Materials Science in Semiconductor Processing 26 (2014) 251–258

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Sol–gel derived nanocrystalline TiO_2 thin films: A promising candidate for self-cleaning smart window applications

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ARTICLE INFO

Available online 21 May 2014

Keywords:
TiO_2 thin films
Sol–gel
Semiconductors
Photocatalysis
Electrochromism

ABSTRACT

In the present work, anatase TiO_2 films are prepared by sol–gel spin coating method. The structural and optical properties of the films have been studied at different post-annealing temperatures. The photocatalytic activity and electrochromic performance of the films are investigated. The films annealed at 400 °C exhibit the highest photocatalytic activity with a rate constant of 4.56×10^{-3} min^{-1}. The electrochromic performance for the films annealed at 400 °C expressed in terms of difference in optical density (ΔOD) at 550 nm between coloured and bleached state is 0.5493. This combination of photocatalysis and electrochromism makes the sol–gel derived titania thin films as promising candidates for self-cleaning smart window applications.

1. Introduction

Anatase titania (TiO_2) has been studied extensively in last few decades for its high efficiency photocatalytic properties [1–3]. Moreover, its biocompatibility and low cost factor are added advantages for real time applications. Therefore, among many candidates for photocatalysis, TiO_2 is considered as the only material which is industrially reliable. The photocatalytic properties of TiO_2 were first realized in 1980s for the detoxication of various harmful compounds both in water and air. In the photocatalytic process, electron–hole pairs are generated when TiO_2 is photo-activated with ultraviolet (UV) light having an energy higher than its band gap [1]. The electrons and holes are used in the red-ox breakdown of organic pollutants leaving CO_2 and other mineral acids as the residue. The holes generated in TiO_2 are highly oxidising and most organic compounds are completely oxidised by it. In the literature, the enhanced photocatalytic activity exhibited by nanocrystalline TiO_2 films is mainly attributed to the increase in surface to volume ratio which results in more number of active sites and the quantum confinement effect [4]. Though, TiO_2 is widely studied and mostly used as a photocatalytic material, its electrochromic properties have not been explored extensively [5–7] as compared to other transient metal oxides like WO_3 [8], Nb_2O_5 [9] and V_2O_5 [10]. The most accepted model [11] for electrochromic reaction in TiO_2 is the injection of electrons, followed by intercalation of monovalent ions into an oxide matrix.

$$\underset{\text{(Colourless)}}{TiO_2} + xe^- + xM^+ \rightleftarrows \underset{\text{(Coloured)}}{M_xTiO_2} \quad (1)$$

where, M^+ is a monovalent ion (H^+, Li^+, Na^+) and x can vary between 0 and 1.

There is no correlation between the electrochromic and photocatalytic phenomena and both are considered to be entirely independent of each other. The electrochromic behaviour is due to the charge intercalation into the lattice resulting in colour change whereas photocatalysis is related to the creation of electron–hole pairs on the semiconductor surface. But, a good combination of photocatalytic and electrochromic properties is desirable for self-cleaning smart window applications. The combination of photocatalysis and electrochromism in a single material allows us for

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http://dx.doi.org/10.1016/j.mssp.2014.05.006
1369-8001/

a one-step, cost-effective and high throughput growth process in the fabrication of self-cleaning smart windows. In these applications, the self-cleaning mechanism works in two stages. The primary and important stage is breaking down of the organic contaminants through photocatalytic activity. This makes the glass surface superhydrophilic which reduces the water contact angle. In the superhydrophilic stage, water forms a thin layer on glass and the dirt is washed away. On the other hand, smart windows work on the principle of electrochromism. Smart windows not only block the visible light but also absorb the near-infrared (NIR) light which is invisible but produces heat.

Hence, the main objective of the present work is to look for a good combination of photocatalytic and electrochromic behaviours of nano-crystalline anatase TiO_2 thin films. In the literature, several deposition methods like radio-frequency magnetron sputtering [12], reactive magnetron sputtering [13], pulsed laser deposition [14], reactive e-beam evaporation [15], spray pyrolysis [16], sol–gel spin coating [17,18] etc. has been prescribed for the growth of TiO_2 thin films. Out of these techniques, sol–gel has got distinct advantage from others due to the atomic scale mixing of the constituents, ease of operation and cost factor [19]. Therefore, in the present work, we have prepared nano-crystalline TiO_2 thin films by the sol–gel spin coating method and have studied their photocatalytic properties at different post-annealing temperatures. The films showing the best photocatalytic property have been checked for their electrochromic behaviour.

