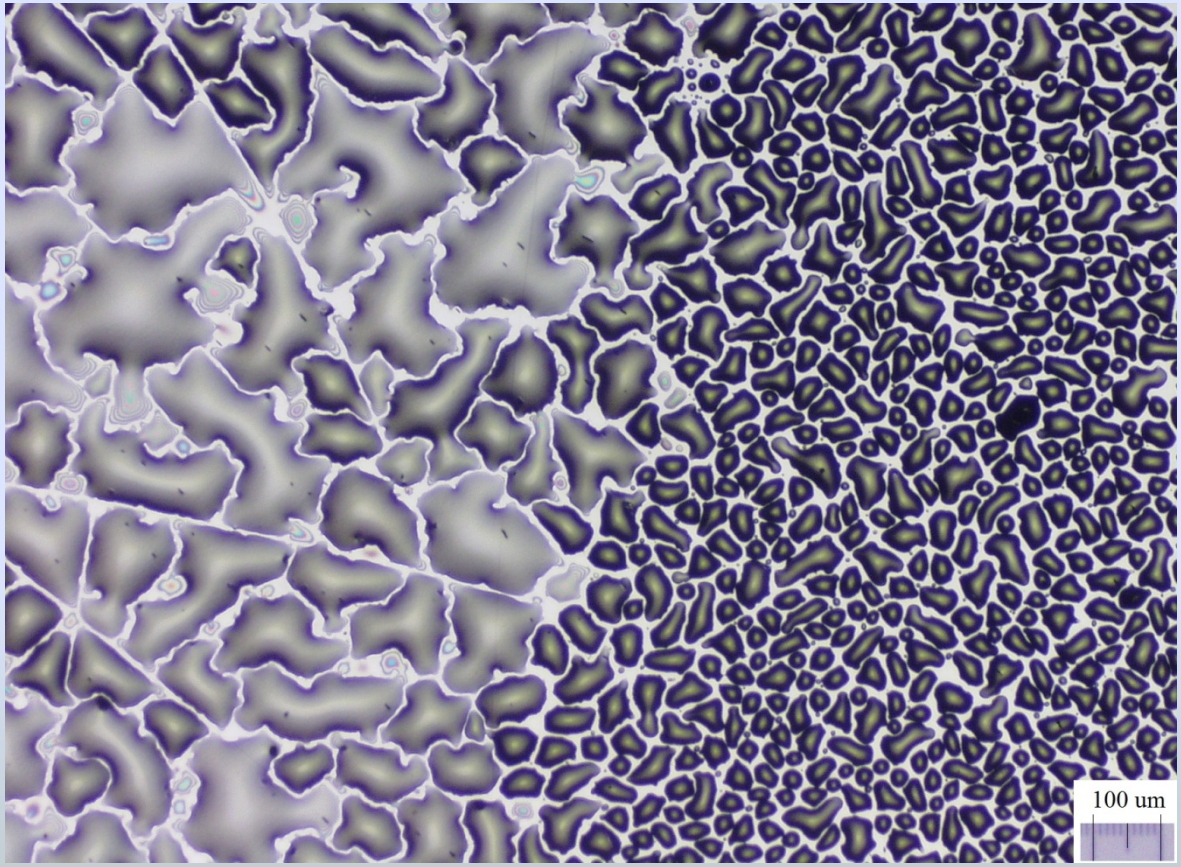
WATER CONDENSATION



Flat region

Ion bombarded region

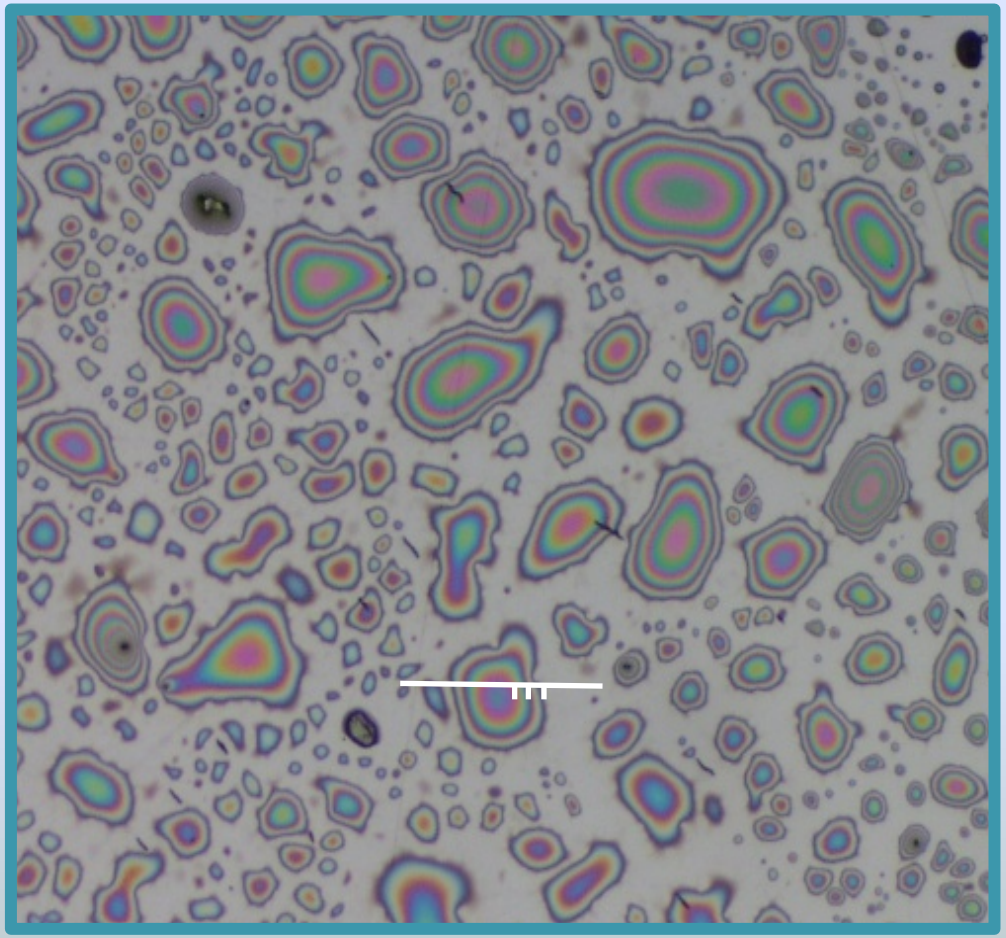
WATER CONDENSATION



Flat region

Ion bombarded region

WATER CONDENSATION

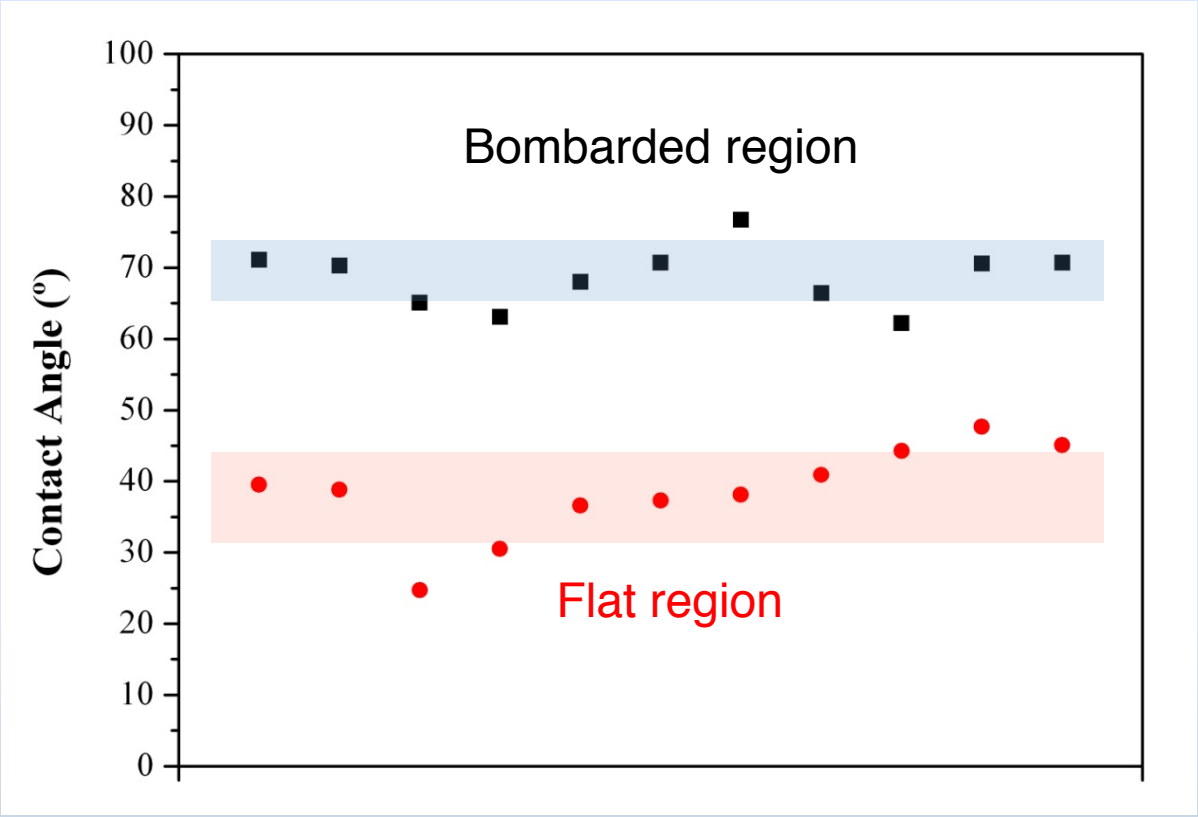


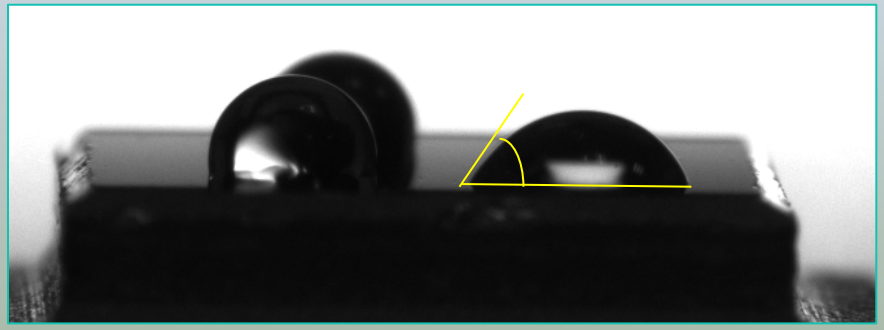
$h = i\lambda/2n$

