



Controlled synthesis of nanoporous tin oxide layers with various pore diameters and their photoelectrochemical properties



Leszek Zaraska^{a,*}, Karolina Gawlak^a, Magdalena Gurgul^a, Damian K. Chlebda^b,
Robert P. Socha^c, Grzegorz D. Sulka^a

^a Department of Physical Chemistry and Electrochemistry, Faculty of Chemistry Jagiellonian University in Krakow, Gronostajowa 2, 30-387 Krakow, Poland

^b Department of Inorganic Chemistry, Faculty of Chemistry Jagiellonian University in Krakow, Gronostajowa 2, 30-387 Krakow, Poland

^c Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland

ARTICLE INFO

Article history:

Received 31 July 2017

Received in revised form 18 September 2017

Accepted 18 September 2017

Available online 20 September 2017

Keywords:

Tin oxide

Porous films

Anodization

Alkaline electrolyte

Photoelectrochemical properties

ABSTRACT

Porous anodic tin oxide films with various pore diameters were synthesized by one-step anodization of Sn foil in 1 M NaOH followed by 2 h of annealing at 200 °C. When the potential of 2 V was applied during anodization, oxide layers with ultra-small nanochannels having diameter slightly above 10 nm were obtained, and an average distance between neighboring pores was ~20 nm. On the contrary, applying the potential of 4 V resulted in the formation of anodic films with much wider channels (~40 nm in diameter) and larger pore spacing (~55 nm). The composition of as formed samples was examined by XRD and XPS measurements. The as obtained anodic films were amorphous even after annealing. However, the greater Sn²⁺ ion content was observed for the sample anodized at 4 V. In consequence, the porous oxide layer grown at the higher potential exhibited a red-shifted absorption edge as well as the lower optical band-gap in comparison to the sample synthesized at 2 V. This fact was ascribed to a higher content of Sn²⁺ defects which are mainly responsible for a significant enhancement of photoelectrochemical activity of the material in the visible range. However, photoelectrochemical activity in the visible range was noticeable for anodic tin oxide films independently of the anodizing potential. We believe that such kind of self-supported electrodes can be promising candidates for photocatalytic and photoelectrochemical applications.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Among various materials that can be used for photoelectrochemical applications (e.g., photoelectrochemical water splitting), recently tin dioxide (SnO₂) has received considerable attention mainly due to its high electron mobility (almost two orders of magnitude higher than that of the most commonly used TiO₂) as well as the more positive conduction band edge potential [1]. In addition, further improvement in electron transport properties have been successfully demonstrated by using various nanostructures instead of bulk materials [2,3]. Moreover, hollow tubular structures can offer some other advantages such as better light-harvesting efficiency and enhanced separation of charge carriers [4].

Within this context, a direct generation of nanoporous tin oxide films with randomly distributed nanochannels by simple anodic

oxidation (anodization) of metallic Sn [5,6] seems to be a very promising strategy for the fabrication of SnO₂-based photoanodes [7–10].

However, the most important drawback of SnO₂ is its relatively high band gap (~3.6 eV) allowing the absorption of the UV light only. Therefore, to improve the energy conversion efficiency a band gap of semiconductor should be reduced in order to increase the absorption in the visible range. Band gap narrowing can be achieved for instance by the doping of oxide with some other elements. However, this often leads to lower thermal stability of the material and greater number of charge carrier recombination centers. In consequence, a significant attention has been recently paid on a self-doping approach, i.e. synthesis of non-stoichiometric metal oxides without incorporation of any impurity elements. For instance, it is widely recognized that a self-doping of SnO₂ nanostructures with Sn²⁺ ions can result in shifting the absorption band of such material to the visible region [11–15].

In addition, Palacios-Padros et al. proved recently that also porous anodic films formed on Sn foil during anodization in an electrolyte containing sulfide and fluoride ions consist of an

* Corresponding author.

E-mail address: zaraska@chemia.uj.edu.pl (L. Zaraska).

amorphous, non-stoichiometric SnO_x with a considerable content of Sn^{2+} defects, which are responsible for a significant enhancement of photoelectrochemical activity of material in the visible range [16,17]. Moreover, simple annealing has been reported as an effective way for the modification of photoelectrochemical properties by a precise tuning of both, the concentration of Sn^{2+} defects and sample crystallinity [16,17]. However, according to our best knowledge this is still the only one report showing the photoelectrochemical activity of electrodes in the form of anodic tin oxide on metallic Sn.

On the other hand, as we recently proved, crack-free nanoporous tin oxide layers with different nanochannel diameters can be obtained during anodization of Sn foil in NaOH electrolyte at low applied voltages [18]. As a continuation of that work, here we present, for the first time, the photoelectrochemical performance of two types of anodic tin oxide films differing in nanochannel diameters being a result of different applied anodizing potentials. A special emphasis is also focused on detailed characterization of the oxide growth itself as well as on possible correlation between anodizing conditions, morphology of anodic layer and, finally, its photoelectrochemical properties.

2. Experimental

The Sn foil (98.8%, GoodFellow) was used as a starting material. Detail information about substrate composition is given in table S1 (see Supplementary Information). Both, substrate pre-treatment and anodization procedures were described in our previous paper [18]. All anodizations were carried out in home-made Teflon cells in an aqueous sodium hydroxide solution (1.0 M) at potentials of

2 V and 4 V for various durations. Then, the samples were annealed in air at the temperature of 200 °C for 2 h with a heating rate of 2° min^{-1} using a muffle furnace (model FCF 5SHM Z, Czylok). The morphology of anodic tin oxide films was characterized using a field emission scanning electron microscope (FE-SEM/EDS, Hitachi S-4700). All structural features of oxide layers were determined directly from SEM images by using scanning probe image processor WSxM v.12.0 [19].