2. Experimental details

TiO_2 thin films were prepared by the sol–gel spin coating method. Titanium iso-propoxide ($Ti(OC_3H_7)_4$) was used as the titanium precursor and ethanol as the solvent. The flow chart for the preparation steps is shown in Fig. 1. Titanium ion concentration was kept at 0.2 M. The films were deposited by spin coating on borosilicate glass (BSG), ITO (10% Sn doped In_2O_3) coated glass and *p*- type Si (100) substrates. Six layers of TiO_2 thin films were deposited in order to obtain the desired uniform thickness for all the samples. After coating each layer, the films were pre-heated at 250 °C for 5 min in air. Finally, all the films were annealed at different temperatures for 1 h in air.

Grazing angle X-ray diffraction (GAXRD) measurements were carried out using a Phillips X'Pert Pro diffractometer with Cu Kα radiation (λ=1.5418 Å) at a grazing angle of 2°. Raman spectra were obtained through a HORIBA Jobin Yvon Raman instrument using He–Ne laser light source (632.8 nm). Scanning electron micrographs were recorded using a field-emission scanning electron microscope (FE-SEM), FEI Quanta 200. The transmittance spectra in the wavelength range 300–2500 nm were recorded using a JASCO double beam UV–vis-NIR spectrophotometer (Model: V-570).

The photocatalytic behaviour of the films was studied by degrading Rhodamine-B (RhB) dye which is a typical pollutant in the effluent stream of dye industry. 5 cm^2 TiO_2 film was immersed in 10 ml aqueous RhB solution (0.5 mg/l). 6 W mercury tube lamp (central wavelength ~352 nm) kept at a distance of 8 cm from the film was used as the UV source. The photocatalytic activity was evaluated by measuring the changes in the optical absorbance of RhB solution in the wavelength range 400–800 nm. The electrochromic property for TiO_2 films deposited on ITO coated glass substrates was evaluated using cyclic voltametry (CV) (CH Instruments model: CHI7081C) in the three electrode electrochemical workstation by

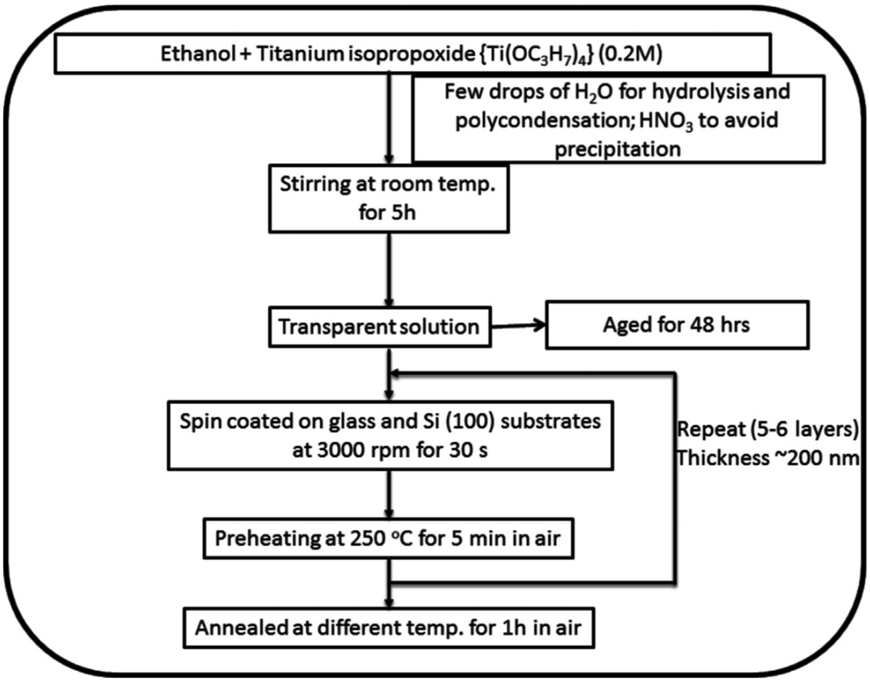

Fig. 1. Flow chart for the preparation of TiO_2 thin films by sol–gel spin coating.