A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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ELECTROCHEMICAL SYNTHESIS OF TETRAGONAL SnO_2 PHASE

ELEKTROCHEMICZNA SYNTEZA SnO_2 O STRUKTURZE TETRAGONALNEJ

The main aim of this research was to determine parameters of deposition of tetragonal SnO_2 phase by electrochemical method. The influence of different parameters like potential of a working electrode, the electrolyte composition and time of deposition on the morphology of the electrodeposited SnO_2 was determined by LSV and QCM techniques. The mechanism of the oxide formation is also discussed. The morphology and structure of films was characterized by AFM and XRD technique.
Keywords: tin dioxide, electrochemical synthesis, electrodeposition, electrogravimetry

Celem badań było określenie parametrów osadzania SnO_2 o strukturze tetragonalnej metodą elektrochemiczną. Określony został wpływ parametrów takich jak: potencjał elektrody pracującej, skład elektrolitu oraz czas trwania elektrolizy na morfologię osadzonego SnO_2. Badania prowadzono z wykorzystaniem technik LSV oraz QCM. W artykule omówiony został również mechanizm tworzenia się SnO_2. Do charakterystyki morfologii uzyskanych cienkich warstw wykorzystano mikroskop AFM. Badania strukturalne wykonano metodą XRD.

1. Introduction

Tetragonal phase of tin dioxide is one of the most important materials for the semiconductors industries. SnO_2 is a transparent n – type semiconductor with a large band gap (3.6 eV) therefore can be used for many applications such as photodetectors [1], gas sensors [2-4] and solar cells [5]. For synthesis of this phase a lot of methods were employed using like chemical vapour deposition (CVD) [6], high-temperature thermal evaporation [7], hydrothermal method [8] or laser ablation [9]. SnO_2 can also be found in the orthorhombic crystallographic structures [10]. Tetragonal phase of SnO_2 is a material with promising electrical, optical and gas sensing properties [11]. The pulsed-laser deposition (PLD) [12] and high temperature-pressures techniques has been developed to synthesize tetragonal phase of SnO_2[11]. These methods require high temperature and pressure conditions as well as expensive equipment in comparison with the electrochemical method. Therefore, electrochemical synthesis can be an alternative methode of the synthesis of inorganic semiconductors.

2. Experimental details

Tin dioxide was deposited from the solution containing KNO_3, HNO_3 and $SnCl_4$ on the gold layer sputtered on the glass substrate. The measurements were performed at the constant temperature 25°C. The saturated calomel electrode (SCE) was used as a reference electrode, and platinum as a counter electrode. Electrodes for deposition were made by sputtering technique, where the gold was sputtered on one side of the glass. The deposited SnO_2 were annealed in air at 400°C for 4h to convert amorphous phase to crystalline phase. The optimal potential and composition of the electrolyte used for synthesis of SnO_2 were determinated using classical electrochemical techniques: chronoamperometry and linear sweep voltammetry (LSV). Voltammetry scans were conducted on potentiostat/galvanostat Autolab PGSTAT30. Electrogravimetric studies were conducted using quartz crystal microbalance Uelko Type M106 connected to potentiostat. All of linear voltammograms and microgravimetry scans were measured at a rate of 20 mV/s. The changes of frequency of quartz resonator is connected with the change of the mass per

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unit area and according to Sauerbrey's [13] can be expressed by:

$$\Delta f = -\frac{2f_0^2 \Delta m}{A\,(\mu\rho)^{\frac{1}{2}}} = -K \cdot \Delta m \qquad (1)$$

where, Δf is the frequency changes, Δm is the changes of mass per unit area f_0 is the quartz's crystal resonant frequency, A is the piezoelectrically active area, μ is the shear modulus of the quartz and ρ it's density. The decrease of resonator's frequency is connected to the increase of the weight of the electrode. Metallographic microscope Nikon LV150 Elipse was used for observation of films morphology. Topography of films surface was registered using AFM microscope NT-MDT Ntegra Prima with probe NSG11. The films were analysed by XRD method using the diffractometer Siemens D5000. The films for XRD analysis were deposited under potential of – 0.4 V for 4 h.

