

UHV - FTIRS investigations of oxide surfaces

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FTIR- AND RAIR - SPECTROSCOPY OF OXIDE SURFACES

Oxides have found numerous applications, e. g. in catalysis, for producing sensors, solar cells and electronic devices. In the past decades numerous IR investigations of oxide powders have been reported. To understand the complex IR spectra recorded for such powder, it is necessary to obtain data for well-defined model systems with reduced complexity, e. g. single-crystal surfaces. Unfortunately, studies on oxide single crystals are extremely scarce. As a result of severe technical problems, in case of rutile TiO_2 so far only one IR-study^[1] has been reported. Reflection-absorption infrared spectroscopy (RAIRS) on metal surfaces is governed by the so-called surface selection rule: Vibrational modes with a transition dipole moment (TDM) orientated parallel to the surface cannot be seen. For dielectric surfaces the situation is more complicated, both s- and p-polarized light couple to adsorbate vibrations. In addition absorption bands of molecular adsorbates on metals can lead to a reduction in reflectivity (positive bands) as in the case of metals, but also to an enhancement of reflectivity (negative bands). For s-polarized light the bands will always be negative, for p-polarized light the bands can be negative or positive depending on the incidence angle Θ and the refractive index n of the substrate (Fig.1). We have designed a new UHV-IR/XPS-apparatus^[2], with which data for molecular adsorbates on oxide single-crystals can be recorded in a routine fashion (Fig.2).

