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Surface properties of TiO2(011) and Mg:TiO2(011)

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Titanium dioxide is a metal oxide with many relevant technological properties for photocatalysis, chemical reactivity, electrical conductivity and solar energy harvesting. TiO2 is an inert insulator in stoichiometric form and it can be easily reduced into a n-type semiconductor TiO2-x with the transformation of Ti4+ to Ti3+ ions. This reduction is also characterized by the excess electrons populating localized Ti3d states in the band gap [1]. These electrons can be well characterized by the presence of a defect state at about 0.8 eV below the Fermi level [2]. Moreover, in the case of very low defect content, Ti3d states signal can be increased through resonant valence-band photoemission process where, at resonance, the direct photoemission of a valence-band electron interferes with the two-step autoionization process leading to the same final state. The angular distribution and the corresponding PhotoElectron Diffraction (PED) pattern of the defect state in resonant conditions have been measured for the rutile TiO2(110) surface and its distribution mapped in the case of a non-stochiometric surface [3] and after deposition of Na on a stoichiometric surface [4]. The main finding was the demonstration that charge distribution of the band gap state is essentially an intrinsic property of the TiO2 (110) surface, because largely independent of the way excess electrons are created. Within this framework we studied another rutile surface –the (011) - in the presence of Mg. Mg is a common contaminant of TiO2 and, by thermal annealing of the sample, it is possible to make it segregate from the bulk of the sample up to the surface. Both core level and valence band photoemission experiments were performed and the spectra show a decrease of the defect state linked to Mg presence. PhotoElectron Diffraction (PED) patterns were also recorded in order to study the localization of magnesium in the TiO2 surface layers. The experimental data set allows to exclude the formation of metallic Mg clusters on the surface and, rather, to point to the substitution of Mg into the Ti lattice sites. The decrease of the defect state intensity in the band gap observed in the presence of Mg is due to the formation of MgO which takes the role of “metal oxide dopant”for the TiO2 , since doping with a metal oxide (i.e. ionic doping) does not induce electron excess. In the case of stoichiometric and contaminant-free TiO2(011), the comparison of the experimental PED patterns with the simulation of the different models proposed so far [5] permits us to indicate the microfacet model as the reconstruction able to explain the specific observed features [6].

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