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ANODIC GROWTH OF NANOPOROUS TIN OXIDE LAYERS IN ACIDIC ELECTROLYTES

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The aim of this work was to synthesize SnO₂ nanostructures with various morphologies by simple anodic oxidation (anodization) of metallic tin in acidic electrolytes. A series of Sn foil anodizations was performed in different electrolytes (oxalic acid, citric acid, tartaric acid) with various concentrations. It was confirmed that anodic oxidation of tin in the oxalic acid results in the formation of nanoporous oxide layers with completely open pores on the surface of the electrode. On the other hand, when citric acid or tartaric acid were used as an electrolyte, porous oxide with a compact layer on the surface was formed during electrolysis.

Tin dioxide (SnO₂), a wide band gap n-type semiconductor has recently become a subject of great scientific interest as a result of its various promising electronic, optical and photoelectrochemical properties offering many potential practical applications, e.g. in solid-state gas sensors, solar cells, and catalysts [1]. Moreover, it is also widely known, that the use of nanostructured oxides instead of bulk materials can significantly improve semiconductor's functionality [2]. Unfortunately, very often the main problem that limits the practical application of such nanomaterials is a relatively high cost of fabrication process. Therefore, a further development of simple and cost-effective methods for fabrication of nanostructured tin oxides is strongly desirable. Among various methods that have been already proposed for fabrication of SnO₂ nanostructures [3], anodic oxidation (anodization) proposed originally by Shin et al. in 2004, seems to be a very interesting, simple and cost-effective strategy [4].

In our recent works we discussed in detail the effect of anodizing conditions on the formation and structure of anodic tin oxides formed during anodization of various Sn substrates in H₂C₂O₄ [5–8] and NaOH electrolytes. This work aims in a brief comparison of the morphology of anodic tin oxide layers grown in various acidic electrolytes at different anodizing conditions.

Results and discussion

Nanoporous tin oxide layers were synthesized by one-step anodic oxidation of Sn foils according to the procedure described in detail in our previous work [7]. The FE-SEM images of the typical anodic layer formed during anodization of Sn in oxalic acid electrolyte are shown in Figure 1 together with a schematic representation of the oxide structure. As can be seen, a completely irregular porous layer with randomly distributed nanochannels was formed during anodization. The typical layered oxide structure with a lot of internal gaps and transversal pores can be recognized in Figures 1A and B. These discontinuities, being a direct consequence of the vigorous gas evolution during anodization, can significantly affect the properties of oxide layers (e.g., electronic conductivity) and dramatically decrease their mechanical stability and integrity.

The FE-SEM images shown in Figures 1C and D indicate that a continuous barrier layer, similar to those observed during anodizations of other metals (e.g. Al or Ti) is also formed at the metal/oxide interface during anodic oxidation of the Sn substrate. Top-view images of the nanoporous tin oxide layer grown via one-step anodization of Sn foil in 0.3 M oxalic acid at the potential of 8 V are shown in Figure 2 A–C. An irregular, porous structure with number of interconnections between individual nanopores can be easily seen on the oxide surface (see Figure 2A). However, it is evident that the inner oxide layer, clearly visible in Figures 2B and C, exhibits a different morphology with more defined, larger and more regular nanopores [5–7].

The FE-SEM top-view images of anodic tin oxide layers after anodization in 0.3 M oxalic acid at various anodizing potentials are shown in Figure 2 D–F. As can be seen, an anodizing potential significantly affects the morphology of the outer oxide layer, and in general, the higher applied potential the more open porous structure is formed (compare Figures 2D and E showing anodic layers grown at the potential of 4 and 7 V, respectively).

It should be mentioned that in our recent works we confirmed a significant increase in the average pore diameter in the outer layer with increasing potential and concentration of oxalic acid. This phenomenon can be attributed not only to the enhanced field-assisted chemical etching of anodic oxide at the oxide/electrolyte interface, but also to a more vigorous oxygen gas evolution at the anode under severe anodizing conditions.

