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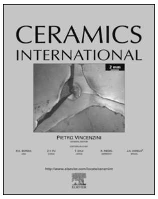

Niobium/Vanadium doped TiO_2 multilayered sol-gel films: Structure, surface chemistry and optical properties

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A B S T R A C T

In this work multilayered TiO_2 films deposited on glass and Si substrates by the sol-gel – dipping method were studied, focusing on the influence of Niobium/Vanadium doping on the structure, surface chemistry and their optical properties. The TiO_2 films doped with 1.2 at% Nb(V) crystallized in anatase phase as evidenced by XRD analysis. It was found that thicker films are obtained in the case of V-doped TiO_2 films, while the values of the optical band-gap show similar values. Bands related to the vibration of oxygen in the Ti–O, Nb–O and V–O bonds were identified based on Infrared Spectroscopic Ellipsometry, proving the incorporation of the dopants in the matrix of the TiO_2 films. Both types of doped films exhibit around 80% transparency on a wide spectral range (300–1700 nm). Niobium and Vanadium have been identified in the surface / subsurface region in the 5+ oxidation state (although a high sensitivity of the Vanadium oxidation states during profiling experiments was found due to the preferential sputtering effect). From a morphological point of view, all titania films show a very uniform and compact microstructure, with a homogeneous superficial structure of small grains with diameters in the range of 10–20 nm.

1. Introduction

When Fujishima and Honda [1] first reported the photocatalytic water splitting properties of titanium dioxide (TiO_2), the material gained attention, especially in the field of photodegradation of different pollutants due to the enhanced photoinduced charge transport, as remarked by Graetzel [2]. To improve this aspect, TiO_2 has been doped with several ionic species [3,4]. The ease of doping TiO_2, especially with transition metals such as Fe, Ni, Cr, Nb, V, etc., has extended the area of applications to electrochromic displays [5], solar cells [6] and gas sensors [7–10]. Among them an increasing interest is shown to vanadium (V), niobium (Nb) or tantalum (Ta) [11]. By doping TiO_2 with group V elements, additional charge carriers are introduced, due to the difference in their valence, as compared to Ti^{4+}. The doping improves the electrical conductivity of the material, [11–13], while simultaneously maintaining the high transparency in the visible light region [14,15] and decreasing the band-gap value [16]. Nb-doped TiO_2 (TiO_2:Nb) is of particular interest as a TCO and has even been proposed as a replacement for the high-cost indium tin oxide (ITO) as electrode in different optoelectronic applications [17]. The doping of TiO_2 with V has also been investigated, mostly in relation to photocatalytic applications [18–20]. Some reports identify V^{4+} as the main doping species present, while oxidation to V^{5+} leads to segregation of V_2O_5 at TiO_2 surface [21]. Besides the well known physical methods of preparation for doped TiO_2-based coatings, the sol-gel method represents a reliable low cost technique due to the good control of the film properties, such as thickness or porosity and of the doping process by modifying the sol concentration, layer number, additives and substrates used [22,23].

Therefore, the aim of this work is to comparatively investigate the Nb- and V-doped TiO_2 thin films deposited on glass and Si substrates from the point of view of the structure, morphology, the chemical state of the dopants inside the TiO_2 host matrix and their influence on the optical properties of the prepared layers.

2. Materials and methods

2.1. Thin film deposition

Multilayered TiO_2 films, doped either with 1.2 at% Nb or 1.2 at% V, were deposited on glass and Si substrates using solutions

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obtained by the sol-gel method [10,24]. In this paper, we report on the properties of 5 and 10 layered films, further denoted as 5TiO_2:Nb(V) and 10TiO_2:Nb(V), respectively. The Nb doped films were obtained starting from tetraethylorthotitanate [$Ti(OCH_2CH_3)_4$], niobium ethoxide [$Nb(OCH_2CH_3)_5$] in ethanol (C_2H_5-OH) with 2,4-pentanedione chelating agent. The solution was aged for 24 h before being dip coated onto the substrates using a 5 cm/min withdrawal rate. A densification treatment at 300 °C for 30 min (heating rate 5 °C/min) was applied after each deposition and a final thermal treatment at 450 °C for 1 h using the same heating rate was used after the last dipping sequence. Similarly, V-doped films with 5 and 10 layers were obtained by the same procedures regarding the deposition and post-deposition parameters. The Vanadium precursor was vanadyl acetylacetonate $VO(C_5H_7O_2)_2$, while the rest of the precursors remained unchanged.

2.2. *Thin film characterization*

Surface analysis performed by X-ray photoelectron spectroscopy (XPS) was carried out on a Quantera SXM equipment, with a base pressure in the analysis chamber of 1.0×10^{-7} Pa. The X-ray source was the Al Kα radiation (1486.6 eV, monochromatized) and the overall energy resolution was 0.65 eV estimated by the full width at half-maximum of the Au 4f7/2 line. In order to take into account the charging effect on the measured binding energies (BEs) the spectra were calibrated using the C1s line (BE=284.8 eV, C–$C(CH)_n$ bonds) of the adsorbed hydrocarbon on the sample surface. A dual beam neutralizing procedure (e^- and Ar^+ ion beams) was used to compensate the charging effect in insulating samples.

