Electrochimica Acta 156 (2015) 283–288

Contents lists available at ScienceDirect

Electrochimica Acta

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

Electrochemical Synthesis of PbO_2, Pb_3O_4 and PbO Films on a Transparent Conducting Substrate

Christopher G. Poll, David J. Payne*

Department of Materials, Imperial College London, South Kensington, London, SW7 2AZ, United Kingdom

ARTICLE INFO

Article history:
Received 14 November 2014
Received in revised form 4 January 2015
Accepted 5 January 2015
Available online 7 January 2015

Keywords:
PbO_2
Pb_3O_4
PbO
Thin Film

ABSTRACT

Through electroplating and thermal decomposition by annealing at various temperatures in an oxygen environment, films of PbO_2, Pb_3O_4 and PbO have been synthesised on transparent conducting substrates of indium tin oxide coated glass. Of these films, Pb_3O_4, α-PbO and β-PbO have a phase pure crystal structure. These films are formed as either nano-scale particles or complete films depending on the electroplating conditions. The complete films demonstrate excellent surface coverage with a thickness of the order of a few microns. The films have been characterised through a combination of x-ray diffraction, scanning electron microscopy and surface profilometry.

1. Introduction

Lead oxide exists in two oxidation states, Pb^{4+} (PbO_2) and Pb^{2+} (PbO), and also with multiple mixed valence states in between ($Pb_{12}O_{19}$, $Pb_{12}O_{17}$, Pb_3O_4) [1]. In both the 4^+ and 2^+ oxidation states lead oxide takes two crystalline polymorphs, tetragonal (β-PbO_2, α-PbO) and orthorhombic (α-PbO_2, β-PbO) [2–5].

PbO_2 has, since 1860, found wide-spread use as an electrode material in the lead acid battery [6], which is utilised world-wide in the ignition process of the internal combustion engine in motor vehicles. PbO_2 is a well studied material from an electrochemical point-of-view with the various phases and surface morphologies comprehensively reviewed [7]. Recent work, undertaken through a combination of photoemission, neutron diffraction and density functional theory has identified the metallic nature of PbO_2 to be due to partial filling of conduction band states due to oxygen vacancies [8–11].

PbO has been demonstrated as a photoactive layer in Schottky-type photovoltaic devices [12,13] and as a surface modification layer in inverted polymer solar cells [14]. α-PbO is a material that has potential in photovoltaic application due to its band gap of 1.9 eV [15,16] whilst β-PbO has suitability as a surface modification layer for lowering work functions [14]. The main issue associated with the incorporation of lead oxide in photovoltaic devices is the fabrication of the lead oxide layer. In the work to date the PbO has been evaporated onto substrates, this however is not a favourable technique due to the health concerns when volatilising lead. Evaporating lead and lead oxide results in contamination of the evaporation system, and hence lead contaminants being present in subsequently synthesised materials. To circumvent this issue it is necessary to have an evaporation system solely for the purpose of lead-based material synthesis, this approach however is certainly not a cost-effective one. Whilst the electrochemical preparation of PbO_2 has been thoroughly studied [7], very little work has been undertaken on the electrochemical synthesis of PbO films [17,18]. In this report we present a novel, low-cost method for the synthesis of PbO and Pb_3O_4 films on transparent conducting substrates by electroplating films of PbO_2 and then annealing in an air. We have produced films of various oxidation states and polymorphs of lead oxide. Through careful control of the initial electroplating conditions, and the annealing temperatures, we have successfully synthesised films of PbO_2, Pb_3O_4 and PbO on indium tin oxide (ITO) coated glass, of these films Pb_3O_4, α-PbO and β-PbO demonstrate phase purity.

