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Increasing surface hydrophilicity of titania thin films by doping ☆

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Abstract

The hydrophilicity of RF sputtered thin films of: (a) pure TiO_2 and (b) TiO_2 doped with 0.3% Ce, 0.4% Nb, and 0.4% N (atomic percents) was investigated macroscopically by measurements of the contact angle between water and film surface. The results are discussed in terms of the connection of the hydrophilic and photocatalytic properties of the materials with their structure, morphology and optical characteristics. The 280 nm thick films were deposited on optical glass substrates at 250 °C. Film structure and surface morphology were investigated by X-ray diffraction and atomic force microscopy. The surface roughness was derived from atomic force microscopy and ellipsometric data. The contact angle of de-ionized water with film surface was monitored during photo-activation and after irradiating with near-UV light. The surface super-hidrophilicity of all the investigated samples decays, when samples are kept in darkness for 48 h after irradiation. The hydrophilic behavior of the doped TiO_2 thin films is discussed in terms of the effects of surface roughness, phase transformations enhanced by doping and charge carrier recombination.

Keywords: Thin films; Doped titanium dioxide; Contact angle; Hydrophilicity; Sessile drop

1. Introduction

Semiconductor-based photocatalysis has gradually focused the interest of materials scientists after the report on photo-induced decomposition of water on the TiO_2 surface [1]. Amorphous TiO_2 and especially its anatase polymorph (with a large band gap, $E_g = 3.2$ eV) are now considered ideal photocatalytic materials, activated with near-UV light radiation ($\lambda \leq 390$ nm). Much effort has been devoted during the last years to increase the photocatalytic efficiency of TiO_2 in terms of widening the wavelength range of photoactivation. Shifting the absorption edge from 387 nm towards the visible region (450–500 nm) leads to increasing the photocatalytic efficiency and allows for photoactivation with interior lighting. Promising results have been reported on doping TiO_2 with transition metals or non-metal elements, but the resulted materials turned out to be thermally and chemically unstable [2,3]. Doping with rare earth (RE) elements and, very recently, with nitrogen [4] revealed new possibilities to increase photo-catalytic performances. The colorimetry and chromatography techniques are the most widespread means to characterize the catalytic efficiency of the photocatalytic materials. It is accepted that the UV-induced photocatalytic properties of TiO_2 are associated with increased film hydrophilicity, despite different intrinsic origins of the two properties [4]. Contact angle (CA) measurements can be used, therefore, as an indirect macroscopic indication of the photocatalytic activity of the thin films, as well. Films are considered super-hydrophilic for CA values below 10° [4].

We present here results on the wettability characteristics of the doped titania thin films acquired through CA measurements. The results are discussed in terms of the combined effects of surface structure and surface morphology, taking into account the role of charge carrier recombination on the defects in the surface region.

2. Experimental

Transparent thin films were prepared in a 13.56 MHz RF magnetron sputtering system placed in a stainless steel processing chamber, 30 cm in diameter and 45 cm high, where a base pressure of 2×10^{-3} Pa could be routinely achieved using a 250 l/s turbo-molecular pump. To grow RE-doped TiO_2

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films, mosaic circular targets of metallic Ti (99.5%) with CeO_2 and Nb_2O_5 (99.99% each) oxide powders were used. The RF supply was operated at constant power, $P = 150$ W. The intensity of the parallel component of the magnetic field strength in front of the target surface, was 60 kA/m. Film thickness was monitored by a quartz microbalance; the deposition rate was 12 nm/min. Gas composition in the discharge was adjusted using mass-flow controllers.

To deposit the pure and RE-doped TiO_2 films, the sputtering was conducted in an ($Ar + O_2$) gas mixture, under the total pressure of 1 Pa and oxygen partial pressure of 3×10^{-2} Pa. The total pressure was adjusted by throttling the turbomolecular pump. To grow the nitrogen-doped TiO_2 films, a commercially available sintered TiO_2 disk target (99.99% Furuuchi Chemicals) and a mixture of ($Ar + N_2$) gases were used. Here, the ratio of partial pressure of the two gases was $p_{Ar}/p_{N_2} = 1.5$. Using the same input RF power conditions, the deposition rate was 1.5 nm/min.

Optical glass slides (Corning 7740 Pyrex® borosilicate with 91% transmittance in the 325–2000 nm range) were used as substrates in all cases. Film thickness, as measured ex situ by a profilometer, was 280 nm for all the investigated samples.

