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Freestanding SnO_2 films produced with anodic polarization in acidic media containing colloidal tin hydroxides

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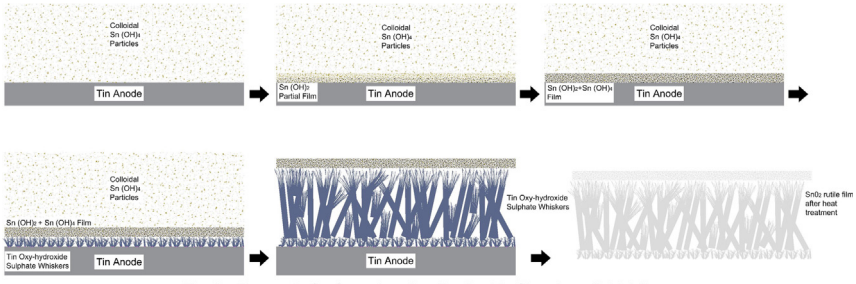
HIGHLIGTS

- Thick anodic oxide films are produced on Sn in $Sn(OH)_4$ containing H_2SO_4 solutions.
- Under the semi permeable anodic oxide layer tin cations are super-saturated.
- Sn oxyhydroxy sulfates crystallized in whisker form in the supersaturated zone.
- High surface area films are easily detached from surface without loosing integrity.
- High surface area thick detached films are converted into SnO_2 by heat treatment.

GRAPHICAL ABSTRACT



Production route for free-standing tin dioxide films in colloidal tin hydroxide containing acidic electrolyte by anodic oxidation

ARTICLE INFO

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ABSTRACT

Within the scope of the study, we aimed to develop a strategy for production of thick self -supporting tin oxide films with high surface area by anodic oxidation of metallic tin in acidic solutions. This has not been achieved before because of the highly porous and non-adherent nature of the oxidation products and high dissolution rate of tin in acidic solutions. Entrapment of the gelatinous colloidal tin hydroxides in the film during anodic oxidation exerted the necessary effect for decreasing the permeability of the oxide and dissolution of tin. Below this adherent and semi permeable film, a tin ion supersaturated zone was created, enabling the whisker type growth of complex tin oxyhydroxides at the metal/oxide interface. Colloidal +4 valent acid insoluble tin hydroxides are prepared by oxidation of dissolved Sn^{+2} ions in sulfuric acid solution with H_2O_2. Moreover by utilizing this approach growing 100–150 μm thick layers was possible, which were easily detached as free standing film from the underlying tin anode. The structure, chemistry and morphology of the films produced by anodic oxidation in acidic solutions were determined by using micro Raman spectroscopy, X-Ray diffraction (XRD) and SEM. Since the films produced by the above stated method consisted of a complex mixture of oxides, hydroxides and sulfates, annealing treatment was applied to convert these structures into stoichiometric SnO_2.

1. Introduction

Tin oxides are thermodynamically stable materials that can exhibit p and n type semiconducting behavior depending on their stoichiometry. These properties make them attractive material for a variety of applications including chemical sensors, supercapacitors and lithium ion batteries. In some of these applications these materials have already found industrial use. In all of these applications, increase of the surface

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area is one of the most widely used approaches for developing the performance of them [1–3]. Physical vapor deposition [4] vapor transport [5], solution and spray techniques [6], hydrothermal [7] and electrochemical methods have been used for producing large area SnO_x materials. Electrochemical methods for oxidizing tin metal surfaces to grow tin oxide layers is a decent alternative to these methods because of its lower cost and suitability for large area and continuous production; however, the complex dissolution mechanism of tin prevents the growth of thick continuous layers [8]. According to Sn−H_2O Pourbaix [9] diagram tin passivates in neutral solutions, hence applying anodic oxidation in neutral solutions results in dense but ultra-thin films. Anodic oxidation in acidic solutions can be a good alternative for the production of tin oxides since during anodic polarization of metallic tin in acidic solutions it is possible to produce acid insoluble Sn^{+2} and Sn^{+4} oxides or hydroxides dependent on the anodic oxidation potential. However, as already been observed in previous studies [10–12] high dissolution rate of tin in acidic solutions and highly porous and non-adherent structure of the oxides does not allow the production of a continuous oxide layer on their surface. Thus if one can develop a strategy for lowering the dissolution rate of tin and/or increasing the density and adherence of the oxide layer, it may become possible to grow thick tin oxide layers by anodic oxidation of metallic tin in acidic solutions.

The aim of this study is to develop a strategy for production of thick tin oxide films with high surface area using anodic oxidation of tin in acidic solutions by using two different approaches. Namely by addition of tin ions to the solution for decreasing the dissolution rate of tin and by decreasing the permeability of the self-formed oxyhydroxide layer by the addition of gelatinous tin hydroxides into the electrolyte that has not been utilized in former studies.

Results of the study revealed the critical role of the presence of tin hydroxides in the electrolyte for attaining thick oxide layers with a whisker like growth on tin surface. Relying on the results obtained in different solutions a mechanism based on the role of tin hydroxides on the integrity and permeability of the anodic oxide films was proposed. The semipermeable stable anodic oxide film formed on the tin surface resulted in the supersaturation of tin ions under this layer that lead to the crystallization of complex tin oxyhroxides in whisker form. These films had the ability to be converted into crystalline SnO_2 by suitable heat treatments. Overall the method proposed with its simplicity could be an alternative to other whisker type tin oxide production methods [13].

