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ScienceDirect
Applied Surface Science 253 (2007) 8560–8567
applied surface science
www.elsevier.com/locate/apsusc

Synthesis of electrochromic tin oxide thin films with faster response by spray pyrolysis

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Received 24 March 2007; received in revised form 17 April 2007; accepted 17 April 2007
Available online 24 April 2007

Tin oxide thin films have been synthesized via pyrolysis of tri-*n*-butyl tin acetate solution at various substrate temperatures. The effect of substrate temperature on electrochromic properties is studied by electrochemical cyclic voltammetry and chronoamperometry. The films deposited at various substrate temperatures (450, 475 and 500 °C) were polycrystalline and their preferred orientation changes from (1 1 0) to (2 0 0). Electrochromic performance indicated faster colour/bleach kinetics with appreciable reversibility in spray deposited SnO_2 films. Maximum colouration efficiency and reversibility was attained for the sample deposited at 500 °C. All the spray deposited SnO_2 thin films showed long term electrochemical stability in proton containing electrolyte.

Keywords: Tin oxide; Thin films; Electrochromism; Spray pyrolysis technique

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1. Introduction

Tin oxide (SnO_2) is a multifaceted transition metal oxide having diverse uses in optical technology [1], consequently leading to almost inexhaustible literature [2]. SnO_2 thin films synthesized by using plethora of deposition techniques have been successfully demonstrated as transparent conductors, optical windows for the solar spectrum, stability resistors, touch-sensitive switches, digital displays, electrochromic display devices, gas sensors and for optoelectronic applications [3–8], due to their outstanding properties. Recently novel nanostructures of SnO_2 have been demonstrated [9–12].

Electrochromism of SnO_2 films have recently been described by Orel et al. [13] and Olivi et al. [14], who prepared samples by dip coating. Isidorsson et al. [1] have prepared SnO_2 films by dc sputtering. They discussed the importance of various properties that SnO_2 should exhibit for attaining pronounced electrochromism. The SnO_2 thin films with preferred orientation along (1 0 0) plane are known to exhibit higher gas sensitivity and those along (2 0 0) plane exhibited higher electrical conductivity [15,16]. It is thus anticipated that the electrochromism (EC) and hence the colouration efficiency (CE) would also be dependent on crystallinity and preferred orientations. SnO_2 easily adopts dual valency of (II) and (IV) upon reduction [17] or a mixture of valencies (Sn, Sn^{2+}, and Sn^{4+}) upon partial reduction [18]. The EC in SnO_2 thin films has been reported to be due to $Sn^{II} \rightarrow Sn^{IV}$ transition [19]. The electrochromic SnO_2 thin films have been synthesized by different methods [20–24]. The details of their processing parameters, charge storage capacity, cyclic voltammetry (CV) features and plausible EC mechanism are given in Table 1. The structural, electrical and optical properties of spray deposited tin oxide thin films have been discussed in our earlier publication [25]. In this investigation, we have employed spray pyrolysis technique for the synthesis of electrochromic SnO_2 thin films at different substrate temperatures (T_{pyr}) and studied the effect of T_{pyr} on crystallinity and electrochromic properties. The deposition of the films has been carried out from the pyrolysis of tri-*n*-butyl tin acetate (TBTA), which has three butyl groups and one acetoxy group in a molecule, dissolved in methanolic solvent.

2. Experimental

The spraying solution was prepared by dissolving TBTA [Tri-*n*-butyl tin acetate, AR grade quality, Merck Make, 98.7% purity $(C_4H_9)_3Sn(OOCCH_3)$] in methanol. A methanolic

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doi:10.1016/j.apsusc.2007.04.029