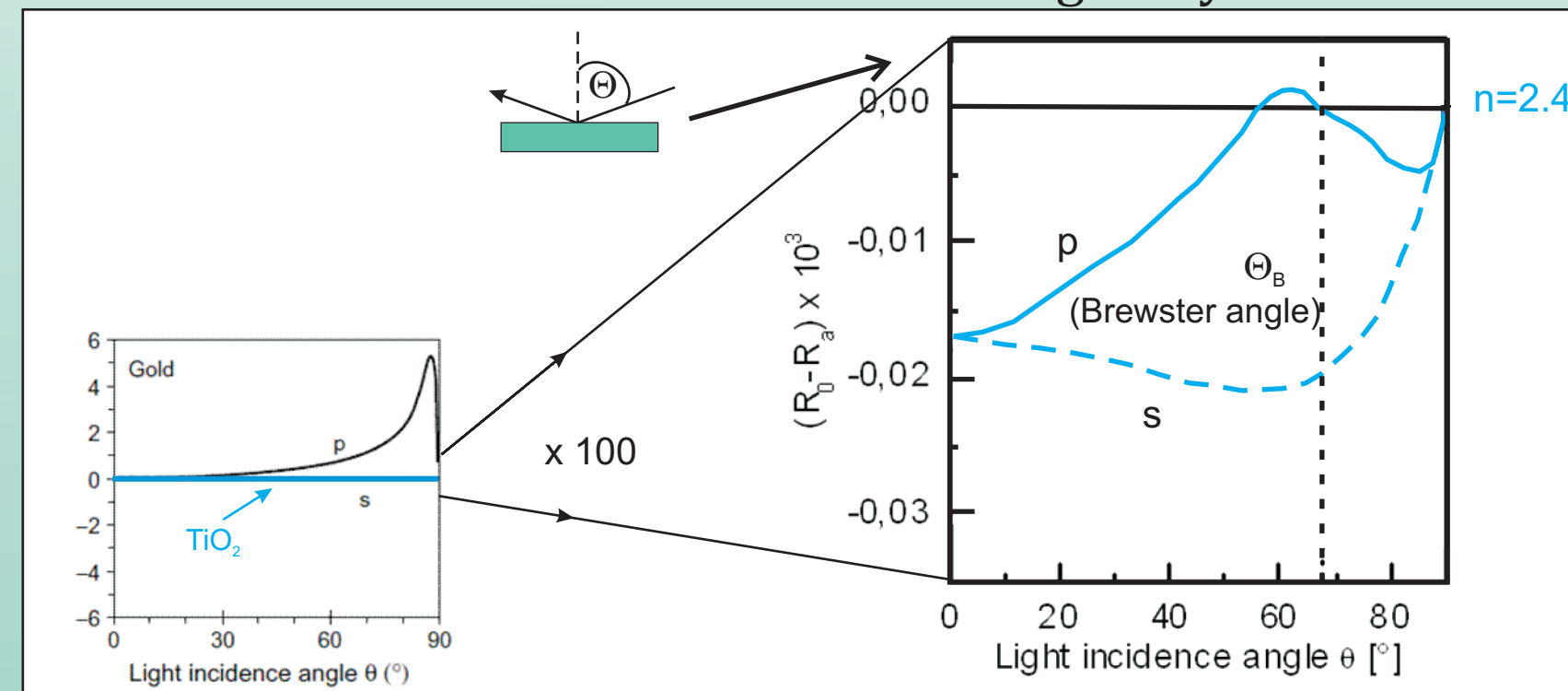


Fig.1: Calculated reflectivity differences between the clean substrate (R_0) and the adsorbate covered substrate (R_a) for different substrate materials as a function of the light incidence angle for p-polarized radiation and s-polarized radiation.

