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Niobia-stabilised anatase TiO_2 highly porous mesostructured thin films

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Abstract

The thermal stability of anatase TiO_2 mesoporous thin films has been considerably increased up to 800 °C by substituting a fraction of Ti cations by Nb. Mesoporous mixed oxide films $Ti_{1-x}Nb_xO_2$, with $x = Nb/(Nb + Ti)$ ranging from 0 to 1, and homogeneous crystalline walls have been successfully prepared from chloride precursors and non-ionic block copolymer templates. They all exhibit a uniaxially distorted *Im3m* bcc mesostructure with the *a* lattice parameter ranging from 14 to 19 nm. Films have been characterised by simultaneous in situ SAXS and WAXS investigations during thermal treatment. Transmission electron microscopy and UV–visible ellipsometry were used to confirm the structure, the porosity and the good optical quality. A high porosity of 40% (pore size estimated at 7 nm) was maintained for the 10% Nb-doped films above the temperature of crystallisation and a bandgap of 3.40 eV has been measured after annealing at 500 °C.

Keywords: Mesoporous thin films; Nanocrystalline; Niobia; Anatase; TiO_2

1. Introduction

During the last decade, niobium– and titanium–oxygen species have received growing attention in the fields of catalysis [1,2], energy conversion [3,4], electrochromic devices [5,6], sensors [7,8], where electron transfer properties are required. Indeed, the anatase TiO_2 phase is one of the most promising since it combines hardness, chemical inertia, and semiconducting properties, being of particular interest in photocatalysis or photovoltaic devices [9,10]. Nowadays, progress has been made in preparing these materials as thin films of high surface area and controlled pore size, aiming at enhancing the transfer efficiency. Generation of these highly controlled materials is achieved by combining sol–gel deposition techniques with the evaporation induced self-assembly (EISA) process taking place in presence of a surfactant templating agent [11–14]. After elimination of the organic template and controlled crystallization of the network [15], one ends up with an organized arrangement of anatase nanoparticles shaped in mesoporous framework with narrow pore size distribution adjusted by the conditions and the surfactant molecular weight [16]. Some of their applications, such as gas sensors, require high temperature work during prolonged periods. These conditions favour crystal growth, sintering and/or phase

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transitions to more stable crystal structures. These three processes tend to diminish the surface area, which is detrimental to the sought properties for mesoporous thin films. In order to increase the stability of the mesoporous crystalline network in such conditions, it is important to prevent the sintering of the metastable nanoanatase and/or their transformation into the rutile phase. Doping an inorganic oxide network with a second cation prevents crystal growth, and in this case, loss of the mesostructure. This usual practice has been extended to mesoporous oxide thin films, leading to an improved resistance to higher temperatures [17,18]. To this end, it is important to conserve the mesostructure, and to homogeneously distribute the cations along the inorganic oxid framework.

The present paper reports the thermal stabilization of nanocrystalline TiO_2 mesoporous networks by Niobia doping which is known to prevent easy transformation from anatase to rutile phase [19]. It will be demonstrated that Nb-containing TiO_2 mesoporous and nanocrystalline thin films with $x = Nb/(Nb + Ti)$ ranging from 0 to 1, can be prepared by the method recently reported for pure titania and other systems [13]. Simultaneous in situ WAXS and SAXS analyses during thermal treatment shows that the ordered mesoporous structure exhibits a stability that is 100 °C higher when anatase nanoparticles that composed the inorganic walls are stabilized with Nb metallic centers. The final meso- and micro-structures have been confirmed by high resolution transmission electron microscopy (TEM) and XRD in Bragg Brentano geometry. The porosity and optical properties were deduced from ellipsometry measurements.

2. Experimental

Dipping solutions were prepared by reacting a mixture of metal chlorides ($xNbCl_5 + (1 - x)TiCl_4$, x varies from 0 to 1) with Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, where EO stands for ethylene oxide, and PO for propylene oxide fragments), in an EtOH/water mixture. Typical molar ratios are Ti + Nb: 1; H_2O: 10; EtOH: 40; F127: 5×10^{-3}. Films were prepared by dip-coating glass or silicon substrates at a constant withdrawal rate (1–2 mm s^{-1}) under controlled relative humidity (RH = 40–60%) and temperature (20–22 °C). In such experimental conditions, film thickness is close to 300 nm. The first drying process of the films took place in the chamber of the dip-coater for 10 min. Thereafter, films were transferred to an RH-controlled (RH = 50%) sealed chamber with constant temperature (20–22 °C) and aged for at least 12 h before annealing at high temperature. Wide-angle X-ray diffraction (XRD) patterns were collected at grazing incidence ($\omega = 0.5°$, 2θ varied from 20° to 50°, Cu-Kα_1 radiation) using a Bruker AXS D8-advance diffractometer. Transmission electron microscopy images in ordinary (TEM) or high (HRTEM) resolution were collected respectively using a JEOL 100 CX II microscope with EDS. Variable angle spectroscopic ellipsometry (VASE) was performed to determine the porosity and the bandgap of the thin films, using a M-2000U Woollam spectroscopic ellipsometer in the range 240–1000 nm. In situ time-resolved small and wide angle X-ray scattering (SAXS and WAXS, respectively) investigations were performed during thermal treatment at the SAXS-beamline of the third generation synchrotron ELETTRA (Italy) with high flux and 8 keV energy. In situ thermal treatment consisted in 8 °C min^{-1} ramps, plus 10 min at the selected temperature; the latter was checked by a temperature probe located at less than 1 mm from the sample. Details of such an experiment are reported elsewhere for pure TiO_2 systems [15].

3. Results and discussion

Under all studied conditions, mesoporous thin films with homogeneous composition walls were obtained, as assessed by TEM and EDS measurements. The typical parameters of the obtained mesostructures are presented in Table 1. Film porosity was evaluated by obtaining the refractive index by ellipsometry, as reported elsewhere [15,20]. Cubic mesophases corresponding to *Im3m* ordering have been obtained, except in the case of pure Nb(V) systems.

3.1. Films with $x = [Nb]/([Ti] + [Nb]) = 0.1$

The TEM analysis of a film prepared with $x = [Nb]/([Ti] + [Nb]) = 0.1$, dried at RH = 50% for 24 h and stabilized at 130 °C is shown in Fig. 1(a). The image corresponds to the typical *Im3m* bcc structure of spherical micelles arrangement in the hybrid material. The periodic distances determined from this image are $d(1\,1\,0)_{TEM} \sim 110$ Å. A regular composition of the inorganic framework ($x = 0.1$) was confirmed by TEM/EDS (i.e., no segregation patterns were observed) [18]. The mesostructures and periodic distances found are in good agreement with those found by the associated 2D SAXS patterns presented in Fig. 2. The (1 1 0) planes are aligned parallel to the substrate, as was reported previously for pure TiO_2 [15]. The complete indexation of a (non-distorted) cubic mesophase typically obtained with F127-templated inorganic matrix can be found elsewhere [21]. HRTEM analysis of the same material annealed at 600 °C is presented in Fig. 1(b). At such a temperature, the inorganic walls are composed of nanometric size crystalline particles while the ordered cubic-based mesoporosity is clearly retained. Pore diameters of around 7 nm can be measured on this picture. The wide-angle diffraction of a material with $x = 0.1$ confirmed that the particles verify the anatase structure. This characterization is provided in Fig. 2, which displays the evolution of the mesostructure (SAXS patterns) together with the apparition of the crystals (WAXS diagrams) during annealing at 8 °C min^{-1}.

In previous works, we used these simultaneous in situ characterizations to understand the formation of the microstructures, and how is the mesoporosity affected by