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Effect of temperature on the growth of TiO_2 thin films synthesized by spray pyrolysis: Structural, compositional and optical properties

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ABSTRACT

Large surface area coatings of oxygen deficient nanocrystalline TiO_2 are of immense use in antifogging mirrors and self cleaning windows. Spray pyrolysis is a simple versatile technique to coat relatively large surface area. A clear understanding of effect of substrate temperature on the coating morphology, structure, composition and optical properties is essential to produce coatings of desired properties. Oxygen deficient nanocrystalline anatase–TiO_2 thin films were synthesized on Si(1 0 0), quartz and glass substrates at 300–550 °C. Well defined platelets like nanograins standing on their edge were obtained at 500 °C. The crystallites were found to be of ~12 nm thickness and ~30 nm major diameter. The secondary ion mass spectrometric studies of the films revealed uniform distribution of titanium and oxygen across the thickness of the film up to the film–substrate interface. Presence of lower valent Ti ions and oxygen vacancies were confirmed from XPS studies. The indirect and direct band gap values evaluated from the Tauc plot for films synthesized at 500 °C are 3.3 and 3.62 eV respectively.

1. Introduction

Titanium dioxide constitutes one of the extensively studied transition metal oxide known for its remarkable photocatalytic and optical properties. Nano-structured TiO_2 thin films find application in photocatalysis [1,2], photovoltaics [3,4] and gas sensors [5,6]. Among the various phases of TiO_2, anatase shows superior photocatalytic activity under UV light irradiation having wave lengths less than 387 nm. Under UV light irradiation organic pollutants gets easily oxidized by the photo-generated holes or by reactive species such as $OH^{\bullet}$ and O_2^- radicals formed on the surface. It has been found that TiO_2 particle size is an important parameter for photocatalytic efficiency. When the size of the particles become comparable with the de-Broglie wave length of the charge carriers, which lies between 5 and 25 nm for oxide semiconductors like TiO_2, the wave function of charge carriers spread over the entire particle and therefore the charge carriers do not need to diffuse anymore to accomplish reactions with species present at the surface [7]. This increases the quantum yield. Experimental investigations support the existence of an optimum particle size of ~10 nm for TiO_2, where photocatalytic oxidation rates of organic pollutants are maximized [8]. Theoretical investigations have also concluded that particle size plays significant role in the photo-activity of TiO_2. A model based on the mechanism of TiO_2 photocatalysis predicts an increase of the quantum yield when particle size decreases from 1000 nm to 10 nm [9]. A stochastic model predicts an increase in quantum yield as particle size increase from 3 to 21 nm, because the e^-–h^+ recombination rates are lower for the larger particles [10]. Based on the above a particle size/confinement of size at least in one dimension around 12 nm seem to be more effective for photocatalytic application.

There are various methods available for making nanostructured thin films of TiO_2, with size confinement at least in one dimension like magnetron sputtering [11], pulsed laser deposition [12], electron beam evaporation [13], chemical vapor deposition (CVD) [14], sol–gel process [15], electro-deposition [16] and spray pyrolysis [17,18]. Among these deposition techniques, CVD, sol–gel dip/spin coating and spray pyrolysis are the commonly applicable large surface area coating techniques. Chemical vapour deposition technique is constrained by the need of vacuum setup and costly precursors. In addition the coating area is limited by the reactor size. Dip coating/spin coating need repeated dipping/spinning and heating to get the required thickness. In the case of spray pyrolysis large surface area coatings are obtained in a single step. The process consists of atomization of the precursor solution and transportation of the resulting aerosols towards the hot substrate by means of a gas stream [19–21]. Within the hot zone above the substrate, the precursors undergo decomposition in the presence of oxygen resulting in the formation of the oxide film on the substrate by surface reaction [22]. The deposition temperature influences the parameters: aerosol transport towards the substrate, solvent evaporation, possibility of the droplets impacting the surface

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and the dynamics of their spreading and most importantly the mechanistic path way involved in decomposition [19,23]. Therefore, the morphology, composition and adherence of the deposited film depend on the deposition temperature. The response of the substrate depends on its heat capacity. Materials with a low heat capacity and high thermal conductivity are cooled much faster by the spray. This influences the performance of the overall process and changes the effective growth temperatures [24,25]. The solvents with lower density and surface tension (such as the alcohol based ones) enable creation of droplets of smaller size. The solvents with lower boiling point vaporize easily and this can have a major impact for achieving pyrolytic decomposition [26,27]. Highly soluble precursors are generally preferred, and volatile molecules are required as co-product for accelerating pyrolysis based decomposition [20,28]. In most cases, the chemical spray pyrolysis process uses metallo-organic compounds in non-aqueous solvents as precursor [29,30]. In spray pyrolysis the flat surface area that can be uniformly coated is limited by the uniform hot zone area of the flat heater. The limitation can be overcome by flame and/laser assisted spray pyrolysis where flame/laser is used as the energy source [31,32]. In flame pyrolysis substrate heating and precursor aerosol pyrolysis are done by the flame. The substrate is mounted on board a Y–Z raster stage in the line of sight incidence geometry and rastered to give large surface area coating [31]. In laser assisted pyrolysis flame is replaced with laser [32].

In the present study, we report the growth of nanocrystalline TiO_2 thin films with grain size confinement in one dimension around 12 nm. The structural and morphological correlations were drawn from grazing incidence X-ray diffraction studies (GIXRD), Raman spectroscopy and field emission scanning electron microscopy (FESEM). X-ray photoelectron spectroscopy (XPS) was used to investigate the elemental composition of the TiO_2 thin films. Compositional depth profiling was performed using secondary ion mass spectrometric (SIMS) analysis. Optical band gap was evaluated using ultraviolet–visible (UV–Vis) absorption spectroscopy.