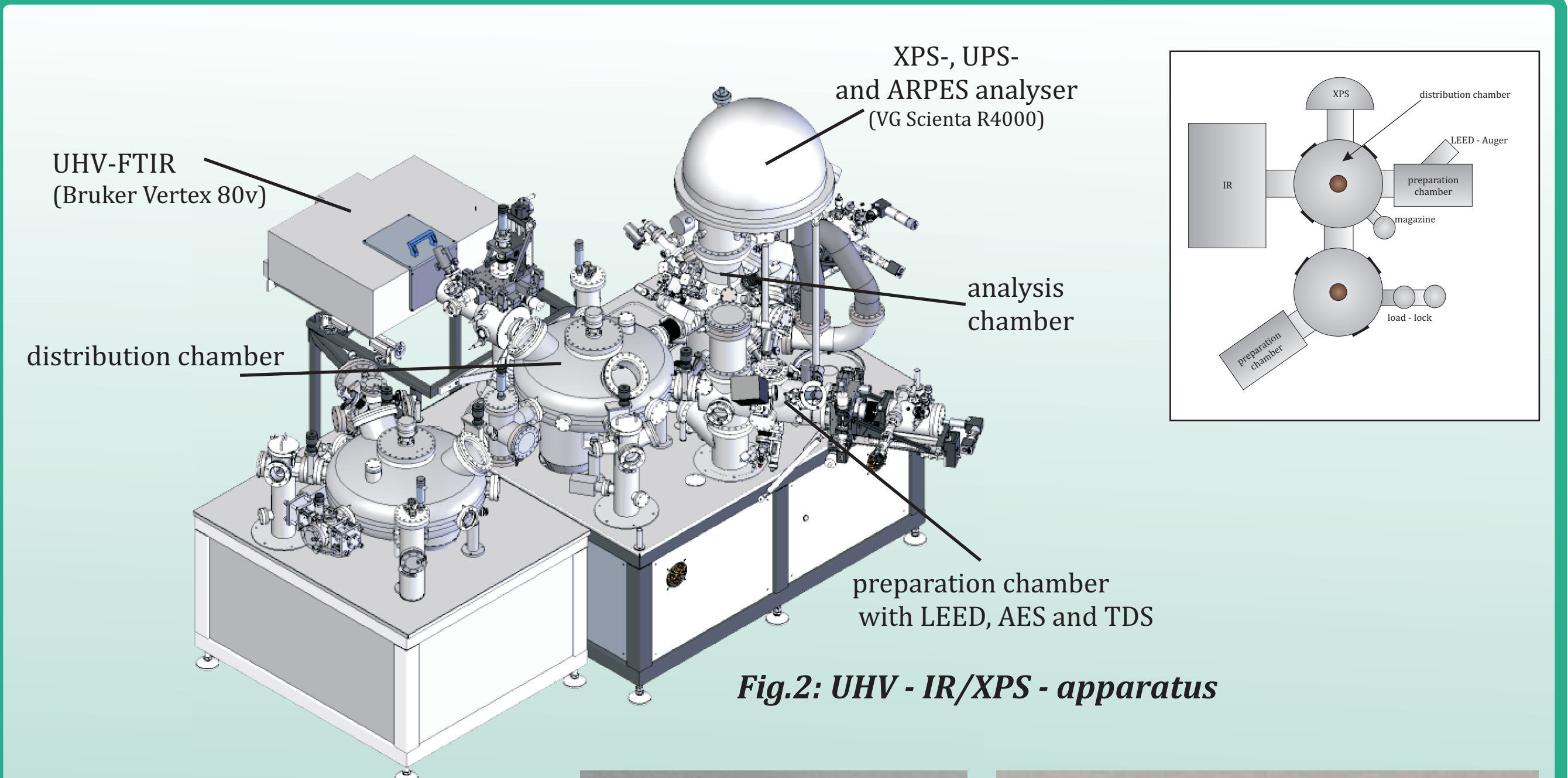
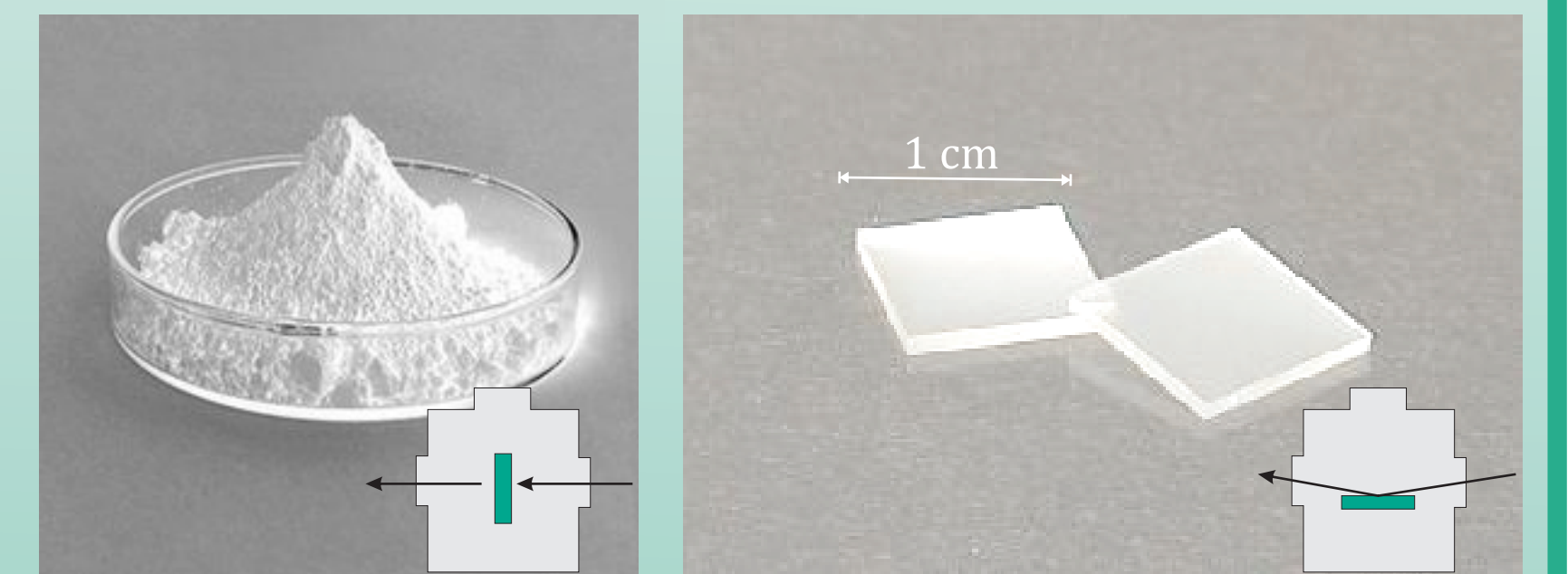


Fig.2: UHV-IR/XPS-apparatus

Fig.3: Powder IR - measurements in transmission mode (left), oxide single crystals IR - measurements in reflection mode (right)