2. Experimental

PbO_2 films have been electroplated onto ITO (8-12 Ω/square, Sigma-Aldrich) from a solution of 375 mM $Pb(NO_3)_2$ + 6.25 mM HNO_3, which has previously been shown to be suitable for the electrodeposition of PbO_2 [8,9,19,20], maintained at 60 °C using a water bath. The $Pb(NO_3)_2$ ($\geq$99.0% purity) and HNO_3 were used as supplied from Sigma-Aldrich and diluted with ultra-pure Milli-Q water. The ITO electrode, assigned as the anode, was prepared

---

* Corresponding author. Tel.: +44 (0)20 759 42585.
E-mail address: d.payne@imperial.ac.uk (D.J. Payne).

http://dx.doi.org/10.1016/j.electacta.2015.01.019
0013-4686/

through ultrasonic cleaning in acetone, isopropanol and ultra-pure Milli-Q water and dried with N_2 gas, a Pt electrode was used as the cathode. A current density of 10 mAcm^{-2} was applied for various plating times using a Keithley 2200-30-5 DC power supply. This current density was chosen as it provided films with optimal surface coverage. Following the electroplating the PbO_2 films were rinsed of any residual solution using Milli-Q water and dried with N_2 gas. The films were then thermally decomposed using a tube furnace at various temperatures in air for 6 hours.

The crystal structure and oxidation state of the films was studied using x-ray diffraction (XRD) with a Panalytical X'Pert Pro X-Ray Diffractometer. The assignment of diffraction peaks has been undertaken using the Inorganic Crystal Structure Database (ICSD) (icsd.cds.rsc.org). Scanning electron microscopy (SEM) images have been recorded with a JEOL JSM5610LV electron microscope and high-resolution scanning electron microscopy (HR-SEM) images with a LEO Gemini 1525 electron microscope. Film thicknesses have been measured using a Dektak profilometer.

3. Results and Analysis

PbO_2 films were electroplated for incremental time periods of 1 second, 2 seconds, 5 seconds and 5 minutes. The films were visually smooth and demonstrated excellent surface coverage. The film colour ranged from a translucent very light brown colour following 1 second of growth through to a dark brown colour following extended growth time. Films grown for 5 minutes were a dark grey / black colour and opaque in appearance. The XRD patterns of these films are presented in Fig. 1.

It can be seen that following 1 second of growth only minimal PbO_2 is present, which appears in the β-phase, however as the growth time continues through 2 and 5 seconds these β-PbO_2 peaks become more intense. The observed In_2O_3 peaks are present due to the ITO substrate. Following 5 seconds of growth, as well as there being β-PbO_2 present, there is additionally α-PbO_2 beginning to appear. After 5 minutes of growth the film has a mixed phase of both α- and β-PbO_2, with the β-PbO_2 dominating the diffraction pattern, at this point there are additionally no diffraction peaks from the In_2O_3, suggesting a thick and complete surface coverage.

The film thicknesses, measured by profilometry, were determined to be 99 ± 10 nm, 134 ± 6 nm, 200 ± 14 nm and 3.2 ± 0.2 μm for the films grown for 1 second, 2 seconds, 5 seconds and 5 minutes respectively. The thicknesses were measured at multiple points on each film with the average then calculated. The uncertainty represents the standard error in the mean. SEM and HR-SEM images of the films are presented in Fig. 2, it can be seen that for the shorter plating times (1, 2, 5 seconds) the films are structured as a series of PbO_2 particles on the ITO substrate, however following the longer 5 minute electroplating a complete film of micro-scale crystallites has formed.

The particles appearing in the HR-SEM images can be attributed to PbO_2, as when recording a control image of bare ITO these were not present. The PbO_2 particles can be seen to grow with increased electroplating time. This result suggests that it is more energetically favourable for the PbO_2 to deposit on PbO_2 nucleation sites rather than directly onto the ITO. The presence of In_2O_3 in the XRD patterns in Fig. 1 for the films electroplated for 1 second, 2 seconds and 5 seconds is clearly due to incomplete surface coverage and large areas of ITO still being exposed. By 5 minutes however there is complete coverage and the films are considerably thicker. The XRD patterns of the PbO_2 distinctly demonstrate polycrystalline films, the SEM images reflect this with the large volume of crystal grains observed with lots of variation in their orientations.

