Shallow trapped electron states and related processes of TiO_2 Probing with UHV-IRRAS

Karlsruher Institut für Technologie

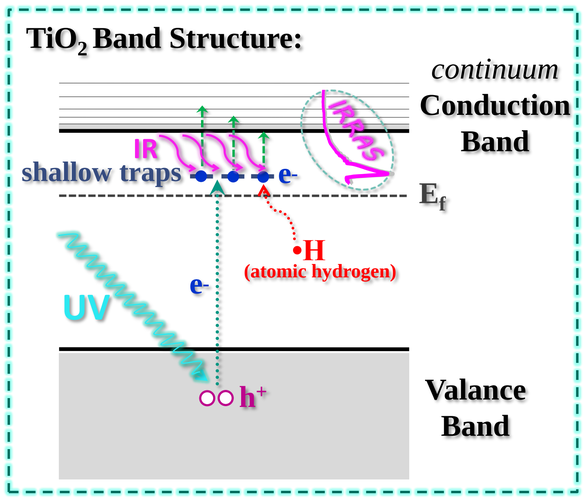
Hikmet Sezen, Carsten Natzeck, Alexei Nefedov, Christof Wöll

Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

1 Scope

❖ Probing trapped shallow state electrons delivering from both atomic hydrogen and UV treatments on powder and single crystal TiO_2 samples by a novel method of the infrared reflection absorption spectroscopy in an ultrahigh vacuum environment (UHV-IRRAS).[1] However, now we have a more furnished UHV system at KIT, which is called as **THEO**!

❖ Tracking related mechanisms utilizing both shallow trapped photoelectrons and photoholes in a time resolved mode of UHV-IRRAS.



