Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 34 (2013) 627 – 636

Energy Procedia

10th Eco-Energy and Materials Science and Engineering (EMSES2012)

Effect of Annealing Temperature on the Photocatalytic Activity of TiO_2 Thin Films

C.-P. Lin, H. Chen, A. Nakaruk, P. Koshy, C.C. Sorrell*

School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

Abstract

TiO_2 thin films were spin coated on soda-lime-silica glass substrates under identical conditions and then annealed for 2 h in air in the range of 300°-500°C in increments of 50°C. The mineralogical, morphological, optical, and photocatalytic properties then were assessed for the films. The techniques used were glancing-angle X-ray diffraction (GAXRD), field emission gun transmission electron microscopy (FEGTEM), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), UV-VIS spectrophotometry (UV-VIS), and methylene blue (MB) degradation. The films had a consistent thickness of ~255 nm. Anatase peaks recrystallised at the annealing temperature of 400°C, with the crystallinity increasing with increasing annealing temperatures. Although recrystallisation caused a significant increase in grain size, the crystalline films showed only a slight increase in the grain size with increasing annealing temperatures. In contrast, the surface roughness of all of the films increased significantly with increasing annealing temperatures. This was associated with increased grain faceting, which was supported by the X-ray diffraction data.

All of the films showed high transparency in the visible region, with the optical indirect band gap of the crystalline films decreasing slightly from 3.49 eV to 3.43 eV with increasing annealing temperatures. Four regimes of photocatalytic performance could be identified, which depended principally on the degree of crystallinity and the level of contamination. In short, a blank was used to negate heating effects, the amorphous films were inert, the onset of crystallisation established photoactivity, and the photoactivity of the films annealed at 400°-500°C decreased in a trend consistent with the trends in increasing grain size, increasing surface roughness, increasing crystallinity, decreasing band gap, and increasing contamination. Since this consistency was the case, these variables could not be decoupled.For the samples that were fabricated using the specified materials and methods, characterised, and tested, the optimal temperature for annealing was found to be 400°C.

Selection and peer-review under responsibility of COE of Sustainalble Energy System, Rajamangala University of Technology Thanyaburi (RMUTT)

Keywords: TiO_2; Thin Films; Spin Coating; Photocatalysis; Crystallinity

*C.C. Sorrell, Tel.: (+61-2) 9385-4421; fax: (+61-2) 9385-6565
E-mail address: c.sorrell@unsw.edu.au

Selection and peer-review under responsibility of COE of Sustainalble Energy System, Rajamangala University of Technology Thanyaburi (RMUTT)
doi:10.1016/j.egypro.2013.06.794

1. Introduction

Over the last decade, extensive research has been conducted on investigating the photocatalytic properties of titanium dioxide (TiO_2, titania) for applications such as photovoltaic cells [1], water purification systems [2], and self-cleaning and self-sterilising materials [3]. For the abovementioned applications, thin films are more extensively used than bulk materials owing to cost considerations, processing flexibility, and suitability for various substrates, types and shapes.

Generally, the optical band gap (E_g) of TiO_2 varies with its structure, with the value for amorphous TiO_2 being ~3.5 eV [4] and the values for crystalline anatase and rutile being 3.2 eV and 3.0 eV [5], respectively. As rutile can absorb light of a wider wavelength range, it would be assumed that the photocatalytic performance of rutile would be superior to that of anatase. However, anatase provides higher photocatalytic activity owing to the higher density of localised states, consequent surface-adsorbed hydroxyl radicals, and slower charge carrier recombination rate relative to rutile [6,7].As a result, there is growing interest in understanding the unique photocatalytic activity of anatase.

TiO_2 thin films can be synthesised using different techniques, including sputtering [8], laser ablation [9], electrophoretic deposition [10], anodic oxidation [11], sol-gel [12], screen printing [13], dip coating [14], gel oxidation [15], spray pyrolysis [16], and spin coating [17]. Spin coating is used widely in the fabrication of TiO_2 thin films due to rapid growth rates, capacity for handling large sample sizes, mass production capability, and high yield rates [18,19]. However, the spin coating technique involves a subsequent annealing process, which is known to enhance the diffusion of contaminants from the glass substrate to the coating [20,21]. This process tends to restrict the grain growth in the film and also increases the number of lattice defects, which decreases the photocatalytic activity of the TiO_2 thin films.

The intentions of the present work were to synthesise TiO_2 thin film coatings on glass substrates using spin coating and to determine the optimal annealing temperature, which should produce the best photocatalytic performance. This is an extension of previous work [17] that focused on the phase transformation of anatase $\rightarrow$ rutile. Further, the present work focussed on the effect of contamination from the substrate (viz., Na, Ca, and Si) on the film properties, including mineralogical, morphological, optical, and photocatalytic.

2. Methodology

The method used to fabricate the TiO_2 thin films by spin coating is described in detail elsewhere [21]. Briefly, the precursors used were titanium isopropoxide (TIP) dissolved in isopropanol at 0.1 M Ti concentration. The solutions were mixed in a Pyrex beaker by hand-stirring for 1 min without heating. Spin coating was done by rapidly depositing ~0.2 mL of solution onto a soda-lime-silica glass substrate that was spun at 2000 rpm in air. The film was dried by spinning for an additional 15 s and the overall process was repeated six more times. Subsequent annealing was carried out in a muffle resistance furnace at annealing temperatures that varied in the range 300°-500°C for times of 2 h; the heating rate used was 5°C/min, followed by natural cooling.

The thickness of the films was determined using field emission gun transmission electron microscopy (FEGTEM, 200 kV accelerating voltage, *Philips CM200*).The mineralogy of the films was examined using glancing-angle X-ray diffraction (GAXRD, 45 kV, 40 mA, *PAN-analytical X'pert Materials Research Diffractometer*). The grain size was estimated by field emission scanning electron microscopy