Nanoporous tin oxides synthesized via electrochemical anodization in oxalic acid and their photoelectrochemical activity

Leszek Zaraska[a],[*],[1], Karolina Syrek[a], Katarzyna E. Hnida[b],[1], Michał Bobruk[c], Aleksandra Krzysik[a], Tomasz Łojewski[c], Marian Jaskuła[a], Grzegorz D. Sulka[a],[1]

[a] Department of Physical Chemistry and Electrochemistry, Faculty of Chemistry Jagiellonian University in Krakow, Ingardena 3, 30-060 Krakow, Poland
[b] AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, A. Mickiewicza 30, 30-059 Krakow, Poland
[c] AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Mickiewicza 30, 30-059 Krakow, Poland

ARTICLE INFO

ABSTRACT

Nanoporous tin oxide layers were obtained by one-step potentiostatic anodization carried out in 0.3 M $H_2C_2O_4$ followed by thermal annealing at temperatures in the range of 200–700 °C. The morphology and crystallinity of as obtained oxide layers were characterized by SEM, and XRD, respectively. It was confirmed, that after 10 min of anodic oxidation at the potential of 8 V, anodic tin oxide consists of a dense array of randomly distributed nanopores with an average diameter of about 50–60 nm. Moreover, such kind of porous structures is maintained during annealing at temperatures up to 500 °C. On the contrary, for higher annealing temperatures a transformation of nanoporous layers into particle-like structures was evident. A gradual increase of the crystallite size with increasing annealing temperature was also confirmed. Finally, photoelectrochemical properties of anodic tin oxide layers, annealed at temperatures in the range of 400–700 °C, were extensively investigated. The best photoelectrochemical performance with the maximum photocurrent densities of above 25 $\mu A\,cm^{-2}$ and conversion efficiency of about 30% was observed for sample annealed at 500 °C. Higher annealing temperatures result in a gradual decrease in photocurrent densities that can be attributed to the change in the sample morphology and decrease in electrochemical reaction sites. Optical band gap energies were determined on the basis of UV–vis reflectance spectra and photocurrent measurements, and a gradual increase in the band gap energy with increasing annealing temperature was confirmed.

1. Introduction

Recently, nanostructured materials based on tin dioxide (SnO_2) have become a subject of great scientific interest due to their many promising electronic, optical and photoelectrochemical properties, and a wide variety of potential applications including solid-state gas sensors [1,2], catalysis [2,3], or even Li-ion batteries [2,4]. This n-type semiconductor with a relatively wide band gap (E_g = 3.6 eV) can be also an attractive material for many photovoltaic applications [2]. Despite the lower conversion efficiency and higher electron recombination rates when compared to the most commonly used TiO_2, tin dioxide has received much attention as photoactive material due to its favorable properties such as much faster electron transport rates ($>100\,cm^2\,V^{-1}\,s^{-1}$) and more positive valence band potential. In addition, further improvement in electron transport properties and lower electron recombination rate can be achieved by using nanochannel or nanotube structures instead of randomly oriented nanomaterials [5,6].

Among many different methods proposed for the fabrication of nanostructured SnO_2 materials, a simple electrochemical anodic oxidation (anodization) seems to be a very promising strategy. This method, widely known for decades as an easy way to obtain nanoporous alumina or titania [7,8], has been recently successfully applied for synthesis of nanoporous layers on the surface of metallic tin [9]. Some reports on fabrication of nanostructured tin oxide layers by anodization in acidic [9–17], alkaline [5,18,19], and fluoride ions containing electrolytes [20,21] can be easily found in the literature. However, the photoelectrochemical performance of such kind of structures were sporadically investigated [5,6,21,22]. For instance, Teh et al. reported the use of photoelectrode based on porous anodic SnO_2 for dye-sensitized solar cells (DSSCs). The nanoporous layer were grown by one-step anodization in aqueous ammonia at a potential of 60 V and detached from the tin substrate

* Corresponding author at: Department of Physical Chemistry & Electrochemistry, Faculty of Chemistry, Jagiellonian University in Krakow, Ingardena 3, 30060 Krakow, Poland. Tel.: +48 12 663 22 64; fax: +48 12 634 05 15.
E-mail address: zaraska@chemia.uj.edu.pl (L. Zaraska).
[1] ISE member

by sonication. After annealing at 450 °C, a crystalline SnO_2 with a optical band gap of 3.15 eV was obtained. It was proved that DSSCs based on such kind of porous electrodes exhibit significantly better performance than that using spherical SnO_2 nanoparticles [5]. Very recently, Kim et al. demonstrated the photovoltaic application of vertically aligned tin dioxide nanochannel arrays synthesized by anodic oxidation of metallic tin in a 0.5 M oxalic acid solution [6]. The authors successfully applied such kind of nanostructured electrodes as photoanodes in DSSCs showing a quite reasonable conversion efficiency (1.29%) under back-side illumination [6]. On the other hand, Palacios-Padrós et al. have shown that controlled thermal annealing can be a feasible way to tune the photo-electrochemical properties of anodic tin oxide films by affecting the concentration of oxygen vacancies and Sn^{2+} defects in the oxide structure [21]. It was proved that the presence of Sn^{2+} defects can significantly enhance the photocurrent response in the visible range. However, it should be mentioned that only annealing temperatures up to 400 °C were examined by these authors due to the peeling off the anodic layers from the molten metallic substrate at higher temperatures.

