Highlights

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Role of oxygen deposition pressure in the formation of Ti defect states in TiO2(001) anatase thin films

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Titanium dioxide (TiO2) is one of the most widely studied oxides because of its specific surface properties, making it a good candidate for photocatalysis of water and for reducing gas pollutants for air and water treatment,5,6 and its photoinduced hydrophilic properties. TiO2 anatase is an insulator with a band gap of 3.2 eV. However, changes in the concentration of oxygen vacancies (TiO2−δ) influence the value of the band gap. This results in the formation of Ti3+-related electronic states located in the band gap, which may overlap with the electronic states at the conduction band minimum (CBM), eventually reducing the value of the gap. We have analyzed the structural and electronic arrangement of TiO2(001)-oriented anatase thin films with different oxygen contents (TiO2−δ).

Anatase thin films growth and advanced electronic characterization by angular-resolved photo-emission spectroscopy (ARPES) and X-ray photoemission spectroscopy (XPS) has been performed at the NFFA-APE beamline end stations receiving undulator synchrotron radiation from the ELETTRA storage ring. All of the surface-related problems have been circumvented by being the characterization chambers UHV connected with the PLD growth apparatus. TEM, LEED, STM, and XRD characterizations contribute to show that our PLD-grown samples, while hosting point defects giving rise to in-gap states whose nature is addressed in the following, show an excellent long-range order and a very high overall quality. Depth-sensitive photoemission spectroscopy (PES) results are able to (i) disentangle the contribution of different Ti ionic states (Ti4+ and Ti3+), (ii) monitor the (homogeneous) diffusion of Al from the substrate through the film, and (iii) reveal the distribution of Ti3+ versus depth. Resonant photoelectron spectroscopy (ResPES) with polarized synchrotron radiation has been used to identify the in-gap defect states as related to Ti states only. By exploiting the PES sensitivity to the electronic state symmetry, we have been able to demonstrate a direct correlation between Ti3+ ions and the intensity of in-gap states. Our results refine the understanding of the defects at the origin of the in-gap electronic state.

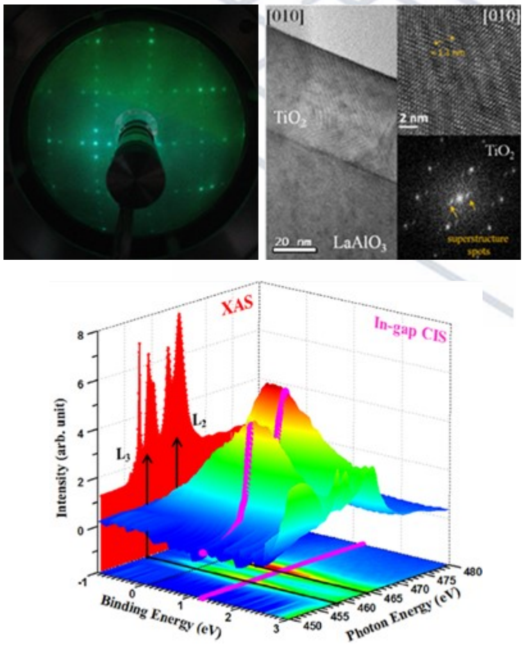

Fig.1: (top-left) Typical LEED pattern of the surface and (top-right) high-resolution TEM image of TiO2-δ film; (bottom) ResPES map of the valence band (VB) as a function of the exciting photon energy (XAS spectrum is also reported in red).