PHOTOCATALYTIC REACTIONS ON TiO_2

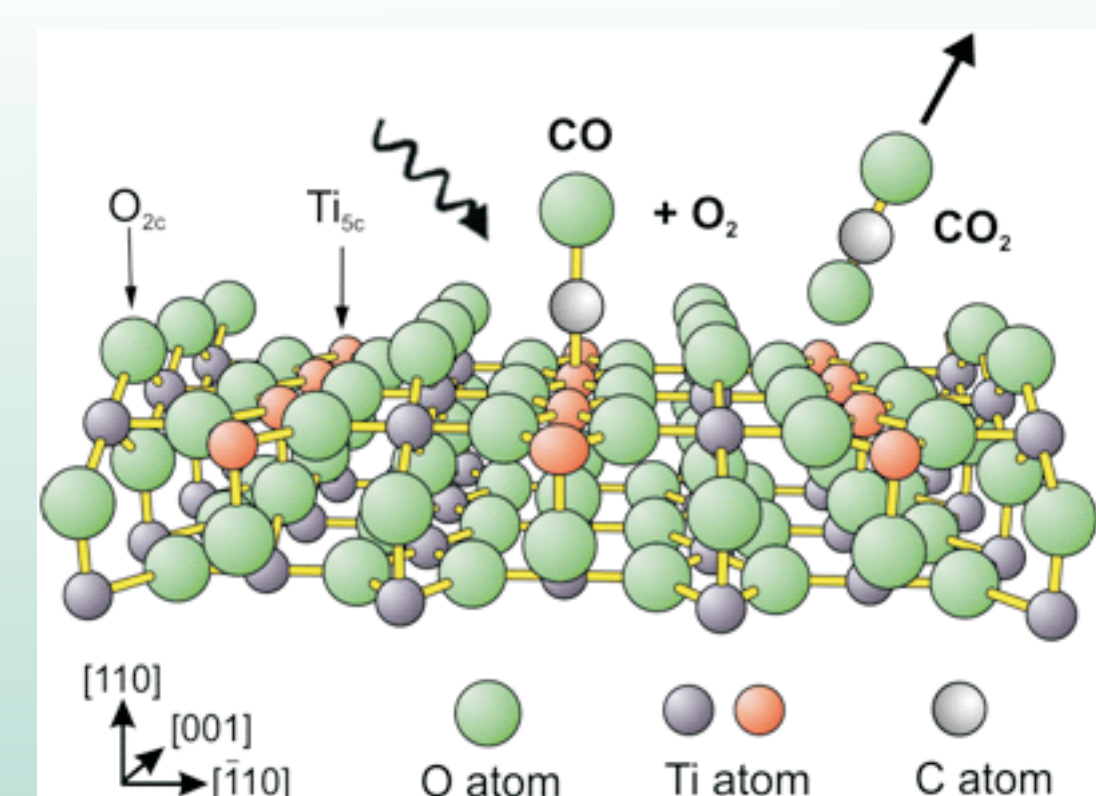
