

Structural characterization of V_2O_5 – TiO_2 thin films deposited by RF sputtering from a titanium target with vanadium insets

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Abstract

Structural and compositional analyses of different series of Ti–V–O thin films synthesized by RF-magnetron sputtering are presented. Vanadium content is changed by means of vanadium insets placed in the titanium target. By micro-X-ray fluorescence (microXRF), the V/Ti atomic ratio of the samples treated at 300 °C was found to be 0.18, 0.25 and 0.82. At low temperature, anatase is the main phase for samples with lower vanadium content. The increase of vanadium content comes along with an increase of the amorphous phase. Rutile phases dominate at high temperatures. V_2O_5 is detected after treatment at 600 °C, then vanishes. MicroXRF and miniSIMS analyses show that the vanadium content decreases as the temperature increases. By microXRF the V/Ti atomic ratio after the thermal treatment at 800 °C was found to be about 0.06, 0.11 and 0.22.

Conductance data are explained on the basis of these observations.

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1. Introduction

Titania (TiO_2)-based thin films are widely investigated in several areas of material science because of their appealing functional properties. In addition to interests in photocatalysis and optical applications, a renewed attention has been recently devoted to the integration of titania thin films in gas sensing devices [1]. The reasons standing behind this interest come from the good chemical stability exhibited by TiO_2 at high temperature and in harsh environments as well. The conductivity of titanium dioxide can be improved by the addition of dopants [2], such as Cr or V, that offer the possibility to tune the electrical response of the sensor devices. Vanadia/titania (V_2O_5/TiO_2) compounds are typically used in selective catalytic reduction, especially for the destruction of chlorinated volatile organic compounds (VOCs) and for alcohol dissociation. V_2O_5 doping improves the catalytic activity and the thermal stability [3]. Thus, the possibility to exploit these features for the production of sensors for some

interesting gases like ethanol or carbon monoxide has been investigated in last years. Radio frequency (RF)-magnetron sputtering is one of the most suitable techniques for the industrial scaling-up of the thin films deposition process, and important progresses for the synthesis of high-quality thin films onto large areas substrates have been obtained by means of the Rheotaxial technique (RGTO) [4]. Recently, a novel technique based on the film deposition starting from a target addicted with a controlled amount of dopant insets has been developed [5]. The possibility to carry out many syntheses in a cheap and carefully controlled way makes this technique very promising for an effective production of sensing devices.

It is now important to understand how this novel approach to deposition influences the structure and the microstructure of the materials and, as a consequence, the functional properties of the devices. Thus, the present work is mainly focused on the structural investigation of different series of V-doped TiO_2 thin films, prepared with the “insets” technique. Due to the novelty of the synthesis applied to vanadium and titanium oxides, it is important to identify the phases that are produced and their stability as a function of different thermal cycles. Bi-dimensional micro-X-ray diffraction

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(μ XRD²), glancing angle X-ray diffraction (GIXRD) and microRaman spectroscopy techniques have been used to investigate the relationship existing between structure and electrical behaviour of these materials. Moreover, microXRF and miniSIMS measurements have been carried out in order to get more insight into the actual chemical composition of the sample as a function of annealing treatments.

2. Experimental

Film deposition was executed by RF-magnetron sputtering (Kenotec plant). Total pressure in the sputtering chamber was 8×10^{-6} bar; Ar/O₂ ratio was 1:1 and RF power was kept at 50 W. The films, after a deposition of 3 h, were about 100 nm thick. The titanium target (purity 99.99% certified) was made of a disc of 101.6 mm diameter with the possibility to insert up to 12 cylinders (5 mm diameter, 4 mm height) of either vanadium or titanium. This option is important in sight of investigating the dependence of film parameters as a function of the V content. During deposition the temperature of the substrate was maintained at 300 °C.

The thin films were characterized both as-deposited and after an oxidation cycle performed in a furnace at controlled flux (0.2 l/min) of humid synthetic air.

The oxidation cycle was constituted by two steps: the first at 250 °C for 4 h and the second at 600 or 800 °C for 12 h. Temperature variations were carried out very slowly (2 °C/min) in order to avoid additional stresses or cracks in the thin layer. Table 1 summarizes the experimental conditions for each sample.