It is well known that β-PbO_2 reduces to α-PbO at 572 °C for powdered samples [9,22,23]. It is also reported that PbO_2 can be reduced to multiple other oxidation states ($Pb_{12}O_{19}$, $Pb_{12}O_{17}$, Pb_3O_4 and PbO) at temperatures in the range of 293 °C to 605 °C [1]. In the work presented here PbO_2 films electroplated for 5 minutes have been reduced in a tube furnace under an air environment at 500 °C, 515 °C, 540 °C, 572 °C, 600 °C and 620 °C for 6 hours. The resulting films ranged in colour from red through to pale yellow, photographs of these can be seen in Fig. 3.

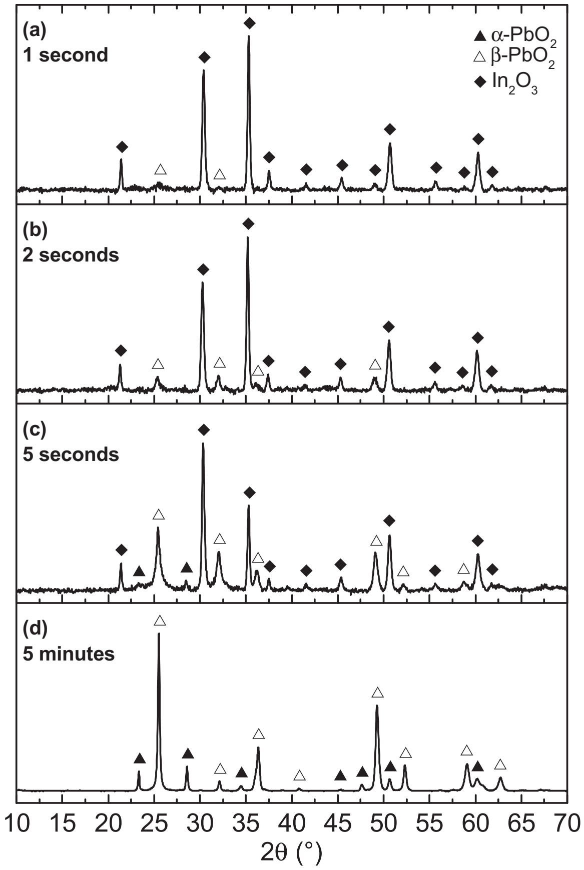

Fig. 1. XRD patterns of PbO_2 films electroplated from 375 mM $Pb(NO_3)_2$ + 6.25 mM HNO_3 with a current density of 10 mAcm^{-2} on ITO for (a) 1 second, (b) 2 seconds, (c) 5 seconds and (d) 5 minutes. The XRD peak assignment has been undertaken using the ICSD with reference patterns of α-PbO_2 [2], β-PbO_2 [3] and In_2O_3 [21].

Fig. 4 shows the XRD patterns of the films reduced at each of the temperatures in the range 500 °C to 620 °C. It can be seen that the films annealed at 500 °C, 515 °C and 540 °C all reduce from PbO_2 to Pb_3O_4, those reduced at 572 °C and 600 °C reduce to phase pure β-PbO, and the film annealed at 620 °C reduces to a mixed phase of α- and β-PbO. The oxidation state of these films corresponds to the colours observed in Fig. 3, Pb_3O_4 is often referred to as “red lead” due to its red colour and β-PbO is often yellow. Previously this reduction method has been applied to the synthesis of films of Pb_3O_4 on nickel substrates [25,26], and recent work has demonstrated the electrochemical reduction of PbO_2 films on transparent substrates [27], however to our knowledge this is the first reported observation of the synthesis of PbO films by this technique, as well as being the first reported observation of Pb_3O_4 and PbO films being produced on a transparent conducting oxide by thermal reduction of PbO_2 films.

SEM images of the PbO and Pb_3O_4 films synthesised by the reduction of PbO_2 films at 515 °C, 540 °C, 572 °C and 600 °C are presented in Fig. 5. The films appear similar to that of the PbO_2 film electroplated for 5 minutes presented in Fig. 2 (d), with the films being structured as a series of micro-scale grains with various