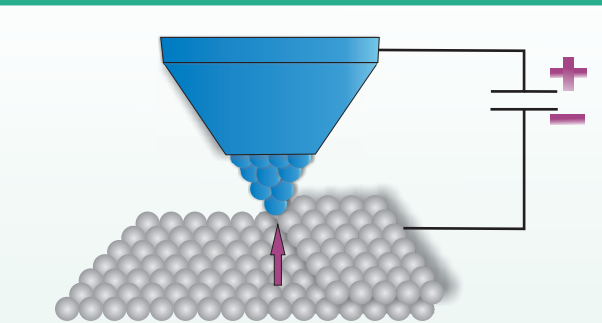
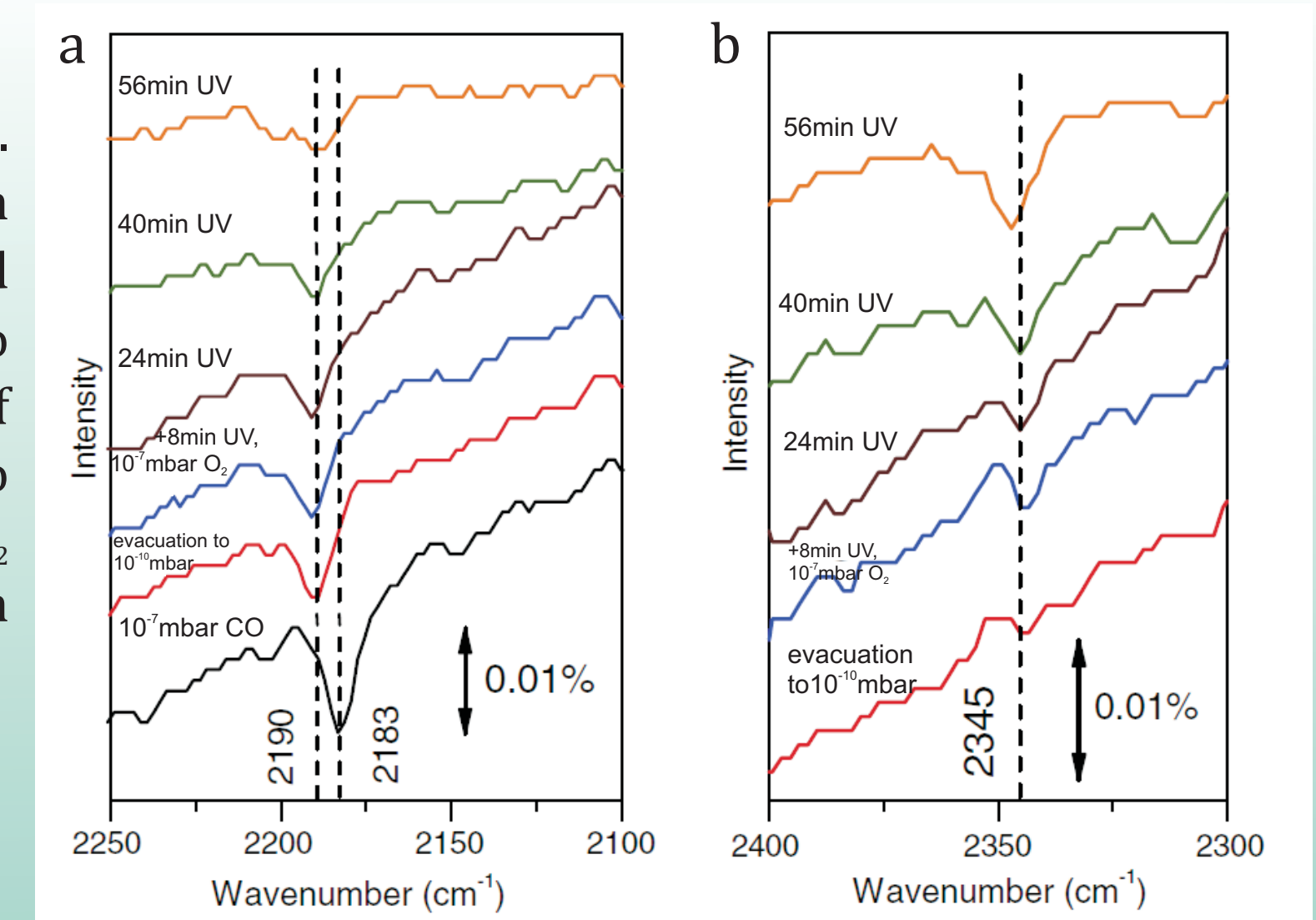


