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Photoinduced effects in TiO_2 nanocrystalline films with different morphology

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ABSTRACT

The complex studies of photoinduced absorption, second harmonic generation and third harmonic generation were performed for TiO_2 films of different morphology. In particular we have studied the influence of a bicolor laser beam treatment by a 300 mW green cw laser emitting at 532 nm on changes of absorption, birefringence and third harmonic generation on TiO_2 films. We have performed the corresponding measurements using as a photoinducing light a glass erbium 10 ns pulsed laser with a fundamental wavelength of about 1540 nm together with its second harmonic generation (SHG) at 770 nm using the method of bicolor laser treatment and a frequency repetition of about 10 Hz. Varying the power density ratios between the fundamental and its SHG we have established the optimal conditions to achieve maximal photoinduced changes of absorption, birefringence and third harmonic generation (THG). We have detected changes of the birefringence and of the THG immediately after the laser treatment. We study an influence of the nanoparticle's sizes on the observed changes of the optical features. Additionally we have studied the role of different chemical treatment on the structural and optical parameters.

1. Introduction

During the last decade, basic and applied research focused on the preparation and characterization of TiO_2 thin films, possessing large energy gap, excellent visible and near-IR transmittance, high refractive index (2.2–2.75 in the visible spectral range) and dielectric constant (within the 120–190) [1–3]. It was found that TiO_2 is antibacterial, self-cleaning, super-hydrophilic, and able to decompose organic substances. Various other applications of TiO_2 thin films are encountered in electronics, optics, environment protection, and medicine. At the same time TiO_2 films present an important class of optoelectronic materials transparent in the visible and infrared (IR) region of the spectrum [4,27].

Besides they have high photosensitivity making them very interesting for integrated optical devices. Dozens of TiO_2 based materials, have been thus widely used in photovoltaic devices, optical gratings, waveguides, fibre and planar optical devices, optical sensors, optical circuits, holography, light amplifiers and generators [5], etc. Especial interest exists for their optically induced optical properties, particularly the nonlinear optical ones for applications in all-optics treatments. The TiO_2 nanocrystallites can play an important role in devices operated by coherent laser beams.

Up to this date, most of the photoinduced effects in films were performed using amorphous as well as partially crystallized chalcogenides both in glass form, and the origin of the effects were determined by the changes of the linear and nonlinear optical constants [6,7]. These effects are a bit similar to those observed in metallic nanoparticles [8], however, for an improved control of the process it would be better to have semiconducting nanoparticles with defined nanocrystallite sizes. TiO_2 nanocrystllallites deposited on different substrates are the perfect candidates for this role. Their photodarkening can be explained within a framework of several models and one of the most probable is a percollative growth of photodarkened local sites after illumination by photon-stimulated site switching, repulsion and slip motion of structural clusters [9]. For comparison, for silver-doped chalcogenides, the aggregation of Ag^+ ions in the illuminated region is the principal mechanism determining phototransparency changes [10], which means a limitation of the photoinduced changes due to the absence of effective photoinduced charge transfer between the substrate and the nano-trapping levels. IR stimulated changes contain two principal contributions: the photo-transient part, which disappears immediately after the switching-off of the laser irradiation, and the long-time relaxed "metastable" part persisting during a relatively long time at room temperature. Traditionally, the metastable contribution is erased after thermal annealing

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at a temperature determined by the glass transition temperature.