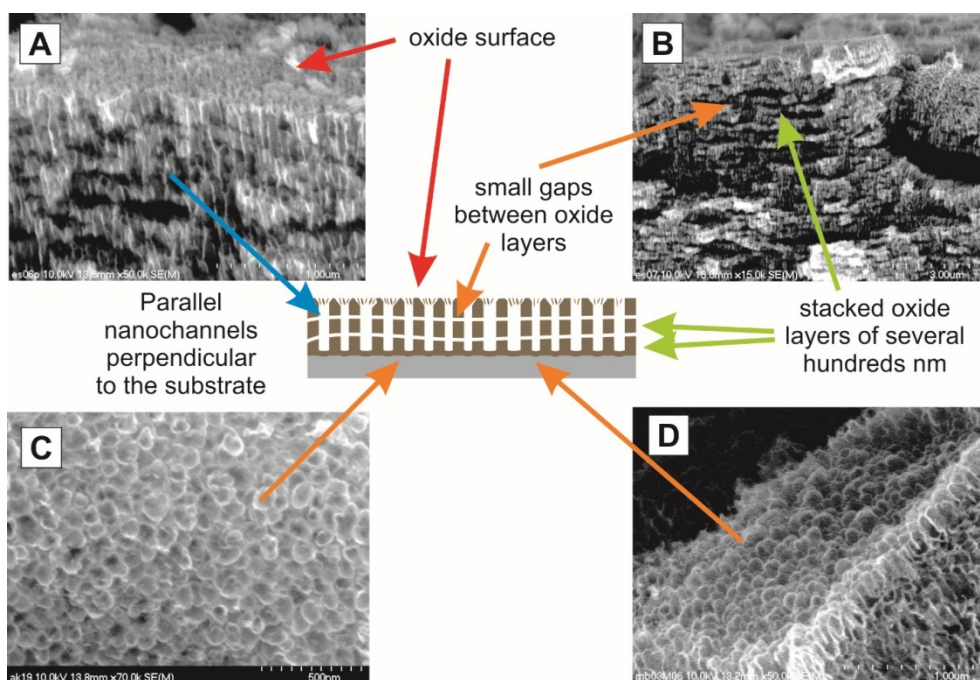


Figure 1. Typical structure of nanoporous tin oxide layers: cross sectional views (A, B, D) and bottom-view of the barrier-layer (C). Anodization was carried out in 0.3 M $H_2C_2O_4$

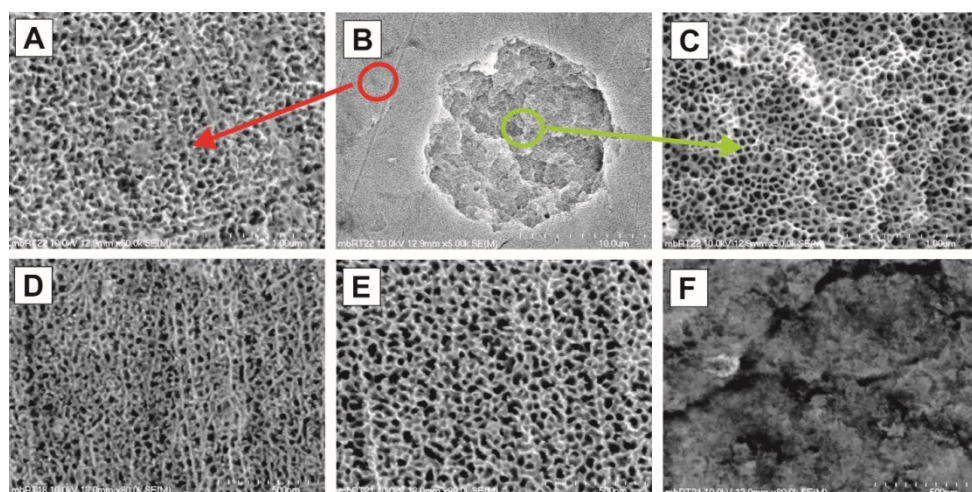


Figure 2. FE-SEM images of the nanoporous oxide layer obtained by anodizing in 0.3 M oxalic acid at 8 V – outer layer (A, B) and inner layer (B, C) and nanoporous SnO_x grown at different anodizing potentials (4 V – D, 7 V – E, 10 V – F)

Contrary to this, no significant effect of anodizing parameters on the structure of the inner oxide layer was recognized [5–7]. However, it is noteworthy that anodizing of Sn foil at potentials of >9 V results in initial formation of the dense, passive outer layer (see Figure 2 F) its further breakdown, and formation of the well-defined, nanoporous inner oxide layer [6]. Anodic films with completely different morphologies were obtained on the surface of metallic Sn when anodizations were carried out in citric or tartaric acid solutions. FE-SEM images of oxide layers grown in these electrolytes are shown in Figure 3.