Fig.4: Side view of the TiO_2 (110) surface and adsorbed CO molecules on top of Ti atoms (red), which are five fold coordinated to oxygen atoms (green); formation of CO_2 via photooxidation of CO.

Titania (TiO_2) presently attracts a lot of interest because of its photovoltaic and photochemical properties. The first RAIRS results^[4] of CO photooxidation to CO_2 on TiO_2 (110) single-crystal surfaces are displayed in Fig.5. In the presence of 10^{-7} mbar CO on TiO_2 (110) at 110K, the internal stretching mode of CO adsorbed on Ti_{5c} sites is seen at 2183cm^{-1} . At higher coverages this band shifts slightly to 2190cm^{-1} . After exposure to UV-light (3.2eV) no photo-induced desorption of CO was detected, only in the presence of O_2 a decrease of the band-intensity reveals photooxidation. In the RAIRS data no intermediates which can be attributed to reaction intermediates like formate or carbonate species were present. We conclude that the activated O_2 molecules react directly with the adsorbed CO to yield CO_2 . Some of the product CO_2 remain adsorbed on the surface, as indicated by the new band at 2345cm^{-1} (Fig.5b).

Fig.5: a) RAIRS data of CO on TiO_2 (110) single-crystal surface at 110K, b) CO_2 region of a)



FORMER RESEARCH WORK

STM-measurements of ultrathin TiO_x - Films on Pt_3Ti (111)

Research Group of Prof. Dr. K. Wandelt, university of Bonn.

Scanning tunneling microscopy (STM) is a powerful technique for imaging surfaces at the atomic level. The STM probes the local density of states (LDOS) of the sample surface and its electronic properties. This method is limited to conductive samples, making experiments on thin and electron-transparent oxide films particularly attractive.

z' - TiO_x	w' - TiO_x	z - TiO_x	rect- TiO_2
rect-($6 \times 3 \sqrt{3}$) commensurate	hex-(7×7)R21.8° commensurate	incommensurate	incommensurate
10 L - 200 L O_2	220 L - 1500 L O_2	900 L - 2700 L O_2	6000 L O_2
1000 K	1000 K	900 K	800 K
$p(\text{O}_2) = 2 \cdot 10^{-5}$ mbar	$p(\text{O}_2) = 2 \cdot 10^{-7}$ mbar	$p(\text{O}_2) = 2 \cdot 10^{-5}$ mbar	$p(\text{O}_2) = 2 \cdot 10^{-5}$ mbar

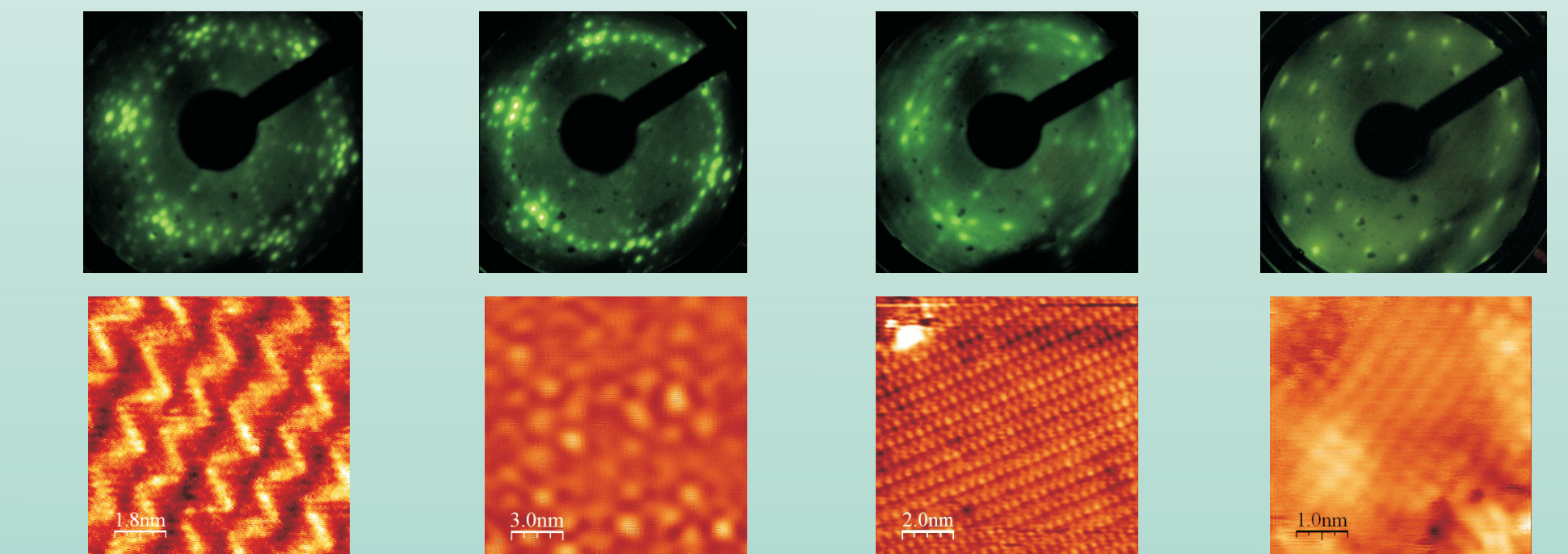


Fig.6: Overview of different titania phases on Pt_3Ti (111), observed with LEED and STM. The structures of the different phases are very similar to them of $\text{TiO}_x/\text{Pt}(111)$ ⁶¹, $\text{VO}_x/\text{Rh}(111)$ ⁷¹ and $\text{VO}_x/\text{Pd}(111)$ ⁸¹ systems.