2. Experimental

For the anodic oxidation studies of tin, high purity tin foils (Sn 99.9%) were used with an active area of 2 cm^2. Anodic polarization studies were conducted in a 500 ml volume water jacketed membrane cell where the electrolyte concentration at the cathode side was kept constant as 30 g/l H_2SO_4. In all the experiments temperature of the electrolyte was held at 15 ± 1 °C. The counter electrode was selected as stainless steel (316 l) with the surface area of 5 cm^2. Vigorous air agitation was applied during polarization for avoiding excessive heating of the substrates. Polarization studies have been conducted by using a potentiostat (Voltalab PGZ 301 Voltammetry) both in potentiodynamic and potentiostatic modes. Hg/Hg_2SO_4 electrode (Monokrystaly RME 121) was used as reference electrode. Anodic polarization studies were conducted in 3 different electrolytes named as Solution A, B and C using potentiodyamic polarization with a scan rate of 0.25 mV/s. Solution A was used as a control group, which consisted of 30 g/l sulfuric acid. Solution B was prepared by adding 30 g/l dissolved tin to the same solution to limit the dissolution rate of the tin anode and enhance the film formation. Solution C was prepared by the precipitation of tin as gelatinous colloidal $Sn(OH)_4$ particles in solution B by introducing H_2O_2. The addition of H_2O_2 was carried out until the detected dissolved tin content in solution was 0 g/l. Ionic tin content of the solution is determined by iodometric titration using starch indicator. The chemistry, structure and morphology the oxide films obtained after anodic polarization in different electrolytes and their heat treated versions was characterized with micro Raman spectroscopy (Horiba Yvon HR800 UV) using He-Ne laser with 632.8 nm line as excitation source with a laser power of 3 mW and Scanning Electron Microscope (Jeol JSM 5410). After the chemical and structural characterization steps, samples are subjected to heat treatment at 800 °C for 3 h under atmospheric conditions to convert the complex oxide-hydroxide film to SnO_2. The structure of the tin oxyhydroxides were also determined with XRD using Cu Kα radiation (Philips PW 3040) in as deposited and heat treated state.

3. Results and discussion

3.1. Selection of anodic oxidation potential

Anodic oxidation of the metallic tin surface in all solutions was performed at 650 mV vs $Hg/HgSO_4$ at 15 °C. The reason for selecting of this potential can be explained with the help of anodic polarization curve of Sn in the sulfuric acid solution (Fig. 1). In this polarization curve, the first peak appearing at - 850 mV is associated to the active dissolution of Sn to Sn(II) species and the second one at −770 mV, is related to the electro-formation of Sn(IV) containing compound. First

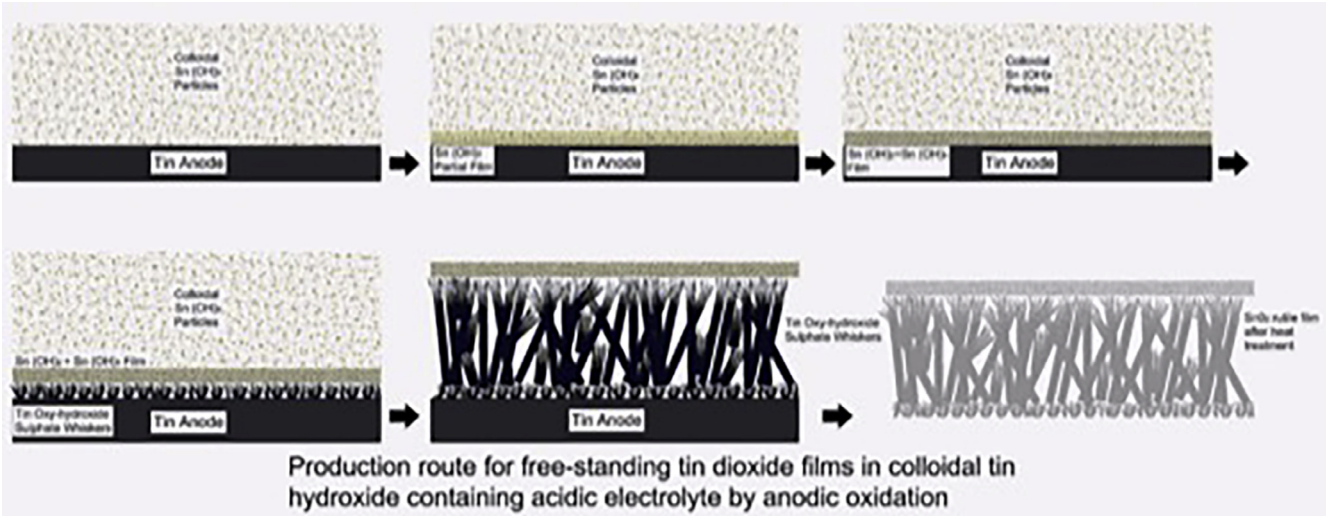

Fig. 1. Linear voltammogram of tin metal in 30 g/l H_2SO_4 solution at 15 °C determined using a scan rate of 0.25 mV/s.