

Synthesis of nanoporous tin oxide layers by electrochemical anodization

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ABSTRACT

Nanoporous tin oxide layers were electrochemically synthesized by a voltage-controlled anodization of the metallic tin electrodeposited on the surface of Cu plate. As-prepared structures consist of number of stacked nanoporous layers separated from each other by thin gaps and the atomic ratio of Sn and O was found to be 1:1. An evolution of morphology of nanoporous tin oxide layer during anodization was investigated in detail. It was found that the oxide layer formed during the initial stage of anodizing is non-porous or exhibits a tiny pores, much smaller than those observed in the inner oxide layer. Under certain conditions (especially at higher anodizing potentials and temperatures), the nanopores in the outer layer widen with time of anodization. On the other hand, nanochannels diameter in the inner oxide layer remain almost constant. The effects of anodizing potential, temperature and electrolyte concentration on structural features of the oxide layer were deeply investigated. It was found that time required for a complete metallic tin oxidation shortens with increasing both anodizing potential and temperature. In addition, the increase in the maximum current density with increasing anodizing potential and temperature was observed. Moreover, the higher temperature, electrolyte concentration and potential applied during anodization, the larger nanochannels and thinner walls of the oxide layer are formed due to the more effective field-assisted dissolution of the oxide at the oxide/electrolyte interface and more vigorous oxygen evolution during anodizing.

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1. Introduction

Tin dioxide is a very important *n*-type semiconductor with a wide band gap ($E_g = 3.6$ eV) offering many unique electronic, optical and photoelectrical properties that make it a promising material for various modern applications in many aspects such as solid-state gas sensors [1–4], solar cells [5,6], UV detectors [7,8] and catalysts [9,10]. Moreover, tin oxides are considered as promising alternative to the commercial graphite in lithium-ion batteries [11–13]. In addition, the use of nanostructured oxides instead of bulk materials can significantly improve the desired functionality due to extremely high surface area and restricted size. Up to now, the main problem that limits the practical application of such nanomaterials is a relatively high cost of nanofabrication process. A variety of methods have been employed for fabrication of nanostructured tin oxides such as thermal evaporation [14], template assisted methods [15] and solution-based synthesis [16].

On the other hand, one of the most popular method for fabricating nanoporous oxide layers on the metal surface is controlled

anodic oxidation (anodization) of metals under specified conditions [17]. Anodization, widely recognized as an easy way to synthesize nanoporous alumina [17] and titania [18] have been recently employed to fabricate nanoporous tin oxide-based layers on the surface of metallic tin [19–29]. This electrochemical procedure for the fabrication of nanoporous tin oxides was originally proposed by Shin et al. [19]. The authors have performed a series of anodizations of a high purity tin foil in a 0.5 M oxalic acid solution under the constant cell voltage (5–14 V) at room temperature. As a result, amorphous tin oxide layers with randomly distributed nanopores having diameter in the range of 30–60 nm were obtained. Although, oxalic acid is typically reported as an electrolyte used for synthesis of nanoporous tin oxides by anodization [19,20,22–25,27], similar nanostructures can be also synthesized in alkaline electrolytes [28,29]. Since, the formation of porous tin oxide by anodization was pioneered on a high purity tin foil [19,25,27–29], an alternative substrate was proposed by Jeun et al. [20] and Jeun and Hong [22]. The porous SnO₂ films were prepared by anodic oxidation of Sn thin films thermally evaporated on SiO₂/Si substrates and gas sensing properties of this kind of structures were investigated [20,22]. On the other hand, Yamaguchi et al. reported the anodization of tin films deposited on an FTO (fluorine-doped tin oxide) film electrode [24]. The resulting anodized nanoporous tin oxide (ANPTO/FTO) multilayers have been electrochemically tested. It was suggested

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that the ANPTO/FTO multilayer film electrode possesses a wider anodic potential window, compared to other transparent metal oxide film electrodes, and could be used as a transparent electrode for various photoelectrochemical and electrocatalytic systems [24]. Very recently, Lee et al. proposed a strategy for fabrication of nanoporous tin oxide layers on a Cu substrate by simple anodizing of the electrochemically predeposited thin tin film [23]. It was found that the preparation of well-defined porous tin oxide layer on a conducting substrate is not a trivial issue. The fabricated pores at the surface were often closed that drastically limit their practical applications to functional devices. Therefore, a pulsed anodization method has been developed as a quite effective way to create a well-defined tin oxide structure with a few internal cracks and completely open pores [23].

A different strategy for electrochemical fabrication of porous SnO₂ nanomaterials has been used by Feng et al. [21]. They reported, for the first time, that flowerlike micropatterns composed of tin citrate complex nanostrips on tin substrates can be formed by anodic oxidation of tin in a dimethyl sulfoxide/water (DMSO/H₂O) mixture containing citric acid. It was found that the ratio of DMSO to water affects strongly the morphology of the tin citrate complex product. By heating it, polycrystalline SnO₂ nanostrips with a porous structure can be obtained. Furthermore, the morphology of oxide films formed in a pure aqueous solution containing citric acid shows a porous structure, similar to that obtained by anodizing in oxalic acid [21].