2 Instrumental

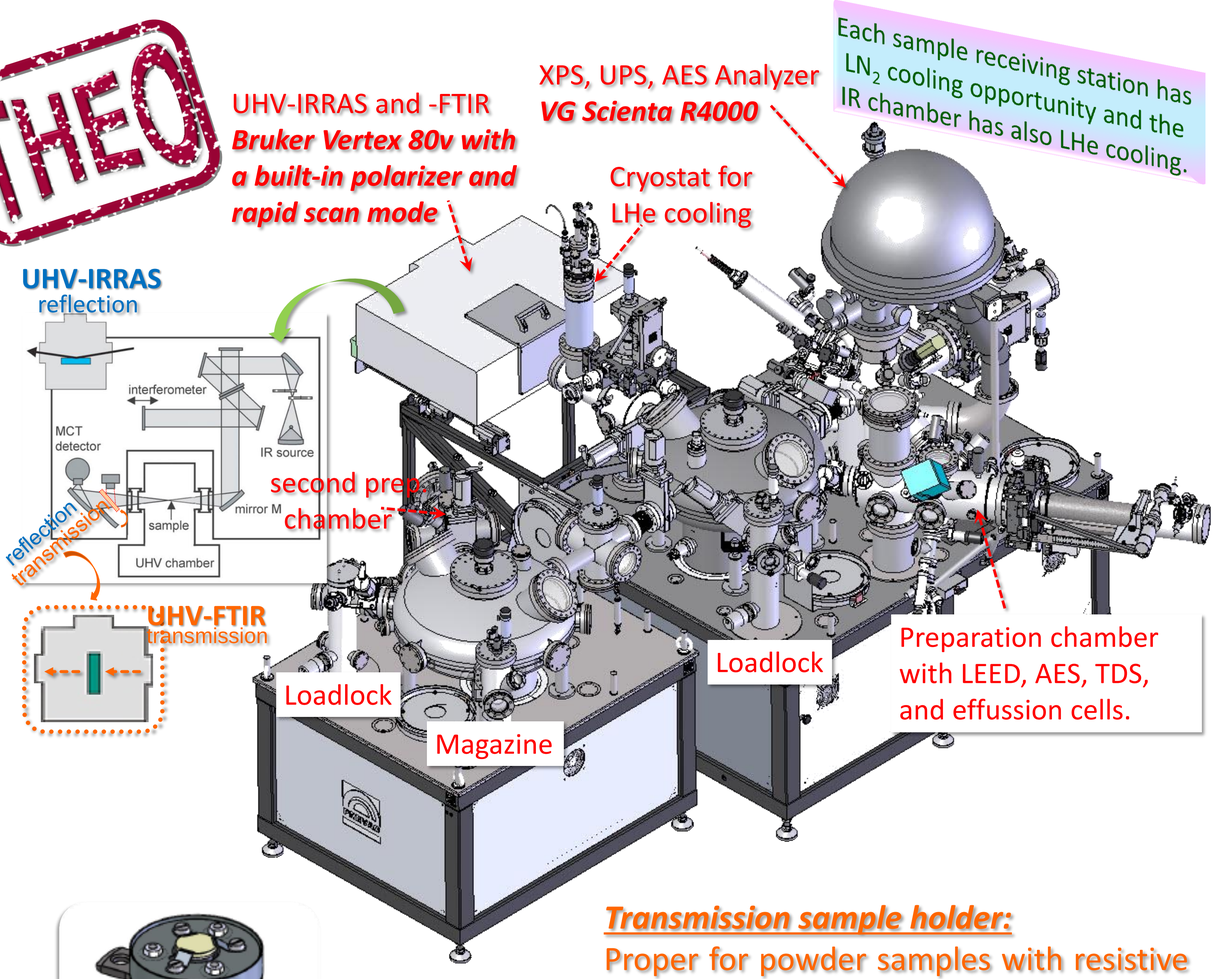
THEO

UHV-IRRAS and -FTIR
Bruker Vertex 80v with a built-in polarizer and rapid scan mode

XPS, UPS, AES Analyzer
VG Scienta R4000

Each sample receiving station has LN_2 cooling opportunity and the IR chamber has also LHe cooling.

Cryostat for LHe cooling

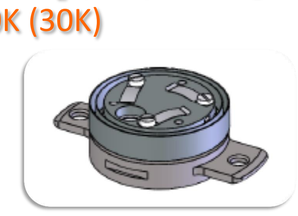


Transmission sample holder:

Proper for powder samples with resistive heater and LN_2 (LHe) cooling in between 1200K-100K (30K)

E-beam sample holder:

Proper for single crystal samples with electron bombardment heater and LN_2 (LHe) cooling in between 1500K-100K (30K)



3 Experiment

Sample Preparation:

cleanness ✓

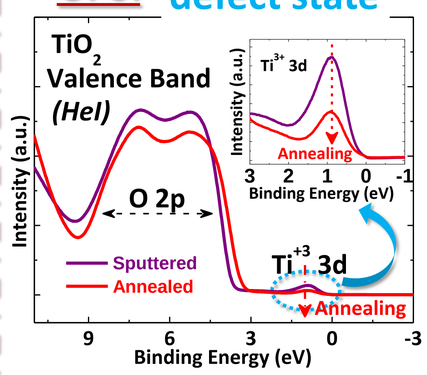
XPS: **oxidation state** ✓

Powder TiO_2 samples were annealed at 600 K for 30 minutes in UHV condition, but never sputtered. Single crystals were prepared a few cycles of Ar^+ ion sputtering and annealing in UHV condition for various durations until reach a satisfactory quality level. The quality of single crystals were qualified by different techniques. For example, x-ray photoelectron spectroscopy (XPS) survey allows to us to check surface cleanness and oxidation state of titania.

Sample Preparation Con't.:

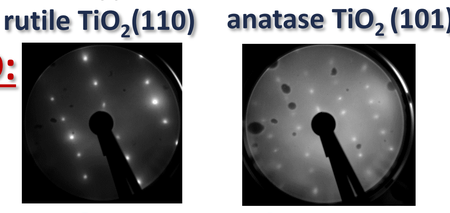
Ultraviolet photoelectron spectroscopy (UPS) provides to us a directly monitoring of the defect state density at the crystal surface by pursuing the Ti3d level appearing around 0.9 eV. Additionally, in the future this capability will be utilized to conduct in-situ type measurement with UPS.

UPS: **defect state** ✓



rutile TiO_2(110) anatase TiO_2 (101)

LEED:



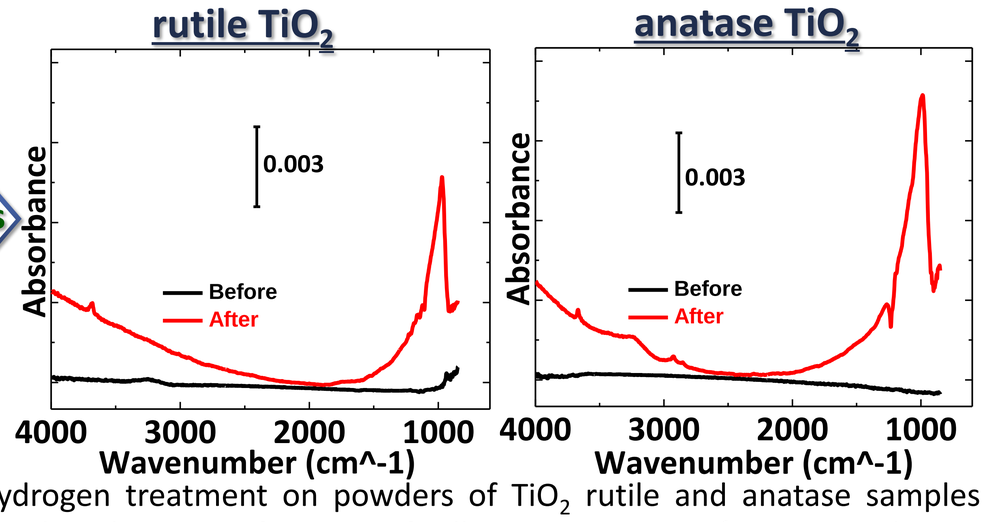
surface crystal structure ✓

Low energy electron diffraction (LEED) can tell us that whether a good quality surface crystallography of single crystals was achieved or keep continuing sputtering and annealing cycles.

4 Results

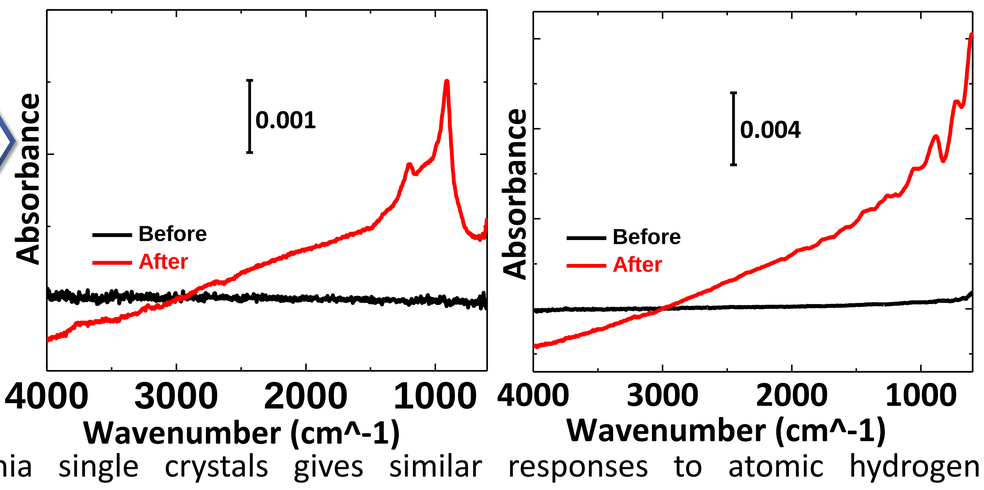
rutile TiO_2 **anatase TiO_2**

powders



Atomic hydrogen treatment on powders of TiO_2 rutile and anatase samples yield a broad IR absorption from specifically 900 to 2000 cm^{-1} corresponding to mostly electron excitation from the shallow state to the conduction band as described in literature.[2-4]

single crystal



The titania single crystals gives similar responses to atomic hydrogen treatment, but much less IR absorption intensities and different attributes than powders. The duration and power parameters of the atomic hydrogen treatment process was carefully adjusted by accompanying XPS survey due to possibility of reduction. The results presenting here were acquired from non-reduced titania samples for both powders and single crystals.

5 Conclusions

UHV-IRRAS technique can probe shallow state electron populations providing from the atomic hydrogen treatment on both powder and single crystal of TiO_2 for different crystal morphologies; rutile and anatase. While the powder results are in good agreement with previous works,[2-4] the single crystal results are reporting the first time here.

6 Outlook

- UV treatment on both powder and single crystal TiO_2 rutile and anatase samples is still a going on project with Theo.
- Time resolved UHV-IRRAS measurements will be integrated to this work to follow related chemical mechanisms dealing with photogenerated electrons and holes on the titania single crystals after accomplishment about the UV treatment.

7 References

1.) M. Xu, Y. Gao, E. M. Moreno, M. Kunst, M. Muhler, Y. Wang, H. Idriss, C. Wöll, Phys. Rev. Lett. 106, 138302 (2011).
2.) D. M. Savory, D. S. Warren, A. J. McQuillan, J. Phys. Chem. C 115, 902 (2010).
3.) D. A. Panayotov and J. T. Yates Jr, Chemical Physics Letters 436, 204 (2007).
4.) D. A. Panayotov, S. P. Burrows, J. R. Morris, J. Phys. Chem. C 116, 4535 (2012).