The TiO_2 films, in the form of nanocrystallites, may be considered as a serious competition to the amorphous chalcogenide films due to the specific origin of the prevailingly 2pO–3dTi ionic valence bonds and the relatively flat conduction bands. These films have a substantial advantage with respect to other semiconductors due to the possibility of occurrence in them of nonlinear optical effects and, due to their high photosensitivity, which may be promising for different photovoltaic devices [11]. Moreover, the absorption edge of bulk anatase (TiO_2) crystal around 3.2 eV is associated with indirect optical band gap transitions. Additionally, widening of the band gap might be expected in nanosized materials [12], so the phonon subsystem may play here also an important role. Indeed, it is shown that decreasing the diameter of the spherical nanoparticles in anatase TiO_2 by 10 nm is accompanied by a band gap variation within 0.2–0.4 eV [13]. Besides the indirect band gap transition mentioned above, a transition at about 3.8 eV has been ascribed to the direct optical band gap in different anatase TiO_2 films [14]. Few direct inter-band transitions with an energy higher than 3.8 eV are also predicted [15,16]. In such kind of nanocrystalline semiconductors the relatively flat bands possessing both properties of delocalized long-range ordered bands and localized states originating from the nanoconfinement effects begin to play a principal role [17]. Also, in the case of TiO_2 amorphous films, the ellipsometrically measured pseudodielectric function spectra have shown three distinct structures at about 3.3, 3.9 and 4.9 eV, which have been assigned to the transitions at the principal van Howe points in the Brillouin zone.

It is crucial to control the synthesis in order to develop an expected material of moderate cost and flexible properties. The use of TiO_2 films with controlled nanocrystalline sizes may open a new step in materials for recording and transformation of optical information and for optical switching. In particular, such nanocrystalline materials may be promising for nonlinear optical effects [18]. For this investigation we have synthesized anatase TiO_2 nanocrystalline films of different sizes with different chemical treatments. In Section 2 are presented the principal parameters of film growth and their structural and morphology monitoring methods. Section 3 presents the principal parameters of the synthesized films and discuss the relation between the film sizes/structure and the photoinduced changes observed.

2. Experimental methodology

2.1. TiO_2 films preparation

Titanium tetra-*n*-butoxide (TTB) obtained from Aldrich Chem Co. was used as the starting material in the preparation the TiO_2 films. The concentration of TTB in the solution was 0.5 mol/L. TTB was first mixed with a small amount of ethanol in a container and stirred for 30 min. A mixture of water containing 3 wt.% HCl and ethanol was poured under stirring into the transparent solution to promote hydrolysis; the molar ratio of H_2O to TTB was 1:1. Finally, poly-ethylene glycol of molecular weight ~600 (PEG 600) was added slowly to this solution and stirred for 1 h. The resulting solution was used for the TiO_2 film coating. The molar ratio of PEG to TTB was 1. Films annealed at 400 °C and below were coated on corning glass substrates, whereas films annealed at temperatures from 500 to 900 °C were deposited on vitreous silica. A dipping solution was also prepared without PEG and used for coating. A custom-built dip-coating apparatus was used for the depositions. The substrate was lowered into the coating solution for 30 s and then withdrawn at a regulated speed of 4 mm/s. After each coating, the films were first dried at 60 °C for 2 min and then heat treated at 90 °C for 1 h in air inside an oven. These samples were then treated in hot water at 90 °C for 1 h. Thereafter, the films were heated at a rate of 0.5 °C to annealing temperatures ranging between 100 and 700 °C. The samples were held at the peak temperature for 1 h and then cooled to room temperature. A thin film prepared in presence of PEG 600 and treated in hot water alone was denoted as sample C1. The thin films prepared in presence of PEG, treated in hot water and heated in air at temperatures of 100–700 °C, were denoted as samples C2–C8. Three samples, prepared without PEG, treated in hot water and thereafter heat treated at temperatures of 500, 600, and 700 °C, were denoted as samples C11, C12, and C13.