3. Experimental results and discussion

The study of the potential of the working electrode was conducted in the electrolyte consisted of 0.1 M KNO_3, 75 mM HNO_3 and 30 mM $SnCl_4$. SnO_2 was deposited chronoamperometrycally upon various potentials from E = – 0.2 V to E = –0.5 V. Fig. 1 shows the morphology of films deposited using different potential values. The results of electrogravimetric's investigations are shown in Figure 2 and Figure 3. Tin dioxide was deposited in potential range form – 0.2 V to – 0.5 V. The decrease of potential affect on the increase of cathodic current density as shows in Figure 3. Consequently, the increase of the cathodic current density have a result in decrease of the resonator's frequency (mass increase). When the potential E = – 0.5 V was used the rate of deposition was the highest in all of the cases, however the intensity of hydrogen reduction was very high. Consequently the next step of investigations were conducted using potential E = – 0.4 V.

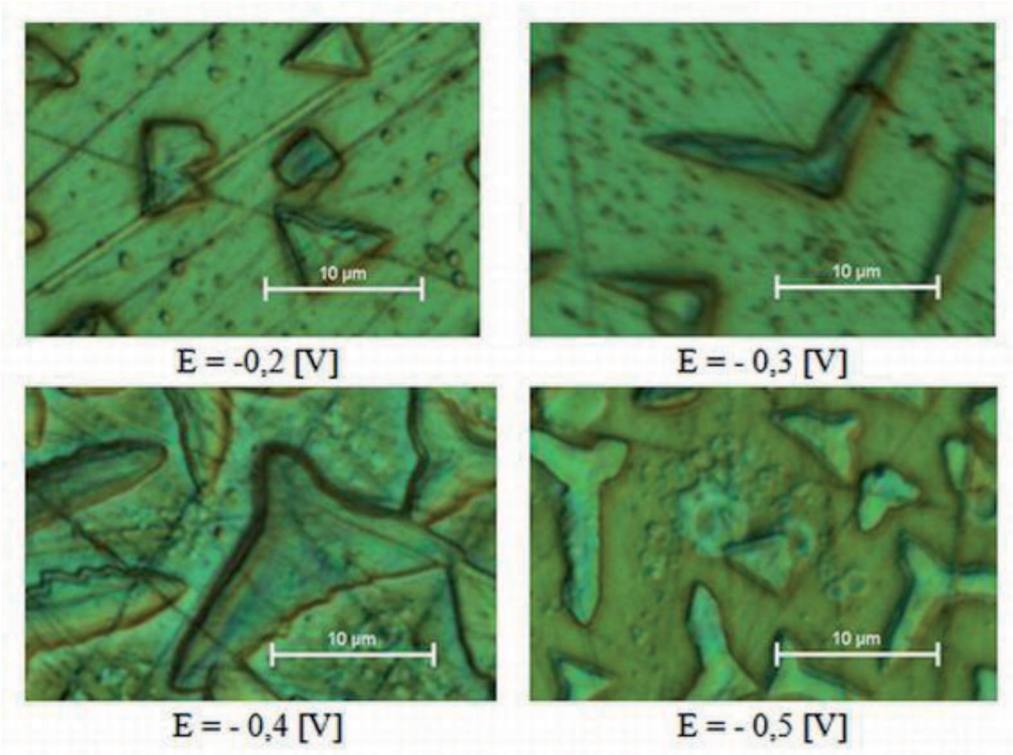


Fig. 1. The images of synthesized SnO_2 using various potentials with deposition time 1h

The process of SnO_2 deposition consisted in two steps. The aim of the first one was to decrease of local pH value near the surface of the electrode. According to the literature [14] decrease of pH is the result of the reaction (1).

$$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O \qquad (2)$$

Then, in the second step, precipitation of tin dioxide is localized in the zone near the surface of the electrode with decreased pH value, according to reaction (2):

