

Molecular Ordering at the Interface Between Liquid Water and Rutile TiO₂ (110)

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TITANIUM DIOXIDE



(lowest surface energy)

[010] 1.983 Å [100]

Diebold, U., et I. (1998). Surface science, 411(1), 137-153.

RUTILE TiO₂ (110) SURFACE – UHV STUDIES...

Adsorption of water vapors



073411.



MOLECULAR OR DISSOCIATIVE WATER ADSORPTION AT THE REAL TIO₂ / WATER INTERFACE?

Pang, C. L., Lindsay, R., & Thornton, G. (2013). Chemical reviews, 113, 3887-3948.

Deposition of organic molecules ex-situ



....THE INTEREST INTO IN SITU STUDIES

"[...] there is an essentially unexplored range of experiments at ambient pressure and liquid interfaces that is now technically feasible. The appropriate techniques include surface X-ray diffraction, SPM, ambient pressure photoemission, and X-ray absorption spectroscopy. Measurements of this type will be vital to explore the fundamental physics and chemistry associated with photocatalysis under more realistic conditions ..."

Chi Lun Pang et al. (2013), *Chemical Review.*, 113, 3887-3948.

"These structures, however, have generally been observed in vacuo, whereas most applications of TiO₂ involve instead an aqueous environment [...]. Therefore, an important question concerns the fate of the surface reconstruction in such an environment [...] surface structures in vacuo and/or at low water coverage can be very different from those present in real photocatalytic applications"

Aschauer and Selloni (2011), *Physical Review Letters*, 106, 166102.

"If one wants to link surface-science studies closer to application, it is also **vital to bring surface science out of UHV**[....]. This would further test the relevance of acquired knowledge for technical applications."

Diebold, U. (2003), Surface Science Reports, 48(5), 53-229.

RUTILE TiO₂ (110) (1x1) – SAMPLE PREPARATION

bulk reduction in UHV (annealing at T~800K)
formation of O vacancies and Ti³⁺ interstitials

- surface preparation (Ar+sputtering and annealing cycles at T~930K)
- LEED and XPS characterization



RUTILE TiO₂ (110) IN HIGH PURITY WATER



- High purity water: milli-Q water (18.2 MΩ•cm)
- No erosion or dissolution in water
- Structure stability after days of immersion in water

Sasahara, A. and Tomitori, M. J. Vac. Sci. Technol. B, 2010, 28, C4C5-C4C10. 300x300 nm²

STM image in water 449x449 nm^2 V_b= -700mV, I_t=1nA



MONOATOMIC STEPS



previous AFM studies reported a degradation of the surface for UHV prepared samples

RUTILE TiO₂ (110) IN HIGH PURITY WATER



RUTILE TiO₂ (110) in HIGH PURITY <u>WATER vs. UHV</u>

Corrugation values from STM in water vs UHV

- along [1-1 0] : about 0.4 Å (as in UHV) - along [0 0 1] : about 0.3 Å (0.1 in UHV)



•Which is the origin of the x2 periodicity along the rows in WATER?



J. Matthiesen..., F. Besenbacher, PRL 102, 226101 (2009)

RUTILE TiO₂ (110) IN HIGH PURITY WATER





x 2 periodicity along [001]



STM image in water 10x10 nm^2 V_b= -700mV, I_t = 1nA

H₂O molecules adsorption: ordered overlayer





c(2x2) cell



9

graphic elaboration from: Murray, P. W., Condon, N. G., & Thornton, G. (1995). Physical Review B, 51(16), 10989.

RUTILE TiO₂ (110) IN HIGH PURITY WATER

Theory: DFT MD simulation

Jun Cheng and Joost VandeVondele Department of Materials, ETH Zürich,





x 2 periodicity along [001]

Molecular Ordering at the Interface between Liquid Water and Rutile TiO_2 (110) 10

CALCIUM SEGREGATED - RUTILE TiO₂ (110)

The presence of a thin calcium layer onto TiO2 has recently raised the interest of medicine to simulate bone growth in biomedical implants.



CALCIUM SEGREGATED - RUTILE TiO₂ (110) IN HIGH PURITY WATER



STM image 167x167nm² V_{b} = -1V, I_{t} =1nA

- Monoatomic steps

- Stripes along [001]: Ca structures 1–5nm long



3.3<u>±0.2</u> nm

10 12 14

Distance (nm)

16 18 20

- distances between stripes along the [001] **x5** ; x4 ; x3 a_[1-10], up to x8 a_[1-10]
- FWHM of 1.2 ± 0.2 nm, height of 2.0 ± 0.5 Å.



