

OR1305

Electronic structure of N-doped TiO₂ films grown by reactive pulsed magnetron sputteringRAUL GAGO-FERNANDEZ¹, Andrés Redondo-Cubero², Javier Palomares¹, Mykola Vinnichenko³, Jens Lehmann³, Frans Munnik³¹ICMM-CSIC, Madrid, Spain ²ITN, Sacavém, Portugal ³HZDR, Dresden, Germany

rgago@icmm.csic.es

TiO₂ is a functional wide band-gap semiconductor with interesting photocatalytic properties [1,2]. However, TiO₂ applications are mostly limited to the ultraviolet spectral range due its band-gap energy (E_g) > 3 eV. Non-metal (anion) doping has been proposed to overcome such drawback, with most of the effort focused on N doping (TiO₂:N) triggered by the visible-light activity reported by Asahi *et al.* [3] and attributed to substitutional N sites. However, controversial results about the effective band-gap narrowing by substitutional N have been found [4]. It should be noted that N solubility limit at substitutional sites is ~2 at.% [2]. Hence, highly-doped TiO₂:N may contain a large fraction of interstitial N, its impact on the electronic structure still remaining an important question [2]. In this work, highly-doped (N up to ~8 at.%) TiO₂:N films grown by reactive pulsed magnetron sputtering (RPMS) have been studied by X-ray absorption near-edge (XANES) and X-ray photoelectron (XPS) spectroscopies. XANES reveals that N sites are preferentially in the form of N₂ or NO_x complexes for low and high ($\geq 300^\circ\text{C}$) growth temperatures (T_s), respectively. Complementary, XPS corroborates the dominance of NO_x bonds together with a small contribution of substitutional N. Spectroscopic ellipsometry (SE) shows a progressive reduction of E_g with T_s in TiO₂:N with respect to undoped films, with a decrease of ~0.3 eV at 450°C. Interestingly, the valence-band spectra from XPS display a rigid *red-shift* that matches SE data. Hence, band-gap narrowing in RPMS TiO₂:N is correlated with the dominant contribution of NO_x interstitials.

[1] A. Fujishima *et al.*, *Surf. Sci. Rep.* 63 (2008) 515; [2] M.A. Henderson, *Surf. Sci. Reports* 66 (2011) 185; [3] R. Asahi, *et al. Science* 293 (2001) 269; [4] M. Batzill, *et al. Phys. Rev. Lett.* 96 (2006) 026103.

Keywords

Titanium oxide
photocatalysis
doping
electronic structure
band-gap narrowing