$\alpha \approx 2^{o}$

Optical interference fringes

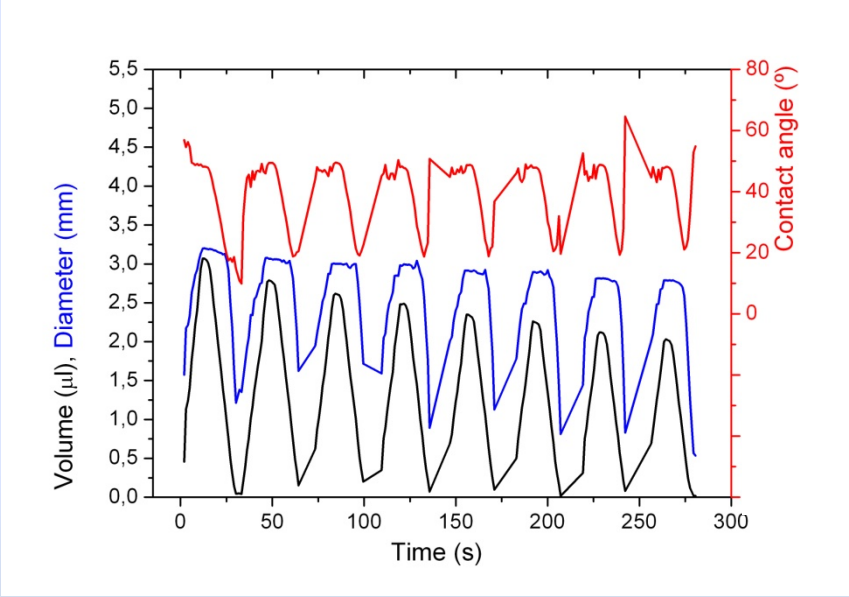
CONTACT ANGLE



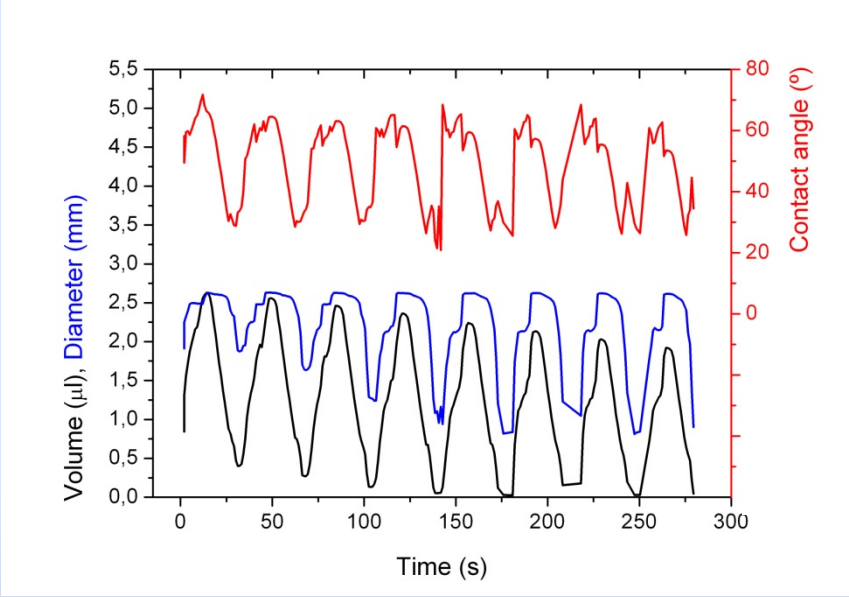


CONTACT ANGLE - DYNAMIC MEASUREMENTS

FLAT SURFACE



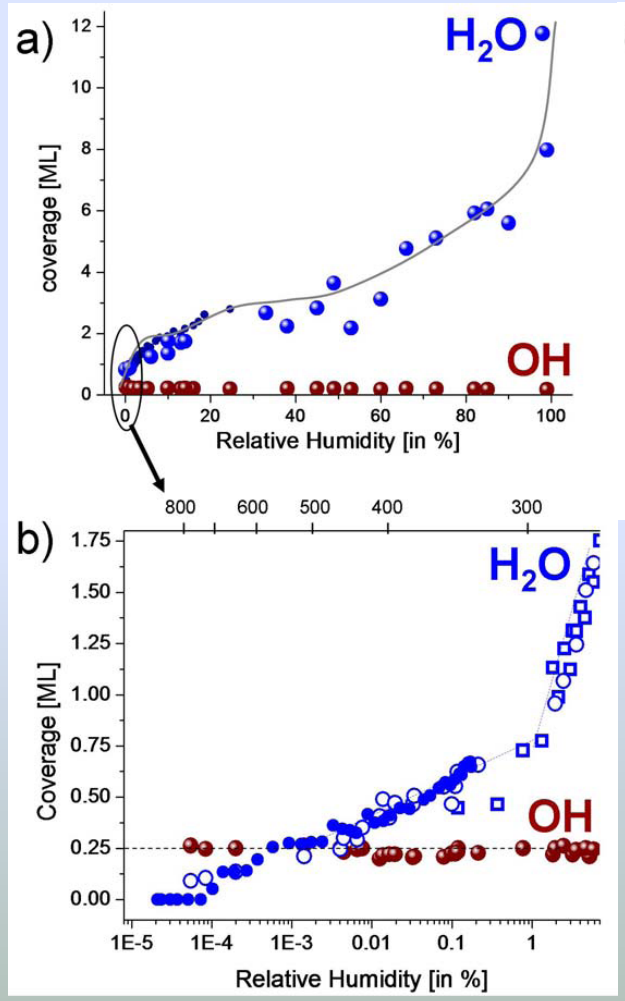
ION-BOMBARDED SURFACE

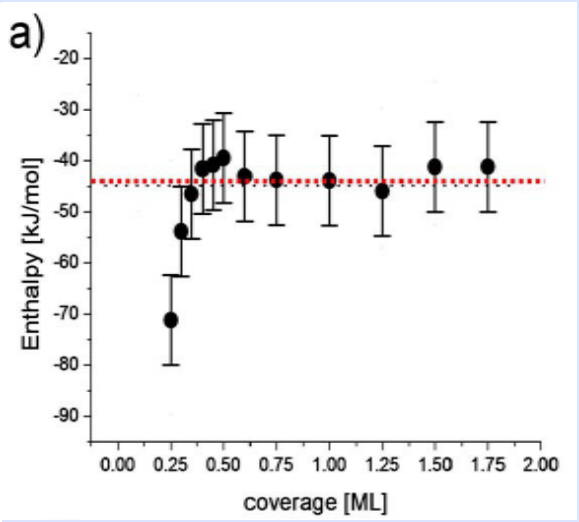