After 48 hours immersion in water



STM image 18x18nm²; inset 5.3x6.8nm² Zhang, et al. Surf.Sci. (1998) 412, 242.

STM image: 74x74m² $V_{b} = -1V, I_{t} = 1nA$

THE TiO_2 (110) SURFACE FOR PHOTOVOLTAIC APPLICATIONS: DYE SENSITIZED SOLAR CELLS



Pang, C. L.; Lindsay, R. and Thornton, G. *Chemical Society Reviews*, 2008, 37, 2328. Ball and stick model of the most likely adsorption geometry for bisisonicotinate on TiO2(110)(1×1)

RUTILE TiO₂ (110) IN ETHANOL

- Preparation of a new sample in UHV: $TiO_2(110) (1x1)$ surface
- Immersion in pure ethanol (>99.8%)
- monoatomic steps

-10]

[001]

STM image: 127.9 x 127.9 nm², V_{b} = +2.7 V, I_{t} =1 nA

- structure at low scale:
- row pattern



STM image 14.2 x 14.2 nm², V_b = +2.6 V, I_t =1 nA.



RUTILE TiO₂ (110) IN ETHANOL

step edge modification, mainly along the <1-11>



RUTILE TiO₂ (110) IN ETHANOL WITH DYE N-719

TiO₂ rutile (110) in pure ethanol



STM image 129x129 nm², V_b = +2,7 V I_t = 1nA

The sample was left left overnight in contact with dye solution (10⁻⁶M) and then rinsed with pure ethanol. All the STM measurements are taken in a solution of pure ethanol.



ethanol + dye N719 (10⁻⁶M)



STM image $174x174nm^{2}$, $V_{b} = +2.6 V I_{t} = 1nA$

web source: http://www.google.com/patents/EP2455955A 2?cl=en

RUTILE TiO₂ (110) IN ETHANOL WITH DYE N-719



STM image about 85x85 nm^{2,} V_b = +2,69 V I_t = 1nA



isolated spots : 1.6 – 2.0 nm wide

dye molecules





isolated dye molecules



STM image 14.2 x 14.2 nm², $V_b = + 2.6 \text{ V}$, $I_t = 1 \text{ nA}$



RUTILE TiO₂ (110) IN ETHANOL WITH DYE N-719

mobility and aggregation of dye molecules on the surface



STM images, sequence: 42.6 x 42.6 nm², $V_b = + 2.6 V$, $I_t = 1 nA$.

CONCLUSIONS

 Study of metal oxide surfaces in realistic and technologically important environment

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O BEILSTEIN JOURNAL

In-situ investigation of the rutile TiO₂/liquid interface

•TiO₂ (110) in high purity water

first atom-resolved images

stability of the surface

ordering of the adsorbed H₂O overlayer

morphology and stability of the calcium-terminated surface

•TiO₂ (110) **in ethanol** with **dye molecules** step edge modification (<u>ethanol</u>) adsorption of isolated and aggregated <u>dye molecules</u>

the interface in bulk liquid is different with respect to UHV !!!

SURF GROUP @ UNITORV

SURF Group: SUrface and inteRFace in liquid and UHV Physics Dept., University of Rome "Tor Vergata"

MEMBERS

Prof. C. Goletti, Dr. B. Bonanni

Post-doc researchers T. Kosmala, S. Breuer

Ph.D. Students G. Serrano, M. Di Giovannantonio, L. Fazi





TECHNIQUES: RAS, SDR, EC-STM, XPS chamber with EC pre-chamber, variable temperature UHV-STM (Prof. K. Wandelt, Bonn Universitat, donation, September 2011)

COLLABORATIONS: Prof. K. Wandelt , Bonn Universitat

Prof. Aldo Di Carlo (Electronic Engineering Dept. University of Rome "Tor Vergata", CHOSE Polo Solare Organico Regione Lazio, Rome)

Prof. Ulrike Diebold (Institute of Applied Physics - University of Technology, Wien)

Prof. Joost VandeVondele (Department of Materials, ETH Zürich, Switzerland)

TIO₂ RUTILE (110) IN ETHANOL WITH DYE Z-907 MOLECULES









STM images, sequence: 115.2 x 115.2, nm² $V_{h} = -1.1 V$, I, = 1 nA