Four different phases of ordered, ultrathin titanium oxide films (Fig.6) can be prepared in UHV by oxidation of a $\text{Pt}_3\text{Ti}(111)$ single-crystal^[5]. These different phases have been investigated by low-energy electron diffraction (LEED) and a home-built STM. Two commensurate phases with zig-zag stripes (z' - TiO_x) and with a wagonwheel-like structure (w' - TiO_x) are obtained at low oxygen pressures. In both cases the resulting homogeneous oxide films wets the complete surface and consist of Ti-O bilayers. At high oxygen partial pressures two incommensurate structures can be prepared: a fully oxidized rect- TiO_2 film, that forms a film which contains holes to release stress, that arises from the lattice mismatch between film and substrate. The second (z - TiO_x) shows a very disordered surface morphology.

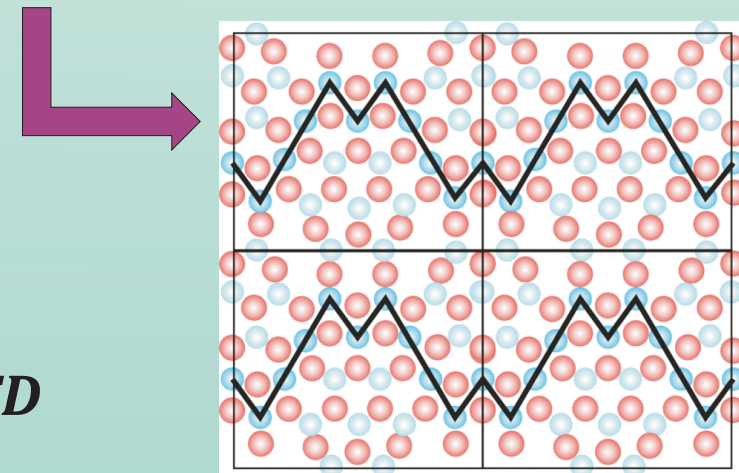


Fig.7: Model of z' - TiO_x - phase on Pt_3Ti (111) getting from the STM-results. Four fold coordinated Ti atoms (dark blue) form the zig-zag structure, three fold Ti (light blue) and oxygen (red) are in between.

FIRST PROJECT: CeO_2

In combination with other catalysts ceria (CeO_2) is used in automobile catalytic converters to reduce NO_x emissions and convert CO to CO_2 . Due to the oxygen mobility and the ability to change the oxidation state of the metal ions cerium oxide is used as electrolyte in solid oxide fuel cells (SOFC). We plan to investigate the adsorption of CO, CO_2 , NO_x , O_2 , H_2O and H_2 on single-crystal surfaces of CeO_2 with UHV-IR- and X-ray-photoelectron-spectroscopy (XPS).

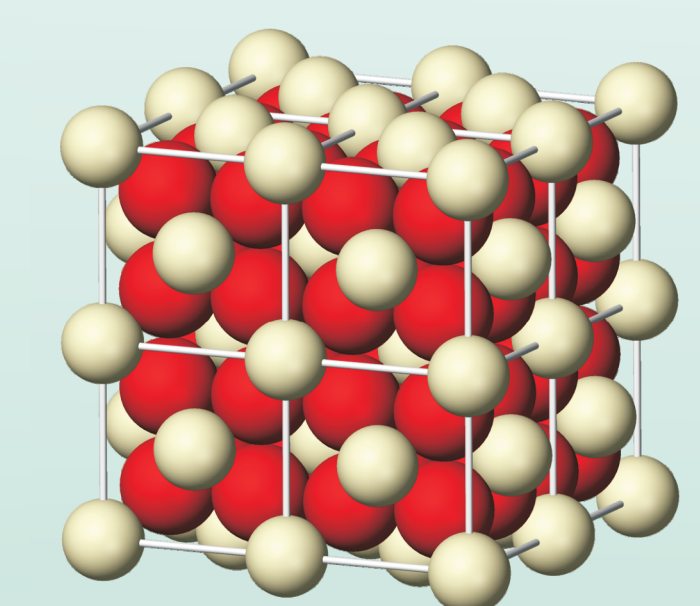


Fig.8: Crystal structure of ceria (CaF_2 -type).

