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ScienceDirect
J. Anal. Appl. Pyrolysis 82 (2008) 83–88
JOURNAL of ANALYTICAL and APPLIED PYROLYSIS
www.elsevier.com/locate/jaap

Properties of chemical vapour deposited nanocrystalline TiO_2 thin films and their use in dye-sensitized solar cells

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Received 8 July 2007; accepted 14 January 2008
Available online 2 February 2008

Abstract

Nanocrystalline titanium dioxide (TiO_2) thin films have been prepared using titanium(IV) isopropoxide as a precursor onto the glass and fluorine doped tin oxide coated glass substrates by chemical vapour deposition technique at 400 °C substrate temperature. X-ray diffraction study confirms the polycrystalline nature of TiO_2 with anatase phase having tetragonal crystal structure. The films are 975 nm thick and transparent having transmittance grater than 80%. Atomic force microscopy (AFM) images reveal the nanocrystalline morphology with grain size of ~200 nm. The film shows a sharp absorption edge near 350 nm. Photoelectrochemical study shows that TiO_2 thin film sensitized with Brown Orange dye is found to exhibit relatively maximum I_{sc} and V_{oc} among the studied dyes. The values of fill factor (FF) and efficiency (η) for the dye-sensitized solar cell (Brown Orange dye-sensitized TiO_2) are 0.54 and 0.17%, respectively. Such films would serve as better prospects for dye-sensitized solar cells.

Keywords: TiO_2 thin films; CVD; X-ray diffraction; AFM; Optical properties; Dye-sensitized solar cell

1. Introduction

Photovoltaic systems present a promising option for future energy needs with several different technologies currently under development [1]. In the field of alternative energy, a dye-sensitized solar cell is now a hot topic due to its high conversion efficiency produced with porous TiO_2 electrode that is composed of several tons of nanometer sized particles [2–4]. In contrast to the all-solid state junction solar cells, the dye-sensitized solar cell is a photoelectrochemical (PEC) solar cell that uses a liquid electrolyte or other ion-conducting phase as a charge transport medium.

In present days, CVD has proved to be the best technique to produce thin films in nano-form having greater surface area, which is the basic need in case of dye-sensitized solar cells. When a volatile compound of substance to be deposited is vapourised and the vapour is thermally decomposed or reacted with other gases, vapours or liquids at the vicinity of the substrate to yield a non-volatile reaction product which deposit atomistically, the process is called chemical vapour deposition. In CVD, flow rate, gas composition, deposition temperature, pressure and deposition chamber geometry are the process parameters by which deposition can be controlled to have nano-forms of the desired material.

Djerdja et al. [5] reported nanocrystalline TiO_2 films by CVD on different substrates at relatively low temperature of 320 °C using $TiCl_4$ as a precursor and found that the nature of substrates influence the size and distribution of nanograins in the films. Byun et al. prepared TiO_2 thin films at 287–362 °C using titanium(IV) tetraisopropoxide (TTIP) precursor and O_2 gas [6]. It is reported that best photocatalytic reaction rate can be achieved with CVD-deposited TiO_2 films, which have the preferred orientation with columnar structure for the formation of larger surface area for dissociative reaction. The study of anatase TiO_2 photocatalysts prepared with different thicknesses using TTIP by low-pressure metal–organic CVD shows that the photocatalytic activity strongly depends on the film deposition time (or film thickness) [7]. The structure of the TiO_2 thin film photocatalysts prepared in two different crystalline forms of TiO_2 using the complex compound precursors of TiO_2 like titanium [bis(dipiraloymethanate) diisopropoxide] and TTIP has a dominating effect on the photodegradation rate of the test compound [8]. It is demonstrated that the alkoxide-based CVD

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0165-2370/$ – see front matter
doi:10.1016/j.jaap.2008.01.004

treatment combined with UV irradiation can improve the efficiency of dye-sensitized photoelectrodes with nanocrystalline TiO_2 deposited on ITO-coated plastic films [9]. The thermal decomposition reactions of TTIP and the deposition processes were studied in detail [10–13]. Ahn et al. [14] demonstrated that the deposition occurs at a lower temperature in oxygen containing atmosphere than in nitrogen.

This paper deals with the synthesis of TiO_2 thin films by CVD technique using TTIP in oxidizing atmosphere on conducting fluorine doped tin oxide coated glass substrates. TTIP is chosen as the TiO_2 precursor due to its non-corrosivity and non-toxicity. Moreover, decomposition of TTIP to TiO_2 is a very clean process [10]. The structural, morphological, optical and photoelectrochemical properties are studied in order to utilize them in dye-sensitized solar cells. This paper provides a new stuff in the context that there are hardly any reports [9] on chemical vapour deposited TiO_2 thin films for dye-sensitized solar cells using as-mentioned dyes in the paper. The possible use of nanocrystalline TiO_2 thin films in dye-sensitized solar cells is discussed.

