SCIENCES SORBONNE UNIVERSITÉ

2023-2024

Master thesis proposal

INSP INSTITUT DES NANOSCIENCES DE PARIS

Campus Pierre et Marie Curie
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Title: Interplay between defects and band bending at TiO_2 surface

Keywords: TiO_2, surface science, x-ray photoelectron spectroscopy, scanning tunneling microscopy, band bending

Scientific description:

Although titanium dioxide (TiO_2) is widely used and studied, its electronic properties are still highly debated. In particular, the band bending profile at its surface is a key parameter of numerous applications in photochemistry[1]. Its magnitude and longitudinal extension control the charge separation of excitons and therefore the photoinduced process efficiency. Its origin is linked to the occurrence of defective sites including surface O vacancies (O_{vac}) and sub-surface Ti interstitials (Ti_{int}) which give rise to excess electrons whose localization on Ti cations distorts the lattice and creates polaronic deep band gap states. However, the relative contribution of these defects to the electronic density, and hence the band bending profile, is still a matter of debate. A clear consensus has not yet been reached both due to the difficulty in distinguishing O_{vac}- from Ti_{int} -induced free charges and their sensitivity to the sample redox history[2–4].

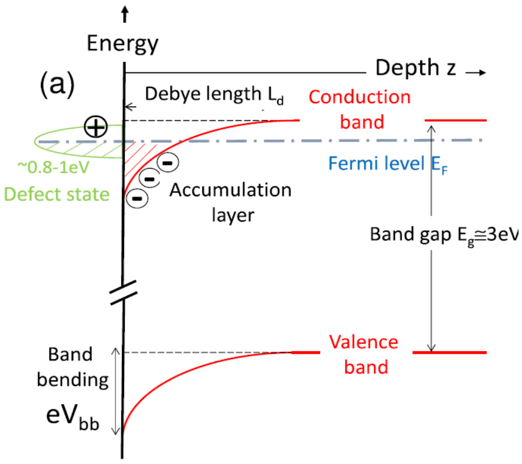

Figure 1. Schematic band diagram for donor surface defects inducing an accumulation layer and a downward

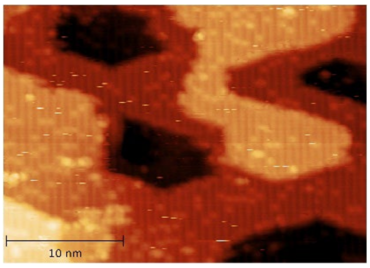

Figure 2. STM image of TiO_2 (110) surface with evidences of O_{vac}.

In a recent experiment performed at DIAMOND synchrotron facility using HAXPES diagnostic (hard x-ray photoelectron spectroscopy), we have characterized the band bending profile at the rutile TiO_2(110) for different redox states using a specific preparation procedure. The interpretation of these data must be completed with additional XPS measurements using laboratory UV and K_α x-ray sources in correlation with surface microscopy at atomic resolution (scanning tunneling microscopy - STM) to diagnose the surface density of defects (O_{vac} and eventually Ti_{int}). This internship will be dedicated to these data analysis and experimental measurements in order to characterize the band bending profile and disentangle the O_{vac} and Ti_{int} contributions. The experiment (XPS/STM) will be performed in an ultra-high vacuum setup of INSP.

1. Zhang, Z. & Yates, J. T. Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces. *Chem. Rev.* **112**, 5520–5551 (2012).
2. Lazzari, R et al. Dual behavior or coexistence of trapped and free states in reducible rutile Ti O 2. *Phys. Rev. B* **102**, 081401 (2020).
3. Lazzari, R. et al. Point Defects and Related Excess Electrons in the Dielectric Profile of the Reduced TiO $_2$ (110) Surface. *J. Phys. Chem. C* **125**, 16652–16663 (2021).
4. Lazzari, R. et al. Contributions of oxygen vacancies and titanium interstitials to band-gap states of reduced titania. *Phys. Rev. B* **97**, 041403 (2018).

Techniques/methods in use: x-ray photoelectron spectroscopy (XPS), scanning tunnelling microscopy (STM), low energy electron diffraction (LEED)

Applicant skills: Good background in material science and solid-state physics. Strong appetite for experiments.

Industrial partnership: N

Internship supervisor(s): Greg Cabailh, cabailh@insp.jussieu.fr, 01 44 27 44 43; Anna Levy, levy@insp.jussieu.fr, 01 44 27 46 46 ; Rémi Lazzari, remi.lazzari@insp.jussieu.fr, 01 44 27 46 28

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Possibility for a Doctoral thesis: Y (application to ED397)