XRD diffraction patterns of the samples were registered using X-ray diffractometer Rigaku Mini Flex II (Japan) with monochromatic Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were scanned from 20° to 80°.

UV-Vis diffuse reflectance spectroscopy (DRS) spectra were collected using the AvaSpec-ULS3648 high-resolution spectrometer equipped with a high-temperature reflection probe (FCR-7UV400-2-ME-HTX, 7 400 μm fibers). As a light source, the AvaLight-D(H)-S Deuterium-Halogen Light Source was used. The spectra were registered in the range of 180–1050 nm. The spectrum of each sample is a result of 128 co-added scans. The instrument was controlled by AvaSoft v 9.0 software. The spectra were collected in ambient conditions.

X-ray photoelectron spectroscopy (ESCA/XPS) measurements were carried out using a system equipped with the hemispherical analyzer SES R4000 (Gammadata Scienta) with a Al $K\alpha$ source (1486.7 eV, 180 W). The analyzer was calibrated according to ISO15472:2010 standard. During the measurements, vacuum was kept at about 5×10^{-10} mbar and the analyzed surface area was about 3 mm^2 . The electron binding energy (BE) scale was calibrated relatively to C 1s at BE of 285 eV. The spectra were deconvoluted with a Voigt profiles (GL=30) while the background was

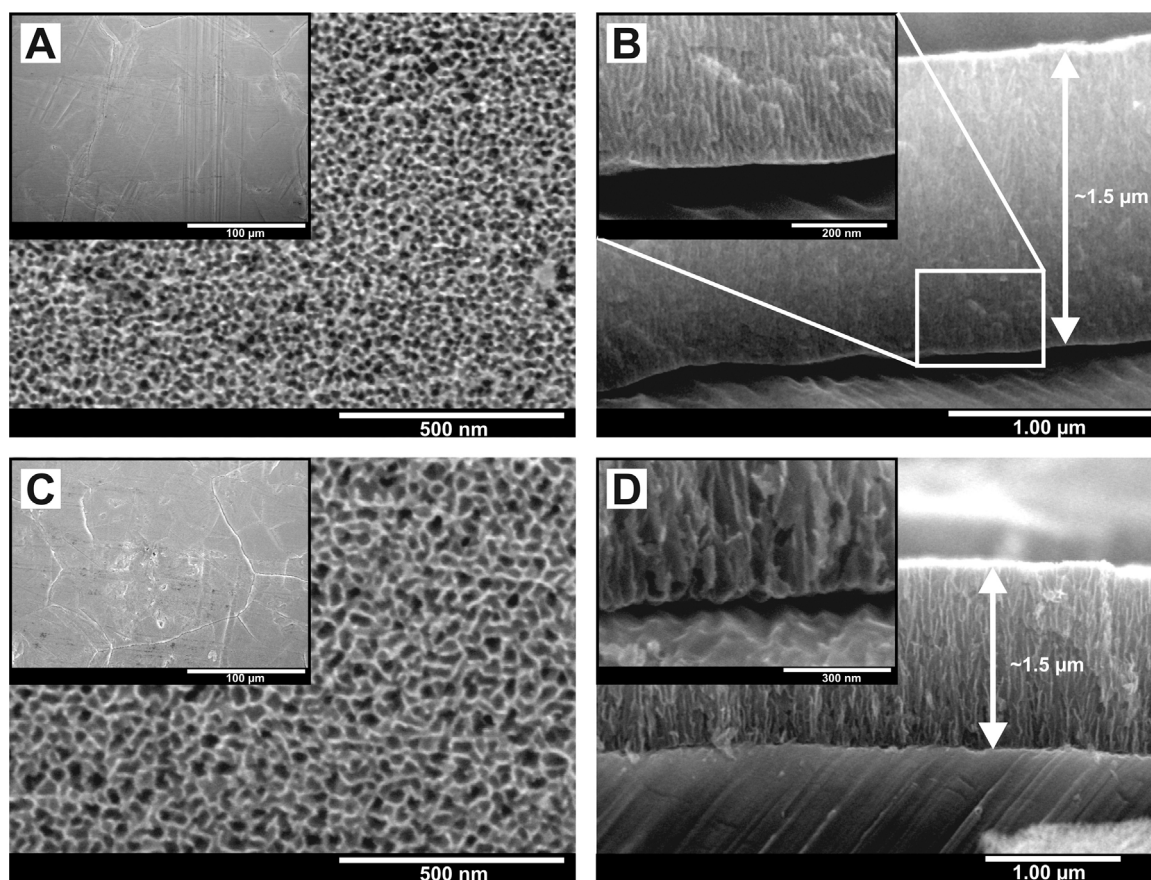


Fig 1. FE-SEM images of nanoporous tin oxide layers grown at the potential of 2 V (A, B) and 4 V (C, D). Top-views (A, C) and cross sectional views (C, D).

Download English Version:

<https://daneshyari.com/en/article/6469821>

Download Persian Version:

<https://daneshyari.com/article/6469821>

[Daneshyari.com](https://daneshyari.com)