2. Experimental details

2.1. Synthesis of TiO_2 thin films

The experimental set up and the parameters employed for the synthesis of nanostructured thin films are published elsewhere [33]. However, for the sake of completeness, a brief account is being furnished here. The spray pyrolysis set up consists of an ultrasonic atomizer, a heater and a quartz column. The precursor solution was prepared by dissolving 0.05 M titanium oxy-acetyl acetonate in methanol. A static ultrasonic nebulizer with 1.7 MHz resonator was employed to generate aerosols having fairly uniform size distribution in the range 1–3 μm. The aerosols were transported to the substrates fastened on to a flat heater. The substrate temperature was varied from 300 to 550 °C. The quartz, Si(1 0 0) and glass substrates were cleaned chemically in acidic and basic baths, and then ultrasonicated in isopropanol before being loaded onto the substrate holder. The aerosols on reaching the hot zone evaporated and the vapors reacted with oxygen at the substrate surface to form the desired TiO_2 thin film.

2.2. Characterization

The thickness and roughness of the films were measured using a Dektak 6M-stylus profiler (Veeco, USA) and atomic force microscope (AFM) (NT-MDT, Solver, The Netherlands) respectively. The crystal structure of the film was characterized by GIXRD (STOE, Germany) using Cu-Kα radiation and 0.5° angle of incidence in back scattering geometry. The Raman spectroscopic studies were carried out using Micro-Raman Spectrometer (Jobin Yvon HR800) 514 nm Ar^+ ion laser, equipped with a power of 0.5 mW and 100× objective lens. The surface morphology of the thin films was characterized using Hitachi made FESEM. XPS study on the thin films was carried out using SPECS make photoelectron spectrometer. Depth profile analyses of the thin films were carried out by CAMECA IMS-4f SIMS machine. Cs^+ ion beam with 1.75 kV impact voltage and 10 mA current with beam diameter of ~5 μm was rastered over an area of 100 μm^2 for the depth profile analysis. Optical absorption spectra of the thin films were recorded at room temperature using double beam UV–Visible spectrophotometer (Shimadzu-3101PC) in the wavelength range 190–890 nm.

3. Results and discussion

3.1. GIXRD studies

Fig. 1a shows the GIXRD patterns of films grown on Si(1 0 0) at 300–550 °C, in steps of 50 °C. Similar patterns were obtained for films grown on quartz and glass. The thin films synthesized on all the substrates at 300 °C are amorphous as seen from the GIXRD spectra. The GIXRD pattern of the thin films synthesized at 350–550 °C corresponds to the anatase phase of TiO_2 (JCPDS 21-1272, space group $I4_1/amd$). The most intense peak appears at a 2θ value of 25.30° which corresponds to (1 0 1) plane. This peak is used to

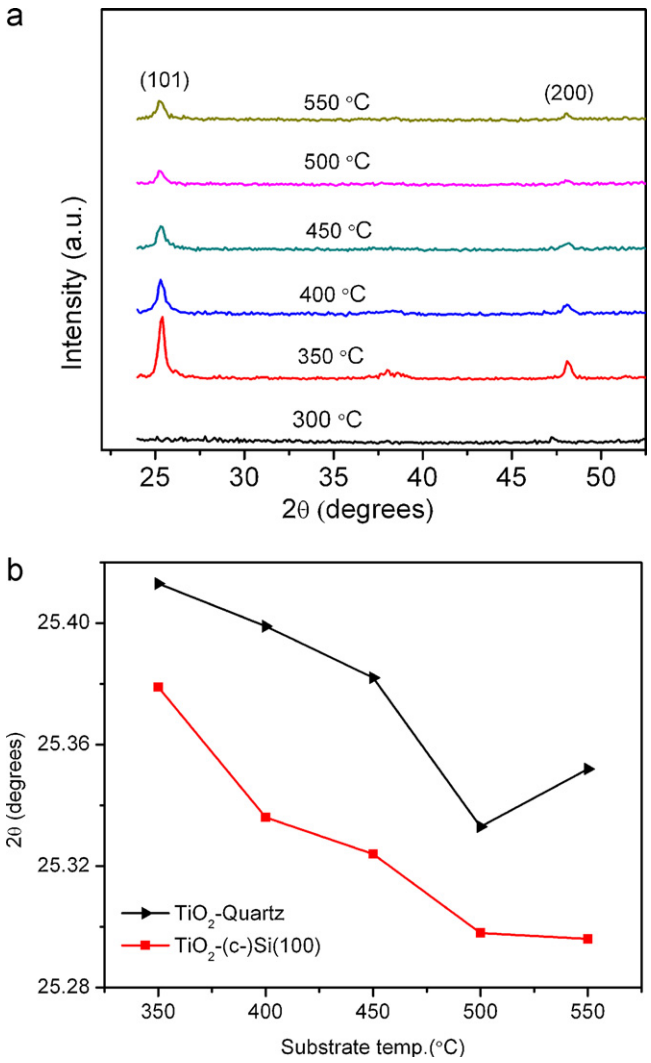

Fig. 1. (a) (Color on line) GIXRD pattern of TiO_2 thin films synthesized on Si(1 0 0) at substrate temperatures of 300–550 °C. (b) (Color on line) Variation of 2θ with substrate temperature for films grown on Si(1 0 0) and quartz.