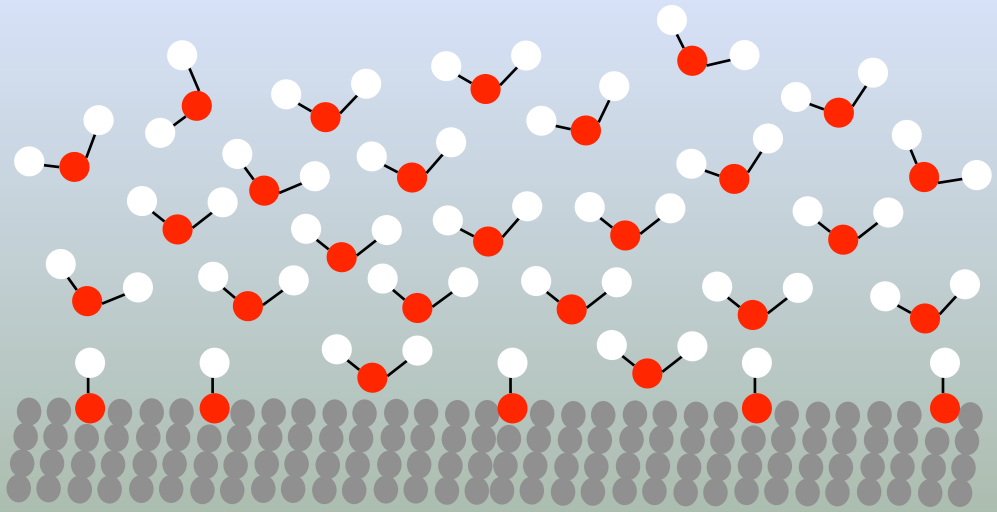
$$\gamma_{SV} = \gamma_{SL} + \gamma \cos \theta_{eq}$$

DISCUSSION

OH^- are the precursors for H_2O adsorption in defective TiO_2







Ketteler et al. J. Phys. Chem. 2007, **111**, 8278

CONCLUSIONS

Low energy ion bombardment of TiO_2(110) causes atomic disorder and chemical reduction of the surface and a structural tilting of small regions around the [001] axis.

Exposure to water partially reoxidizes the upper layer.

When continuously exposed to water vapour, the density of nucleation points of microdroplets is larger for the flat surface, where they lye with a lower angle than in the defective surface.

After coalescence and saturation, the microdroplets are finally larger in the flat surface.

The as-placed static contact angle, as well as the advancing and receding angles in dynamic measurements, are higher for the defective surface.

This can be due in part to the formation of a non-favourable, frustrated, H-bond network.