Herein, we present some results on the electrochemical synthesis of nanoporous tin oxides by anodization of metallic tin electrochemically deposited on a Cu substrate in an oxalic acid electrolyte. The effect of anodization conditions such as anodizing potential, temperature and electrolyte concentration on the morphology of nanoporous layers is reported. According to our knowledge, the detailed inspection of structural features (pore diameter and wall thickness) of the both outer and inner layer of anodic tin oxide synthesized in oxalic acid at various anodizing conditions have not been reported yet. In addition, the evolution of the morphology of anodic oxide during anodizing is discussed.

2. Experimental

The nanoporous tin oxide layers were synthesized by a one-step electrochemical anodization of the metallic tin electrodeposited on the surface of Cu plate. A schematic representation of the experimental procedure is shown in Fig. 1A. At first, the Cu foil (0.5 mm in thickness) was cut into specimens with dimensions of 0.5 cm × 3 cm. The Cu specimens were electrochemically polished in a 10 M H₃PO₄ solution under the constant current density of 80 mA cm⁻² for 1 min. Then, a working surface area of 1 cm² was selected and the rest of the sample was insulated with an acid resistant paint. Just before the electrodeposition, the samples were dipped into stirred 0.5 M H₂SO₄ to remove a native oxide layer from the copper surface. Sn layers were deposited on Cu plates by galvanostatic electrodeposition from the electrolyte containing 7 g dm⁻³ SnCl₂·2H₂O and 25 g dm⁻³ sodium citrate. The constant current density of 2 mA cm⁻² was applied during electrodeposition and the duration of the process was 10 min. All electrodeposition experiments were carried out in a three-electrode cell powered by a Reference 3000 potentiostat (Gamry Instruments) with a Cu plate and Pt plate as a working electrode and counter electrodes, respectively. After electrodepositions, the samples were rinsed with water and ethanol, then dried. A top-view SEM image of the electrodeposited Sn layer is shown in Fig. 1B.

The Cu plates covered with Sn layers were used as a starting material for anodization. Several series of one-step anodizations under various operating conditions, including different anodizing potentials, temperatures and electrolyte concentrations, were carried out in oxalic acid. The anodization experiments were performed in a two-electrode electrochemical cell thermostated by a powerful circulating system. A Pb plate was used as a cathode and the duration of anodizing was 5 min.

The morphology of anodized samples was investigated by a Field Emission Scanning Electron Microscope (FE-SEM/EDS, Hitachi S-4700 with a Noran System 7) and the composition of oxide layers was determined by energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) measurements. Structural features of nanoporous tin oxides were determined directly from SEM images.

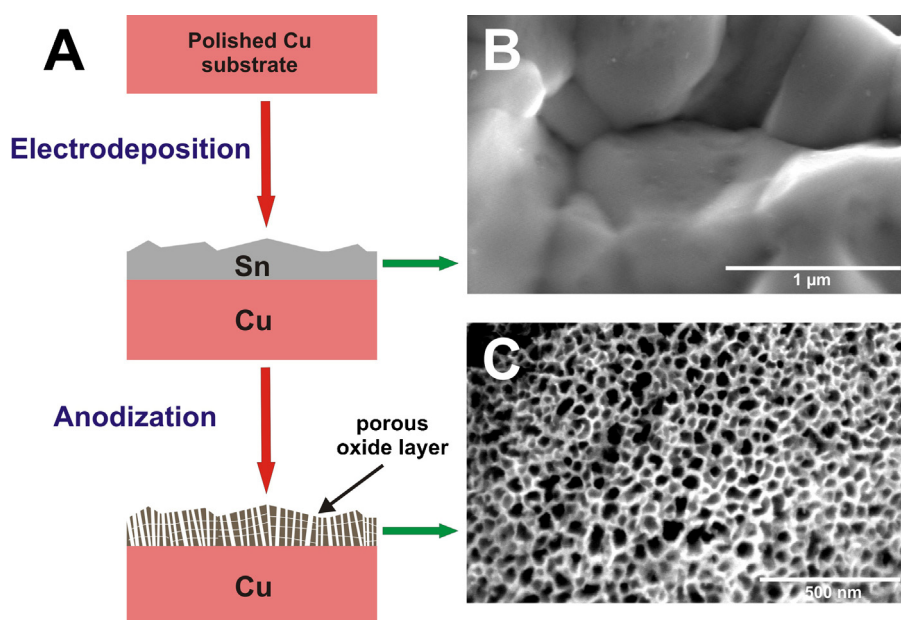


Fig. 1. Schematic representation of the experimental procedure (A) together with the top-view SEM images of the Sn layer after electrodeposition (B) and nanoporous tin oxide after 5 min of anodization in 0.3 M oxalic acid at 8 V and 20 °C (C).

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