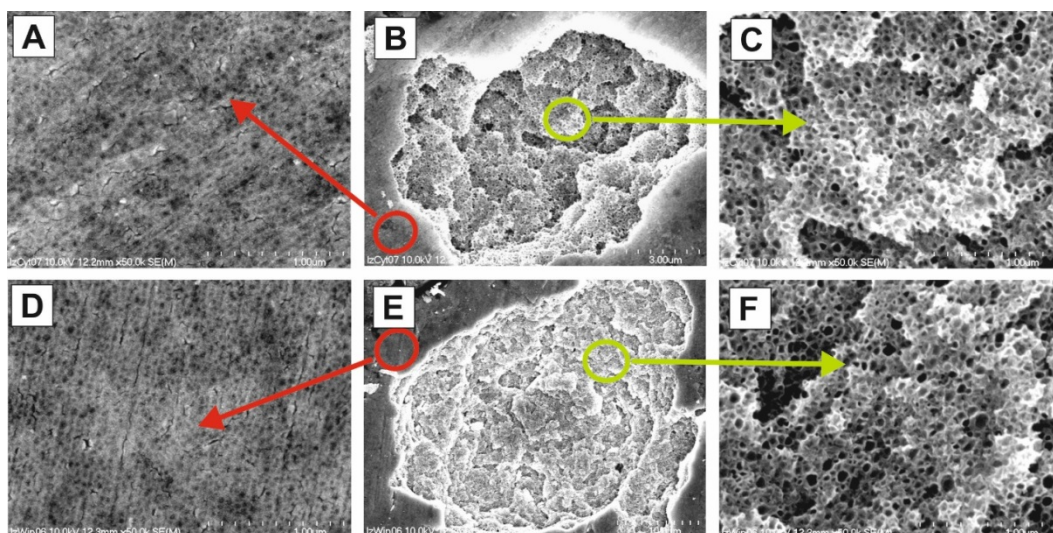


Figure 3. FE-SEM images of anodic layers on Sn foil after 30 min of anodization in 0.3 M citric (A–C) and 0.3 M tartaric acid (D–F) at the potential of 7 and 6 V, respectively

It was confirmed, that almost a compact passive layer was initially created on the surface of metallic substrate and further anodization did not lead to the pore opening. In consequence, the pores were still completely closed at the oxide surface even after 30 min of anodic oxidation (see Figures 3A and D). On the other hand, it is evident that the inner oxide layer exhibits the porous morphology and consists of quite well defined nanochannels (see Figure 3C and F), however an average pore diameter (~ 30 nm) is still much lower from that observed in anodic layers grown in oxalic acid (~ 50 nm). We also confirmed that the surface area of nanoporous inner anodic layer exposed to the electrolyte increases with increasing anodizing duration.

However, this can be attributed not to the enhanced field-assisted etching of the passive layer, but rather to the peeling of the outer part of the film as a result of vigorous oxygen evolution and formation of internal cracks and transversal pores in the anodic layer. It should be also mentioned that even if anodization was carried out in more concentrated electrolytes (up to 1 M) and higher anodizing potentials (to 20 V) as created anodic films still exhibited a non-porous morphology of the outer layer. It is obvious that this phenomenon hinders the potential application of such kind of porous anodic tin oxides.

Since the species cannot access the internal pores of oxide layers, its application to functional devices is limited. Taking above into consideration it should be stated that citric and tartaric acid solutions are not very promising electrolytes within the context of fabrication of nanoporous tin oxide layers.

Conclusions

In summary, nanoporous tin oxide layers can be easily obtained via extremely simple one-step anodic oxidation carried out in acidic electrolytes. However, the character of the electrolyte strongly affects the morphology of anodic tin layers. Nanoporous films with well-defined and open pores can be obtained when anodization is carried out in oxalic acid at the potentials <9 V. On the contrary, the use of weaker acids as electrolytes (citric acid, tartaric acid) results in formation of anodic oxides with a completely compact outer layer and nanoporous inner structure.

Acknowledgements

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