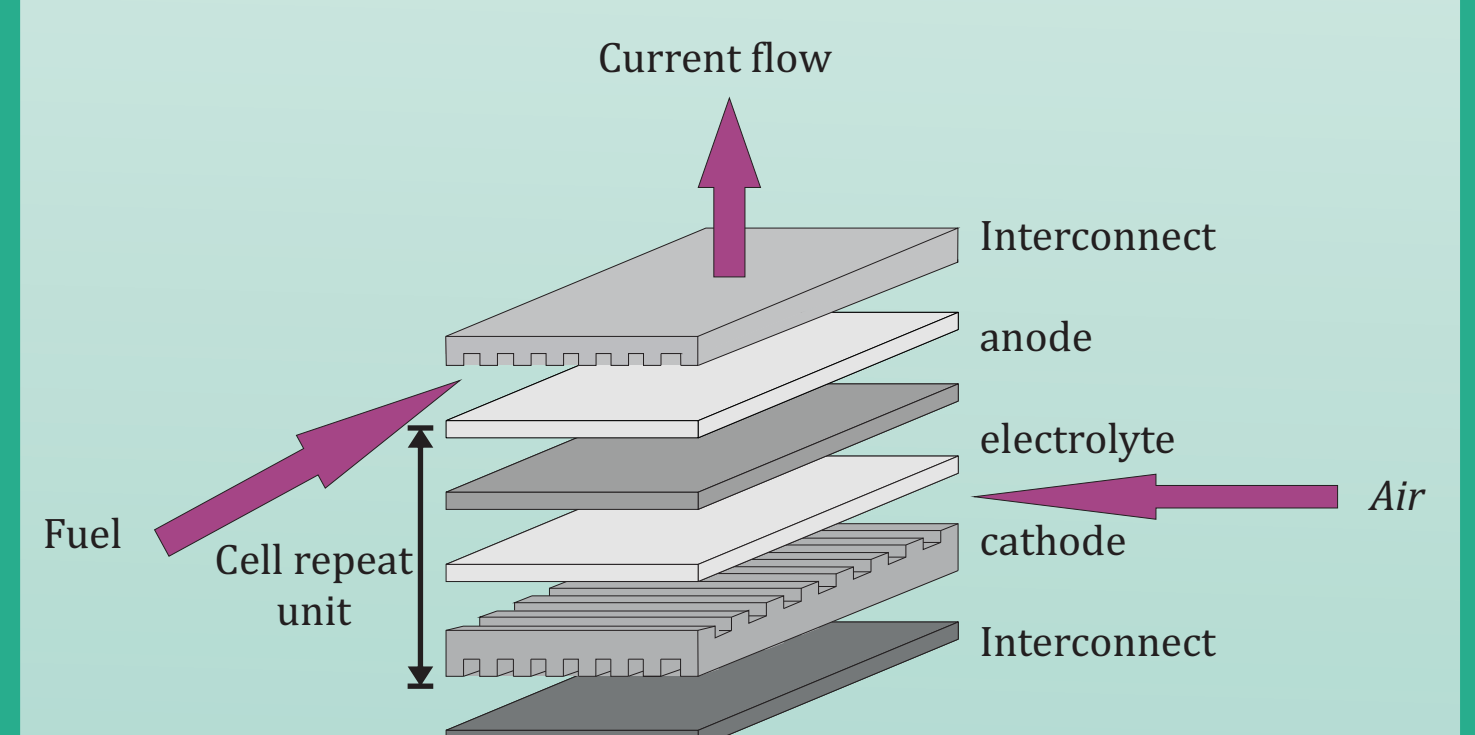


Fig.9: Application of CeO_2 as electrolyte in SOFC

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PERSONAL DETAILS

Maria Kesting, Diplom - Chemikerin
08 / 2010 diploma thesis *Struktur und Templateigenschaften von ultradünnen TiO_x - Filmen auf Pt_3Ti (111) - Untersuchungen mit STM, LEED und AES*, university of Bonn.
Supervisor: Prof. Dr. Ch. Wöll ; Cosupervisor: Prof. Dr. O. Deutschmann
Institute for Functional Interfaces, KIT.