Table 1
Survey of electrochromic tin oxide thin films

Deposition method	Nature of the films	Charge storage	CV features	Electrochromic mechanism	Remarks	Ref.
RF magnetron sputtering	Polycrystalline: D.P. = 4 mTorr (dense); D.P. = 30 mTorr (porous); $t = 0.22–0.32\ \mu m$ undoped	$\Delta Q = 1–15\ mC/cm^2$ in $LiClO_4$/PC electrolyte	$PW_1 = 1–2.5$ V (Li), $PW_2 = 2–4.5$ V (Li), voltammetry did not give evidence for longevity of the samples	$SnO_2 + xLi^+ + xe^- \rightarrow Li_xSnO_2$; absorption at $\lambda < 600$ nm and NIR is observed; $(CE)_{400\ nm} = 30\ cm^2/C$; $(CE)_{630nm} = 5\ cm^2/C$; $(CE)_{2000nm} = 75\ cm^2/C$	Porous films exhibit better EC	[1]
Dip-coating	Polycrystalline: D.T. = 140 °C; A.T. = 500 °C/1 h; $t = 1\ \mu m$ undoped	$\Delta Q_i = 4–10\ mC/cm^2$; 0.1 M $LiClO_4$ + A.N.	Reduction peak at +0.05 V (SCE) corresponding to reduction of SnO_2, $D = 5.8 \times 10^{-9}\ cm^2/s$ at 0.6 V, PW = −0.5–1 V (SCE)	Predicted Li^+ insertion and change in transmittance $(CE)_{650\ nm} = 3\ cm^2/C$	SnO_2 is a prospective material for ECDs	[14]
Co-precipitation	Nanocrystalline SnO_2:Sb (highly doped porous) $t = 1.2\ \mu m$	$\Delta Q_d = -5\ mC/cm^2$; 0.2N $LiClO_4$/PC TBAP/PC	PW = −1.4 to +1.4 (NHE), CV featureless in TBAP/PC; increased current in $LiClO_4$/PC is observed; lack of well-defined peaks	Flips between colourless-blue; strong absorption in the blue is caused by $Sb^{3+} \rightarrow Sb^{5+}$ charge transfer transition; two reactions are proposed: 1. SnO_2: $Sb + xLi^+ + xe^- \rightarrow Li_xSn_{(1-2)}{}^{IV}Snx_{/2}{}^{II}$; 2. SnO_2: $Sb + xLi^+ + xe^- \rightarrow Li_xSnO_2$: $Sb_{(1-x/2)}{}^{V}Sb_{x/2}{}^{III}$, $(CE)_{650} = 18\ cm^2/C$	OD scales with the number of electrons injected; absorption by free carriers (NIR) is the dominant process contributing to EC; absorption in blue region is due to Sb^{III}-Sb^{V} charge transfer transition, which occur at the particle surface	[19]
Sol–gel (dip-coating)	Nanocrystalline SnO_2 and Sb: SnO_2 (0–10 at.%); A.T. = 150, 300 and 500 °C; $t = 0.03–0.1\ \mu m$	$Q_c = -0.36–6.4\ mC/cm^2$, $Q_a = 0.15–6\ mC/cm^2$, 0.1 M $LiClO_4$ + water and 0.1 M $LiClO_4$ A.N.	PW = +0.2 to −0.8 V (SCE); absence of well defined peaks; $x = 0.01$ for SnO_2, $x = 0.02$ for Sb:SnO_2	EC is due to $Sn^{4+} \rightarrow Sn^{2+}$ reduction; no contribution by ‘Sb’ ions to the EC	ˋSb’ doping results in increased conductivity, which is responsible for large charge capacity of doped films	[13]
Sol–gel	Nanostructured SnO_2:Sb (highly doped) $t = 2.5–3.0\ \mu m$	$\Delta Q = -3.8\ mC/cm^2$ $LiClO_4$/PC	PW = +1.4 V to −0.8 V (Ag/AgCl); no well-defined peaks capacitive behaviour; electrochemical reactions are observed only when applied potential is more negative than V_{fb}	$(CE)_{700\ nm} = 25\ cm^2/C$; $(CE)_{350nm} = 60\ cm^2/C$; two reaction mechanisms proposed: 1. $SnO_2 + 2H^+ + 2e^- \rightarrow SnO + H_2O$; 2. $SnO_2 + 2xH^+ + 2xe^- \rightarrow H_2x\ Sn_x{}^{II}\ Sn_{1-x}{}^{IV}O_2$	Reaction (1) is limited to the surface layer of nanostructured electrode; reaction (2) extends in to the bulk of the electrode H^+ and Li^+ ions intercalate into SnO_2 at sufficiently negative applied potentials	[20]
Sol–gel	SnO_2 and Mo:SnO_2 thin films	$Q_c = -3.1\ mC/cm^2$, $Q_a = -1.2\ mC/cm^2$ for undoped SnO_2, $Q_c = -32.2\ mC/cm^2$, $Q_a = 29.8\ mC/cm^2$ for Mo:SnO_2 in $LiClO_4$ electrolyte	PW = ±1.5 (SCE)	Mo:SnO_2 films exhibit largest charge storage capacity, owing to its amorphicity.	Mo doped SnO_2 films exhibit reversible charging–discharging behaviour; due to their excellent storage capacity they are promising as CE for ECDs	[21]
Pulsed laser deposition	SnO_2:Sb (40% doping) $t = 370$ nm porous-film1; 550 nm dense-film2	$Q_c = 34\ mC/cm^2$ and $Q_a = 10\ mC/cm^2$ in 0.1 M H_3PO_4	1. PW = ±0.8 V (SCE) reversible, well-defined peaks observed; $E_{pa} = 0.05$ V (SCE) and $E_{pc} = -0.65$ V (SCE); 2. PW = −0.6 V to 1.5 V (SCE) coupled of broad peaks centered on 1.0 V and −0.2 V appeared; 3. PW = ±0.3 V (SCE) revealed pseudo-capacitive behaviour	$(CE)_{550\ nm} = 15\ cm^2/C$ for porous films; $(CE)_{550\ nm} = 26\ cm^2/C$ for dense films; $(\Delta OD)_{650nm} = 30$ for film1; $(\Delta OD)_{650\ nm} = 30$ for film2; contrast ratio for film1 = 2.3 at 550 nm and for film2 = 2.1 at 550 nm	EC behaviour depends on film morphology; the electrode can act both as switching electrode and counter electrode in different potential windows	[23]