2. Experimental details

2.1. Materials

The fluorine doped tin oxide ($F:SnO_2$) conducting coatings with 90–95% transparency and sheet resistance less than $10\ \Omega\ cm^{-2}$ were first deposited onto the ultrasonically cleaned glass substrates (3.5 cm × 1 cm × 0.125 cm) using stannic chloride ($SnCl_4{\cdot}5H_2O$) and ammonium fluoride (NH_4F) precursors by spray pyrolysis technique. These $F:SnO_2$ electrodes and ultrasonically cleaned bare glass substrates were then used for deposition of TiO_2 thin films by CVD technique.

Titanium(IV) isopropoxide (TTIP, $Ti[OCH(CH_3)_2]_4$, AR grade, 99.99%) was used as a precursor for deposition of TiO_2 thin films by CVD. The films deposited on glass substrates were used for structural, morphological, optical characterizations and those on $F:SnO_2$ were used for photoelectrochemical characterization and dye-sensitized solar cell.

Four different dyes such as Brown Orange (BO), Turkish blue (TB), Red HE 8B (RH) and Yellow HER (YH) were used to sensitize the working TiO_2 electrode.

2.2. CVD apparatus and reaction conditions

Fig. 1 shows a schematic diagram of the experimental set-up of chemical vapour deposition in our study. It consists of two furnaces which are adjacent to each other with a fused quartz tube (4 cm inner diameter and 100 cm in length) traversing both of them; one is called vapourising furnace which provides temperature zone to the quartz tube where the vapourisation (sublimation) of the precursor takes place and another one is pyrolyzing furnace which provides the uniform temperature zone to the tube where the pyrolytic decomposition of vapours on the substrate occurs. Initially, nitrogen gas was flushed through the tube for 15 min to

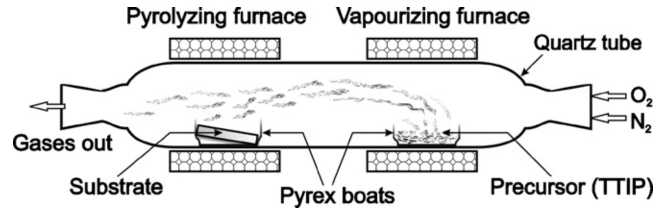

Fig. 1. Schematic diagram of the CVD apparatus. N_2 as carrier gas and O_2 as reactant gas.

remove the air inside the tube completely. The substrates were kept horizontally over the Pyrex boat in the reaction chamber (pyrolyzing furnace). The temperature of the pyrolyzing furnace was maintained constant at 400 °C. The precursor TIPT was kept in Pyrex boat inside the quartz tube region surrounding the vapourising furnace (maintained at 100 °C temperature) and the vapours of TTIP thus created were guided into the reaction chamber by means of high purity ($N_2 + O_2$) gas flow. The gas was purged at the flow rate of 400 cc min^{-1}. The nitrogen gas was used as a carrier gas while oxygen was used as reactant gas. The deposition time was 20 min. Table 1 shows the CVD deposition conditions used to prepare TiO_2 thin films.

2.3. Characterization of the deposited films

Structural properties were studied using Philips PW 3710 X-ray diffractometer (operated at 25 kV, 20 mA). The surface morphology of TiO_2 thin films was observed using scanning electron microscope JEOL JSM-6360. TiO_2 film was coated with 10 nm platinum layer using Polaron sputter coating unit prior to recording the micrographs. The surface topography of photoanodes was analyzed from the atomic force microscopy (AFM) images taken by means of the atomic force microscope Nanoscope instruments, USA, in contact mode, with V shape silicon nitride cantilever of length 100 mm and spring constant 0.58 N/m in the contact mode.

The optical absorption and transmission spectra were recorded in the wavelength range of 200–1000 nm using a SYSTRONICS make UV-Vis Spectrophotometer (Model 119). Thickness was measured from transmission data of the TiO_2 thin films prepared at 400 °C. The films were uniform and pass the scotch tape test for adherence.

Table 1
CVD conditions used for deposition of TiO_2 thin films

Precursor	Titanium(IV) isopropoxide (TTIP)
Substrate temperature	400 °C
Vapourising temperature	100 °C
Carrier gas-flow rate	Ar—400 cc min^{-1}
Reactant gas-flow rate	O_2—400 cc min^{-1}
Total pressure	1 Torr
Deposition time	20 min
Substrates	Soda glass and $F:SnO_2$ (3.5 cm × 1 cm × 0.125 cm)