Grazing incidence X-ray diffraction (XRD) measurements were done using the Cu Kα radiation (λ = 1.54178 Å). The weight percentage of the anatase phase, W_A, in the total amount of crystalline phase within the film was estimated using the equation [5]:

$$W_A = 1/(1 + 1.265 I_R/I_A), \quad (1)$$

where I_A and I_R stand for the intensity of the strongest anatase A(1 0 1) and rutile R(1 1 0) reflections in the XRD patterns, respectively. The ratio I_A/I_R is independent on the fluctuations in diffractometer characteristics [5,6].

The surface morphology of the films has been investigated by atomic force microscopy (AFM) in non-contact mode. From the topographical data, the average surface roughness coefficient, R, is defined by the equation [7]:

$$R = \frac{1}{D}\int_0^D |z_0 - z(x)| \mathrm{d}x, \quad (2)$$

where z_0 is average height over the interval from 0 to D along the x axis.

$$z_0 = \frac{1}{D}\int_0^D z(x)\,\mathrm{d}x. \quad (3)$$

The surface roughness coefficient was calculated, in our case, over an area of 5 μm × 5 μm. Apart from AFM, the surface roughness of the films was derived from ellipsometry data, acquired from a home-made equipment. The ellipsometric arrangement and the procedure is described elsewhere [8].

Film composition was investigated by electron probe microanalysis using a JEOL 5600LV Oxford Instruments equipment. Optical transmittance measurements were done using a Perkin Elmer Lambda 3 UV–VIS double-beam spectrophotometer.

Film hydrophilicity was assessed by measuring the CA with a home-built goniometer allowing advancing- and receding-angle measurements in the sessile drop arrangement. The motorized syringe (Hamilton, 10 μl) of the set-up, operated by a computer, allowed controlling drop volume with 0.5 nl accuracy. The measurements were performed at room temperature (24 °C) under 65% environment humidity conditions. The drop image was acquired by a CCD camera (1280 pixels × 960 pixels) attached to the microscope, then transferred to the computer for processing with an image analysis software. Drop volumes of 0.5 and 1 μl were chosen to avoid drop shape alteration due to gravitational force and to diminish the evaporation effects.

Surface photoactivation was done by irradiating the samples with filtered UV light (photon energy ranging between 3.18 and 3.65 eV) from a high-pressure 150 W mercury lamp. The lamp ensured a flux value of 100 mW/cm^2 at the surface of the samples. Before each experiment in which the CA versus UV dose was monitored, the sample surface was conditioned to remove surface contaminants. The procedure consisted in sonication for 20 min in acetone and ethyl alcohol, followed by UV irradiation for 2 h. Then, the samples were maintained in darkness at room temperature and 65% relative humidity for 7 days until the de-activation state of the surface was reached.

The CA angle was monitored as a function of the UV dose, until the saturation of the angle was reached. In a second series of measurements, the UV irradiation was removed and the measurements were repeated for 63 h, with a 7 h step, while keeping the samples in the dark room between measurements.

3. Results and discussion

As the XRD plots reveal (Fig. 1), the undoped TiO_2 film (sample S) consists of a mixture of anatase and rutile structures spread in an amorphous phase. Weight percentage ratio of anatase/rutile phases in the film, as calculated using Eq. (1), is 7/3. The XRD patterns of the RE-doped samples display a clear anatase structure, with A(1 0 1) and A(0 0 4) as the most intense peaks, and no rutile signal. The average roughness values do not exceed 6 nm, as evidenced by both AFM and ellipsometric data (see Table 1). Polycrystalline facets are

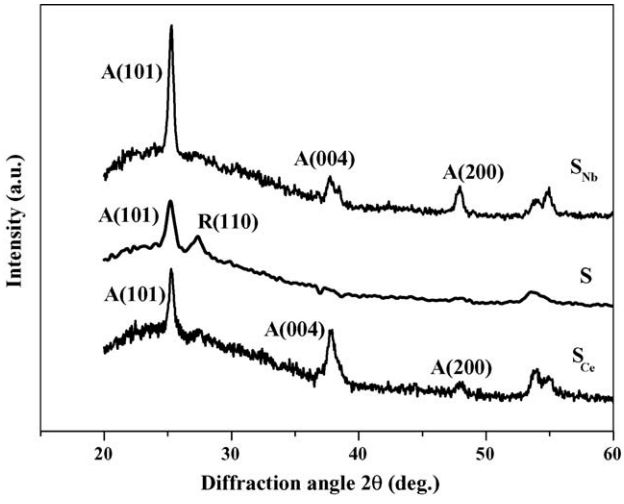

Fig. 1. XRD-patterns of the undoped (S) and RE-doped samples (S_{Ce} and S_{Nb}) using the Cu Kα radiation (λ = 1.54178 Å).