Applied Surface Science 257 (2011) 9498–9502

Contents lists available at ScienceDirect

Applied Surface Science

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

Chemical synthesis of nanocrystalline SnO_2 thin films for supercapacitor application

S.N. Pusawale, P.R. Deshmukh, C.D. Lokhande*

Thin Film Physics Laboratory, Department of Physics, Shivaji University, Kolhapur 416004 (M.S.), India

ARTICLE INFO

Article history:
Received 4 December 2010
Received in revised form 31 May 2011
Accepted 8 June 2011
Available online 15 June 2011

Keywords:
Chemical synthesis
Nanocrystalline SnO_2
Thin films
Supercapacitor

ABSTRACT

Nanocrystalline SnO_2 thin films were deposited by simple and inexpensive chemical route. The films were characterized for their structural, morphological, wettability and electrochemical properties using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy techniques (SEM), transmission electron microscopy (TEM), contact angle measurement, and cyclic voltammetry techniques. The XRD study revealed the deposited films were nanocrystalline with tetragonal rutile structure of SnO_2. The FT-IR studies confirmed the formation of SnO_2 with the characteristic vibrational mode of Sn–O. The SEM studies showed formation of loosely connected agglomerates with average size of 5–10 nm as observed from TEM studies. The surface wettability showed the hydrophilic nature of SnO_2 thin film (water contact angle 9°). The SnO_2 showed a maximum specific capacitance of 66 F g^{-1} in 0.5 Na_2SO_4 electrolyte at 10 mV s^{-1} scan rate.

1. Introduction

Nanometer sized materials are attracting great interest in recent years due to the promising technological applications in various fields. Among these materials, transition metal oxides attracting much attention due to their fascinating electrical and chemical properties. In particular, due to the wide range of applications, SnO_2 in thin film form has engrossed considerable interest. It is an n type wide band gap semiconductor material with promising technological applications in various fields such as catalysis [1], gas sensors [2], solar cells [3], Li-ion battery [4], and supercapacitors [5]. The hydrous RuO_2 electrode with its extraordinary capacitance properties is the most suitable electrode material for supercapacitor. However, due to its rarity and high cost, wide usages of RuO_2 in supercapacitor applications are limited. Therefore, efforts have been made to find inexpensive materials such as MnO_2 [6], NiO [7], SnO_2 [8] and Co_3O_4 [9] for supercapacitor applications. Due to the non-toxic nature and low cost, SnO_2 is attracting much attention in the field of supercapacitors. SnO_2 is noted as co-material for RuO_2 due to its chemical stability and high electrical conductivity [10]. In studies of nanocrystalline SnO_2 as supercapacitor electrode, Mane et al. [8] have reported a specific capacitance of 40 F g^{-1} for electrochemically prepared SnO_2 electrodes.

Nanocrystalline SnO_2 thin films have been deposited by various chemical deposition methods such as chemical vapor deposition [11], sol–gel [12], spray pyrolysis [13], electrodeposition [7], Among the various chemical methods successive ionic layer adsorption and reaction (SILAR) is an excellent method for deposition of metal oxide thin films at sufficiently low temperature. In this method, thin films are obtained by immersing substrate into separately placed anionic and cationic precursor solutions. The SILAR method results in pinhole free and uniform deposits, since the basic building blocks are ions instead of atoms. The various advantages of SILAR method are; it is simple and inexpensive which comprises excellent material utilization efficiency, good control over deposition process along with film thickness and convenient for large area deposition on virtually any type of substrate [14,15]. Solution based low temperature SILAR method for deposition of metal oxides may offer low cost technology for production of electrodes for supercapacitors.

In the present work, we report synthesis of nanocrystalline SnO_2 thin films by SILAR method on glass and stainless steel substrates. The films are air annealed at 673 K for 2 h. The annealed films were characterized for their structural, surface morphological, optical properties. Further, the cyclic voltammetric study was carried out in order to study the supercapacitor properties.

2. Experimental

2.1. Preparation of SnO_2 thin films

The SnO_2 thin films were deposited by SILAR method on glass and stainless steel substrates. For the deposition, the cationic precursor was aqueous solution of $SnCl_2$ (0.05 M), as a source of Sn^{4+} ions and anionic solution was 1% H_2O_2 (pH 9) solution as a source

* Corresponding author. Tel.: +91 231 2609225; fax: +91 231 26092333.
E-mail address: l.chandrakant@yahoo.com (C.D. Lokhande).

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doi:10.1016/j.apsusc.2011.06.043

of oxygen ions. Both the cationic and anionic precursor solutions were kept at room temperature (~300 K). The previously cleaned substrate when immersed in the $SnCl_2$ solution the stannic species are adsorbed on the surface of the substrate. After immersion of substrate in 1% H_2O_2 solution, the reaction occurred to form SnO_2. The adsorption time required to adsorb the stannic species on the substrate was optimized to 20 s and the reaction time for stannic species to react with 1% H_2O_2 solution to form SnO_2 was optimized to 40 s. These two steps complete one cycle for formation of SnO_2 layer. Such cycles were repeated to increase the overall film thickness. The as deposited films were air annealed at 673 K for 2 h to remove hydrous content.