In our previous papers we presented a detailed quantitative inspection of the effect of various anodizing conditions such as: anodizing potential, temperature and electrolyte concentration on the growth and structure of anodic tin oxides formed by anodization of Sn foils [16,17] and Sn layers deposited on Cu plates [14] in oxalic acid electrolytes. We also examined the effects of different cell geometry and type of Sn substrate on morphology of as grown oxide layers [17].

Here, we present a detailed inspection of photoelectrochemical properties of anodic tin oxides synthesized by one-step anodization carried out in a 0.3 M oxalic acid solution followed by thermal annealing at a temperatures in the range of 200–700 °C. A special emphasis is put on the correlation between annealing conditions, morphology, structure and photoelectrochemical performance of SnO_2 layers to find the optimal procedure allowing for the synthesis of such kind of materials offering the best photoelectrochemical efficiency. The dependences between photocurrent density, incident light wavelength and electrode potential were recorded for all obtained samples. Optical band gap energies were also calculated for all studied materials.

2. Experimental

2.1. Synthesis of nanoporous tin oxide layers

Nanoporous tin oxide layers were grown on the Sn surface via a simple anodic oxidation procedure described in our previous works [16,17]. Briefly, a low purity Sn foil (98.8%, Goodfellow) was used as starting material for anodization. At first, the substrate was cut into specimens with dimensions of about 0.5 × 3.0 cm. Before anodizing, Sn specimens were degreased by immersing in ethanol and acetone and dried, and the working surface of electrodes was defined using an acid-resistant paint. Then, the nanoporous tin oxide layers were obtained by a voltage-controlled one-step anodization carried out in 0.3 M oxalic acid at room temperature. The anodizing potential was 8 V and duration of the process was 10 min. All anodizations were carried out in a typical, two-electrode cell with vertically arranged electrodes without stirring of the electrolyte. A Pb plate with a surface area of about 6 cm² was used as a cathode, and the distance between both electrodes was about 2 cm. Just after anodization, the samples were rinsed with water and ethanol, and dried in the stream of warm air. As formed oxide was mechanically detached from the Sn substrate, and the anodizing-detaching procedure was repeated several times in order to obtain a sufficient amount of the nanoporous tin oxide

powder. As synthesized material was then annealed in the air at a temperature ranging from 200 to 700 °C using a muffle furnace with a heating rate of 2 °C min⁻¹.

2.2. Characterization of nanoporous anodic tin oxides

The morphology of as obtained nanoporous tin oxide layers was analyzed by a Field Emission Scanning Electron Microscope (FE-SEM/EDS, Hitachi S-4700 with a Noran System 7). The crystallinity and phase composition of the obtained SnO_2 nanostructures were examined with a Panalytical Empyrean diffractometer in a 10–90° 2θ range with a step size of 0.013° at 25 °C. As X-ray source Cu-lamp (λKα = 1.5406 Å) was used. For the analysis of diffraction patterns, the ICDD (International Centre for Diffraction Data) database, PDF Cards No. 98-001-6635, 98-002-6597 were used.

The UV–vis spectra were collected for the 240–1000 nm range with the use of the AvaSpec-ULS2048 spectrophotometer (Avantes), halogen and deuterium lamps (SL1 and SL3, Stellar Net), integrating sphere (AvaSphere-30, Avantes), UV-grade optical fibers (Avantes), spectrometer calibrated on Spectralone white standard (Labsphere), and data were presented as % reflectance. Each tin oxide sample was crushed to prepare a thin tablet for measurements.

All photoelectrochemical tests were carried out in a standard three-electrode system with a Teflon cell with a quartz window (35 mm × 35 mm). Porous anodic tin oxide layers deposited on the surface of ITO foil (Sigma Aldrich) were used as a working electrodes. Every time the area of 4 × 4 cm of ITO foil was covered with 40 ± 5 mg of oxide powder dispersed in 3 ml of ethanol and dried. Since all the samples were prepared in the same manner, the surface area of electrodes as well as the thickness of the oxide layer should be comparable. Pt foil and saturated calomel electrode (SCE) were used as a counter and reference electrodes, respectively. The photoelectrochemical characterization of samples was carried out using a photoelectric spectrometer (Instytut Fotonowy) equipped with a 150 V xenon arc lamp, combined with a EG&G 273A (Princeton Applied Research) potentiostat. All photocurrent vs. time curves were recorded in 0.1 M KNO_3 under a potential range of 1000–0 mV vs. SCE. Working electrodes were sequentially illuminated with the UV light (in the range of 300–400 nm) with a 10 nm wavelength step and 5 s light and 10 s dark cycles.

3. Results and discussion

A structure of the anodic film, after 10 min of anodization in 0.3 M oxalic acid at 8 V, is shown in Fig. 1. A completely irregular porous structure with poorly defined nanochannels and with a lot of interconnections between neighboring pores is clearly visible on the surface of anodic tin oxide layer (Fig. 1A). On the other hand, as can be seen in Fig. 1C, the inner oxide structure exhibits a significantly different morphology. Much larger, well defined and more regular nanopores with an average diameter of about 50–60 nm can be easily recognized. The presence of such kinds of an outer and inner oxide layers with different morphologies in as grown anodic tin oxide was observed and explained in our previous works [14,16,17], as well as by other research groups [6]. It should be mentioned that the nature of the outer oxide layer is strongly dependent on conditions applied during anodization. For instance, it has been reported that the surface pores of anodic tin oxide, grown in oxalic acid electrolytes carried out even under typical anodizing conditions, can be completely closed, especially for anodization of Sn deposited on other conductive substrates [12,23]. On the other hand, recently, we proved that similar porous oxides with the completely closed outer layer can be also obtained in this type of electrolyte, if the anodization is carried out at too