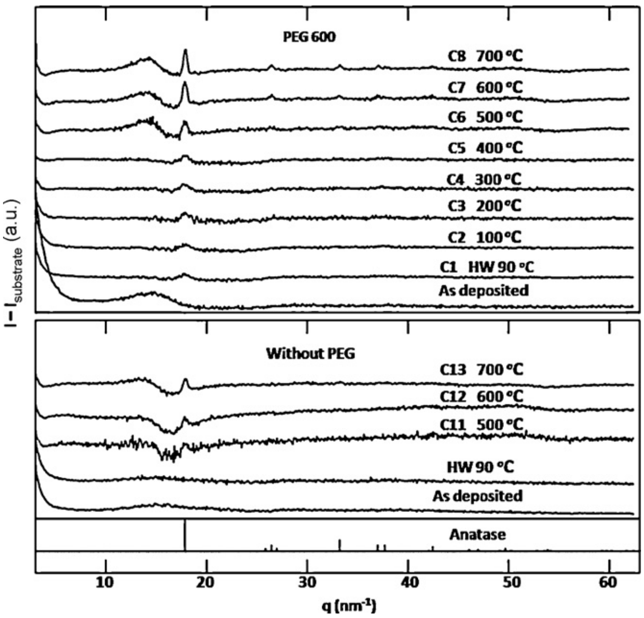

Fig. 1. X-ray scattering intensities of the TiO_2 films prepared in presence of PEG 600 as a function of the scattering vector (top portion) and of those prepared without PEG (bottom portion). The scattering originating from an empty substrate was subtracted. The films were annealed at the indicated temperature. The powder scattering intensities for anatase are shown at the bottom of the diagram.

2.2. TiO_2 films characterization

X-ray diffraction measurements were carried out with a custom-built diffractometer equipped with graphite monochromator and analyzer crystals. The data were taken in reflection mode with Cu Kα radiation ($\lambda = 0.1542$ nm), and the signal measured from the glass and quartz substrates was subtracted from the data. The crystalline phases were identified using the ICDD/JCPDS database [Powder Diffraction File, ICDD, JCPDS, Swarthmore, PA, 1988 (Card Nos. 21-1272, 21-1276 and 29-1360)]. Crystal sizes were determined based on the anatase (1 0 1) and (2 0 0) peaks using the Scherrer formula [19].

Raman spectra were recorded at room temperature with a Jobin-Yvon Labram HR microanalytical spectrometer equipped with a motorized *xy* stage and autofocus. The spectra were generated with a 17 mW, 632.8 nm He–Ne laser excitation and were dispersed with the 1800 g/mm grating across the 0.8 m length of the spectrograph. The laser power was 9 mW on the sample surface. The spectral resolution of this apparatus is estimated to be less than 0.5 cm^{-1} for a slit width of 150 μm and a confocal hole of 300 μm.

Scanning electron microscope (SEM) images were recorded for the films before and after hot water treatment at 90 °C, using a JEOL JSM-5600 SEM (JEOL USA, Peabody, MA). The microscope was operated at 10 kV, at a working distance of 10–15 mm, and with a 45° specimen tilt.

Transmission electron microscopy (TEM) of a powder sample was performed by placing a small amount of the sample into a glass vial. Ethanol was added and the solution was sonicated for 10 min. A drop of the solution was placed onto a carbon coated 200 mesh copper grid and left to dry overnight. The sample was imaged using a 2011 JEOL STEM at 200 keV. Images were captured on a 4 k × 4 k multiscan CCD camera using Digital Micrograph from Gatan.

For the band gap measurements, the transmission spectra of the films were recorded at normal incidence with a Biochrom Ultrospec 2000 UV–Visible spectrophotometer.

2.3. Optical measurements

Optical spectra were measured by spectrophotometer with a resolution of about 1.5 nm. We also have performed the photoinduced measurements using as a photoinducing light a glass erbium 10 ns pulsed laser with a fundamental wavelength of about 1540 nm together with its second harmonic generation at 770 nm (so-called writing beam) using the method of bicolor laser treatment [20] at a frequency repetition of about 10 Hz. Varying the power density ratios between the fundamental and the writing beams, we have established the optimal conditions to achieve the maximal photoinduced changes, both linear as well as nonlinear. We have detected changes of the birefringence and of the third harmonic generation during, and immediately after the cw 532 nm laser treatments at a power of about 300 mW. The photoinducing beam possessed a Gaussian-like beam profile. The Senarmont