2.2. Characterization techniques

To study the structural property of SnO_2 films, X-ray diffraction patterns were obtained using a Philips (PW-3710) diffractometer with a Cr Kα (λ = 2.2870 Å) target. The FT-IR spectrum of the sample was obtained using PerkinElmer, FT-IR spectrum one unit. The microstructure of the films was observed using Scanning electron microscopy (JEOL, JEM-6360, Japan). Static water contact angle measurement was carried out using RameHart Instrument Co., USA equipped with CCD camera. The transmission electron micrograph was obtained by Jeol JEM-2100F unit. The electrochemical study was performed in a three-electrode configuration cell consisting of SnO_2 as a working electrode, platinum as a counter electrode and saturated calomel electrode (SCE) as a reference electrode.

3. Results and discussion

3.1. Reaction mechanism

The mechanism of formation of SnO_2 film can be elucidated as follows. To prepare clear cationic solution, 0.05 M $SnCl_2{\cdot}2H_2O$ was dissolved in concentrated hydrochloric acid and the mixture was kept for heating at 363 K for 5 min. The effect of addition of HCl on the oxidation state of Sn is described in the detail by Fang et al. [16]. Without addition of HCl in $SnCl_2$ there is formation of $Sn_4(OH)_2Cl_6$ colloidal particles as a result of the hydrolysis of $SnCl_2$. The reaction proceeds as,

$$4SnCl_2 + 2H_2O \rightarrow Sn_4(OH)_2Cl_6 + 2HCl \quad (1)$$

The $SnCl_2$ solution is transparent after HCl, indicating that no $Sn_4(OH)_2Cl_6$ colloidal particle exists, and tin composition exists as Sn^{2+} cations in the $SnCl_2$ solution. These Sn^{2+} cations were adsorbed on the substrate surface immersed in it. After immersing the substrate in dilute H_2O_2 solution Sn^{2+} cations were oxidized to Sn^{4+}. The pH of the H_2O_2 solution is made basic (pH 9) therefore the

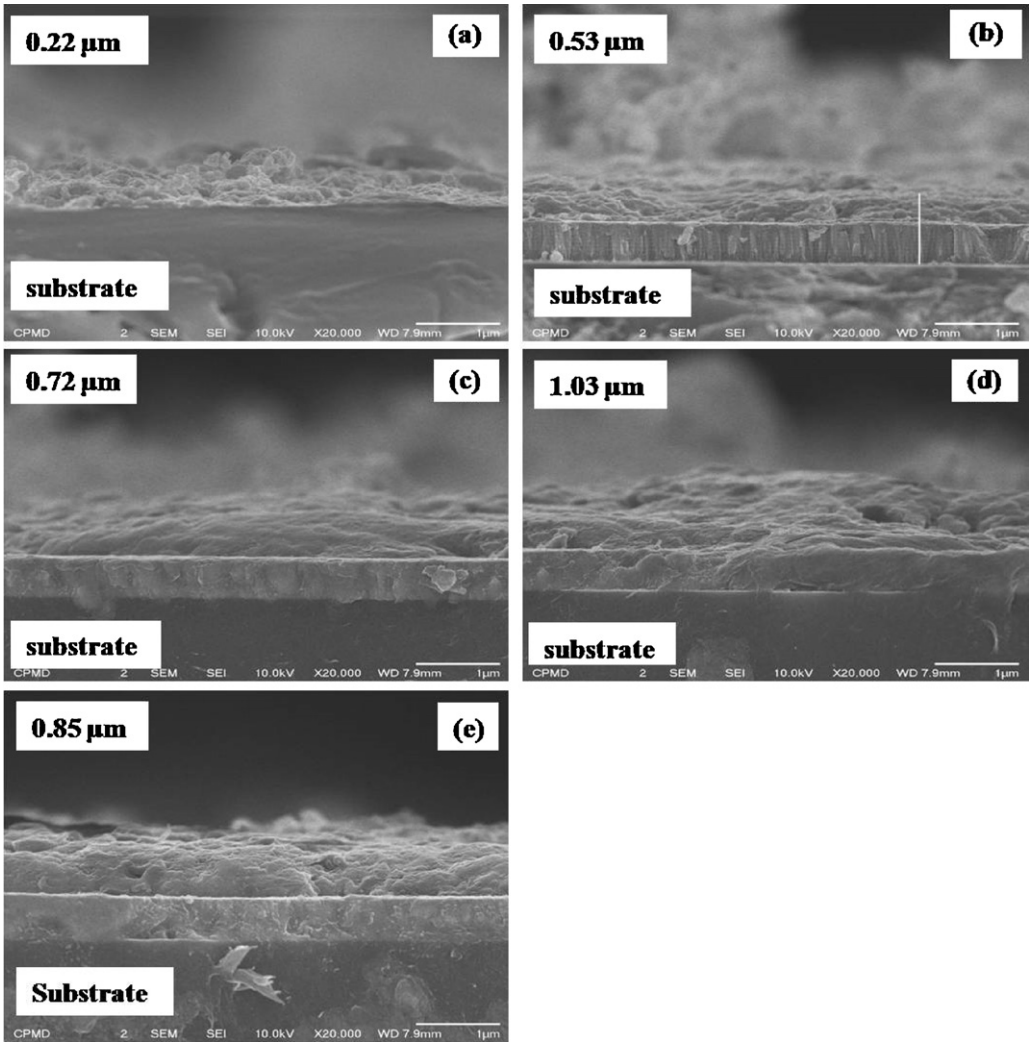

Fig. 1. The cross sectional SEM images of SnO_2 thin films with, (a) 25, (b) 35, (c) 50, (d) 75 and (e) 100 deposition cycles.