The transparency of the multilayered TiO_2 films was examined by UV–vis ellipsometric measurements on a Woollam Co. Inc apparatus in the 200–1700 nm spectral range.

The infrared spectroscopic ellipsometry measurements in the 400–1400 cm^{-1} range were performed on VASE-Woollam equipment from Woollam Co. Inc. The spectra were fitted using a General Oscillator model which involved five Lorentz oscillators and the assignation of the characteristic vibrational bands of the components was done from the dielectric loss function.

The morphology and thickness of the multilayered TiO_2 films was studied by scanning electron microscopy (SEM) images in top and tilted view using a FEI Quanta 3D microscope operating at 10 kV.

AFM measurements were performed with XE-100 apparatus from Park Systems (2011) working in non-contact mode, using sharp tips – PPP-NCHR type from Nanosensors™ – with less than 8 nm radius. In order to establish the morphology of the samples, topographical AFM images were taken over the area of 1×1 μm^2 area. The AFM data analysis was performed with XEI Image Processing Program (v.1.8.0) from Park Systems.

3. Results and discussion

3.1. *Structural considerations*

Our earlier studies have shown that, after several deposition cycles, the doped multilayered TiO_2 films possess similar structure [25]. After 5 deposited layers, the films are crystalline and the nanocrystallites show TiO_2 anatase phase (ICDD file number 00-021-1272). No peaks related to other TiO_2 polymorph phases could be detected in the XRD pattern [24]. For the films with 10 deposited layers, the XRD intensity increases but the position and shape of the Bragg reflections remain the same. This points out that the TiO_2: Nb(V) films grow in stable anatase nanocrystalline structure and only the thickness of the films is different, with thinner films giving a smaller intensity of the diffracted beam.

Table 1
Lattice constants and crystallite size of the 5 (10) TiO_2:Nb(V) thin films.

Sample	Lattice constants			Crystallite size (Å)
	a (Å)	**b (Å)**	**c (Å)**	
TiO_2 anatase*	3.7852	3.7852	9.5139	–
5TiO_2:Nb	3.7881(15)	3.7881(15)	9.495(4)	87(5)
10TiO_2:Nb	3.7870(2)	3.7870(2)	9.500(6)	108(3)
5TiO_2:V	3.7813(11)	3.7813(11)	9.478(3)	119(7)
10TiO_2:V	3.7810(11)	3.7810(11)	9.487(3)	130(13)

* JCPDS card no. 21-1272.

Although the presence of V_2O_5 and Nb_2O_5 in the investigated TiO_2 sol-gel films is not visible from the XRD spectra, it was evidenced from the infrared ellipsometric data (Table 3) and XPS analyses, as discussed further. However, calculating the lattice parameters of Nb/V-doped TiO_2 films, some changes in their values were observed (Table 1). In the case of Nb doping an increase of lattice constants (**a, b**) was established, while in the case of V doping films, an opposite behavior was noticed. This is in agreement with the ionic radii [26] which have the values of 68 pm for V in the 5+ oxidation state, 74.5 pm for Ti^{4+} and, respectively, 78 pm for Nb^{5+}.

3.2. *Optical characterization*

From the transmittance spectra of the doped films on glass, obtained by UV–vis–NIR ellipsometry, the similarity of the film structures is suggested. This fact is illustrated for the 10TiO_2:Nb(V) films (Fig. 1). As it can be seen, all films exhibit 80–90% transparency on a wide spectral range. The maximum of the optical transmission is located in different spectral ranges: for undoped TiO_2 films, the maximum is in the VIS range, while for doped (Nb/V) films it is shifted in the NIR range.

In the UV–vis ellipsometric data analysis, the "General Oscillator" model [27] was applied to the TiO_2/Si structure considering one Tauc-Lorentz oscillator. The surface roughness as top layer was taken into account by considering the top layer consisting of 50% voids and 50% film within the effective medium approximation [27], even though the films are very smooth, [10,24,25]. The thickness of the film (d_{film}) and of the roughness (d_{rough}) layers, the refractive index (n) at 550 nm, the mean square error (MSE) and the optical band gap (E_g) evaluated from the best fit are presented in Table 2. It can be observed that the layer thickness

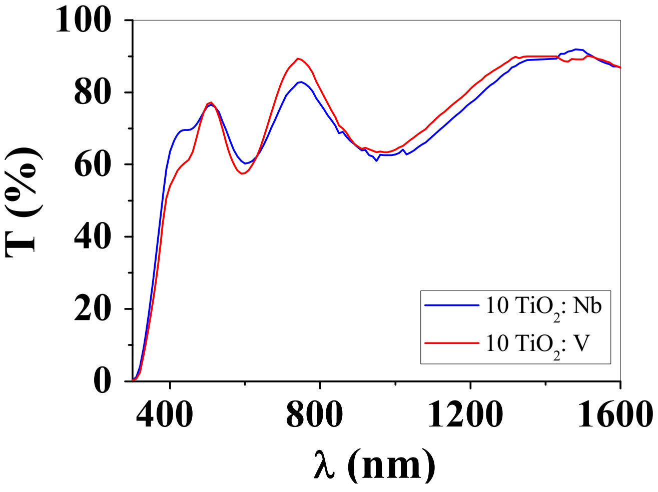

Fig. 1. Optical transmission of the 10 TiO_2:Nb(V) thin films.