



Photoelectron spectroscopy of nanocrystalline anatase TiO₂ films

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Abstract

Nanocrystalline TiO₂ (anatase) films were prepared using either colloidal suspensions or a sol–gel route. The electronic structure of these films was analyzed using X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). Apart from pristine films, films containing defects introduced by annealing under ultra-high vacuum conditions or by ion bombardment were investigated. Generally, annealing in the temperature range up to 720 K results in no significant changes in the XPS and UPS spectra as compared to the pristine state, indicating that the amount of defect formation is too low to be observable by these techniques. On the other hand, ion irradiation causes the appearance of distinct defect states; these could be identified in agreement with previous data from photoemission studies on rutile and anatase single crystals. From UPS, a valence-band width of ~4.6 eV was determined for the nanocrystalline anatase films.

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1. Introduction

Nanocrystalline titanium dioxide has been investigated extensively in recent years because of its many (potential) applications; in particular, the utilization in photocatalysis appears to be a very attractive route to the purification of air and water from contaminants [1–3]. These processes are based on the feature that

(nanocrystalline) TiO₂ is able to photocatalyze many organic substances under UV irradiation. It is generally assumed that electrons and holes created by the absorption of a (UV) photon may oxidize or reduce species adsorbed at the surface of nanocrystalline TiO₂ particles [4,5]. Generally, the defect chemistry of metal oxides has often an important influence on their electrical and electronic properties [6,7]. For instance, TiO₂ is an n-type semiconductor due to donor-like oxygen vacancies [8]. The defect chemistry in non-stoichiometric TiO₂ has been discussed usually in terms of the formation of distinct

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atomic defects like Ti^{3+} ($\text{Ti}_i^{\bullet\bullet\bullet}$) or Ti^{4+} ($\text{Ti}_i^{\bullet\bullet\bullet\bullet}$) interstitials, or O^{2+} ($\text{V}_\text{O}^{\bullet\bullet}$) vacancies [9]. Such defects are expected to play also a crucial role for the doping of nanocrystalline TiO_2 . The aim of our ongoing research is the determination of these defect states in nanocrystalline TiO_2 films using photoelectron spectroscopy. In the present work, defects were created in two different ways. (i) Annealing the samples in ultra-high vacuum produces defects extending over the complete film thickness. (ii) Sputtering, on the other hand, results in defects in the surface-near region only. First results of these studies will be presented in this article.

2. Experimental methods

Anatase TiO_2 thin films with nominal particle sizes of 6, 12 or 20 nm were deposited on various substrates (glass, silicon, sapphire). By means of an organic solvent (normally ethanol), suspensions were prepared from these TiO_2 particles. Nanocrystalline thin films were deposited by spraying or spin-coating these colloidal suspensions of nanocrystalline TiO_2 particles onto the substrates. A second preparation method employed a sol–gel route: Titanium tetraisopropylate [$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$] is added slowly, under continuous stirring, into a mixture of isopropyl alcohol and nitric acid (65%); the latter serves to keep the sol below pH 6.0, the point of zero charge of TiO_2 . In order to stop eventually the aggregation, ethyl acetoacetate (acetoacetic acid ethyl ester) is added, whereupon the solution is kept at least for 24 h for aging. Films were deposited on the substrate by dipping or spin-coating. In both preparation methods, the films were then dried in air at room temperature for 24 h and subsequently annealed at 720 K in air for 1 h.

Photoelectron spectroscopy was performed in an ultra-high vacuum (UHV) system (base pressure $\sim 2 \times 10^{-10}$ mbar), equipped with a Phoibos 150 MCD-9 energy spectrometer (Specs), a non-monochromatized X-ray source for producing Mg $K\alpha$ irradiation, and a He discharge lamp source for UPS, providing He I ($h\nu = 21.2$ eV) or He II ($h\nu = 40.8$ eV) photons. For XPS, the binding energy scale was calibrated using Ag $3d_{5/2}$ (368.1 eV), Au $4f_{7/2}$ (84.0 eV) and other peaks of these elements. For UPS, the sample was biased at -6 V and the energy

scale was calibrated via the Fermi edge of a polycrystalline Au specimen. Photoelectrons emitted perpendicular to the surface were monitored.

Sputtering was done with Ar^+ ions at an energy of 600 eV produced in a broad-beam ion source. The flux density amounted to about 5×10^{12} ions/cm² s.

3. Results and discussion

Structural investigations of these nanocrystalline films were carried out previously [10]. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) revealed that, as in the primary titania particles, only the anatase phase of TiO_2 occurs and that no preferential orientation of the nanoparticles exists. The average particle sizes in the films determined from the XRD data agree within about 10% with the above-quoted size values of the primary particles. Depth profiles by secondary ion mass spectrometry (SIMS) showed a homogeneous distribution of Ti and O throughout the films and a low concentration of impurity species [10].

Whereas *single crystal* TiO_2 surfaces (mostly rutile) have been investigated for quite a while by XPS [11–13] and UPS [14–17], corresponding studies for *nanocrystalline* TiO_2 films are very rare and more recent [18–20]. Those data may serve as a reference for the XPS and UPS spectra acquired from the various nanocrystalline TiO_2 films in the present work. Fig. 1 shows the Ti 2p and O 1s core-level photoemission from a film prepared by the sol–gel route, comparing films in the pristine (as-prepared) state, after sputtering, and upon reduction in UHV at 720 K for 180 min. The pristine specimen exhibits the well-known Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks (Fig. 1, left panel) due to the Ti^{4+} state of stoichiometric TiO_2 . The O 1s peak (Fig. 1, right panel) of the pristine film exhibits a shoulder at a higher binding energy; fitting the O 1s peak a second component located at 532.6 eV is found which might be ascribed to the presence of adsorbed species, possibly CO or OH [21]. The binding energies of Ti $2p_{3/2}$ (459.3 eV) and O 1s (530.7 eV) in these as-prepared nanocrystalline anatase TiO_2 films are in good agreement with results obtained from rutile TiO_2 single crystals [8].

Annealing the films in UHV leads to the creation of point defects and a partial reduction of TiO_2 . Although

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