For electrical characterization, films were deposited onto alumina 3 mm × 3 mm substrates equipped with a platinum meander on the backside, acting as a heater and temperature sensor. Platinum interdigitated contacts were sputtered onto the layer after the annealing treatment.

Electrical characterization was carried out by volt-ampereometric technique; the sensor was biased by 1 V and film resistance was measured by a picoammeter.

For structural analyses, thin films were deposited onto ultra-thin Si (1 0 0) single crystals, in order to avoid the overlapping of alumina peaks on the titania and vanadia signals. The chemical composition resulted to be the same for films

deposited on alumina and Si substrates and no evidence of preferred orientation has been detected.

X-ray diffraction (XRD) data were collected by using a Bruker “D8 Advance” diffractometer equipped with a Göbel mirror; measurements were carried out with both glancing angle and conventional Bragg–Brentano ($\theta - 2\theta$) setting. The Cu K α line of a conventional X-ray source powered at 40 kV and 40 mA was used in both the cases. Further measurements of bi-dimensional diffraction (μ XRD²) were acquired with a D-max Rapid Rigaku diffractometer, equipped with a 2D Image Plate detector. In this case, the spot size of the beam focused onto the sample was 0.8 μ m.

MicroRaman spectra were collected by a Labram Dilor J-Y spectrometer, with a 632.8 nm He–Ne laser source focused using a 100 $\times$ (N.A 0.9) objective confocally coupled to the spectrograph. Beam diameter was less than 2 μ m, and power at the sample did not exceed 10 mW.

Chemical composition maps, as well as depth profiling scans have been obtained by means of secondary ions mass spectrometry (SIMS) with a miniSIMS Millbrook apparatus (ion source Ga⁺, mass resolution: 1).

The micro-X-ray fluorescence (microXRF) analysis was carried out by an XMF 104 Unisantis instrument, with a Si detector with a resolution of 200 eV. This instrument is equipped with a Mo X-ray tube and the beam spot is about 100 μ m.

3. Results and discussion

3.1. Structural and compositional characterization

Three different series of V–Ti oxides have been synthesized by using 4, 6 and 12 insets of vanadium. The phases present in as-deposited films and their changes as a function of thermal treatments are reported in Table 1. TiO₂ can exhibit three different crystal phases: rutile, anatase and brookite, the stable phase being the rutile. Structural differences depend on the way the TiO₆ octahedra are linked with each other. In samples Ti4V300 and Ti6V300, TiO₂ appears to be mainly present as anatase. This phase may appear at low temperature, and its formation is promoted by the 1:1 Ar:O₂ ratio in the vacuum chamber during the deposition. Indeed, Miao et al. [6] have recently shown that the synthesis of TiO₂ via RF-magnetron sputtering at about 300 °C leads to the formation of anatase in case of low oxygen pressure introduced into the vacuum chamber, while the argon atmosphere favours the rutile phase. Our samples also contain an amorphous phase that is formed by two phases of titanium and vanadium oxides. Moreover, μ XRD² spectra of both the samples Ti4V300 and Ti6V300 show weak and broad rings at about 27.4° (Fig. 1) that are attributed to the most intense reflection of the rutile phase. The signal is very low and it could not be distinctly detected either by conventional Bragg–Brentano diffraction or GIXRD experiments. The anatase fraction, calculated by Spurr and Myers [7] formula ($(1/1 + 1.265(I_R/I_A))$), results to be 0.94 for Ti4V300 and 0.72 for Ti6V300. The amorphous

Table 1
Annealing conditions and crystallographic phases detected by XRD

Sample name	V insets	Annealing	Structure
Ti4V300	4	As-deposited	Anatase
Ti4V600	4	600 °C	Rutile
Ti4V800	4	800 °C	Rutile
Ti6V300	6	As-deposited	Anatase + amorphous
Ti6V600	6	600 °C	Rutile + V ₂ O ₅
Ti6V800	6	800 °C	Rutile
Ti12V300	12	As-deposited	Amorphous
Ti12V600	12	600 °C	Anatase + V ₂ O ₅
Ti12V800	12	800 °C	Rutile

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