$$Sn^{4+} + 4OH^- \rightarrow SnO_2 + 2H_2O \qquad (3)$$

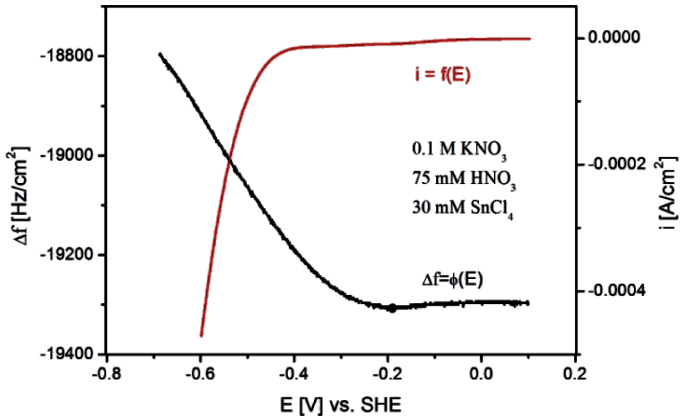
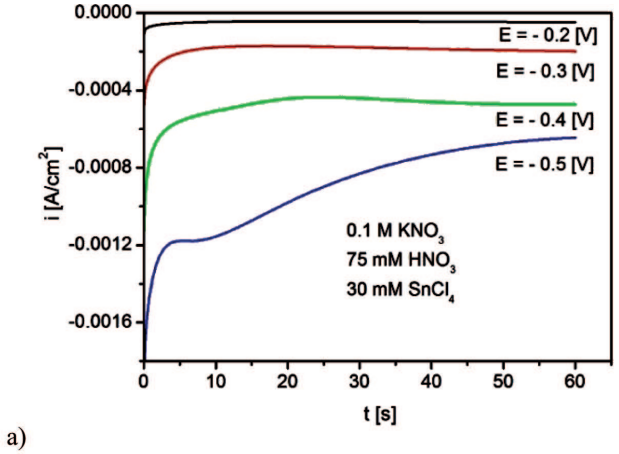
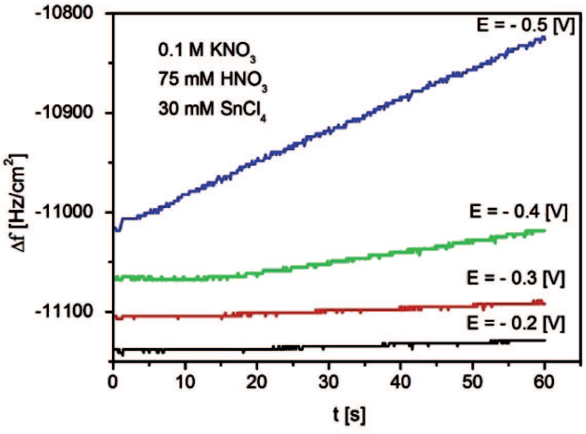


Fig. 2. The linear voltammogram for cathodic polarisation and registered frequency of vibration of quartz resonator



a)



b)

Fig. 3. The potentiostatic curves (a) and frequency of resonator's vibration (b) registered for different potential of deposition.

Nitric acid reduces pH to value near which $SnCl_4$ doesn't hydrolyze and is the source of nitric ions in the electrolyte like potassium nitrate. The presence of potassium nitrate changes equilibrium of reaction (2) to the right according to Le Chateliere-Brown rule. For determination of the influence of concentration of KNO_3, HNO_3 and $SnCl_4$ on deposition process the anodic stripping voltammetry technique was used. SnO_2 was first deposited using potential E = – 0.4 V in 1 h and subsequently polarized from negative to positive potential's value (Fig. 4). In resulted voltammograms (Fig. 5a, 5b, 5c) for E ≈ – 0.5 V cathodic peak's which may be attributed to reduction of SnO_2, according to the reaction (4) were observed. For E ≈ 0.7 V in voltammograms the anodic peak's corresponding to corrosion process of Sn after breakdown of passive film are visible.

$$SnO_2 + 4H^+ + 4e \rightarrow Sn + 2H_2O \qquad (4)$$

According to the literature the similar mechanism was observed for corrosion of tin in acidic media by Fahmy and Hassan [15]. The quantity of deposited SnO_2 is proportional to the area under the cathodic peak. Fig. 5a and 5c suggest that the best electrolyte composition for SnO_2 synthesis is 0.1 M KNO_3 and 75 mM HNO_3. Dependences shown in Fig. 5b suggest that the quantity of deposited SnO_2 increases with the increase of the concentration of tin chloride (IV). After reaching the concentration level of 30 mM of $SnCl_4$, it begins to hydrolyze in the whole volume of the electrolyte.

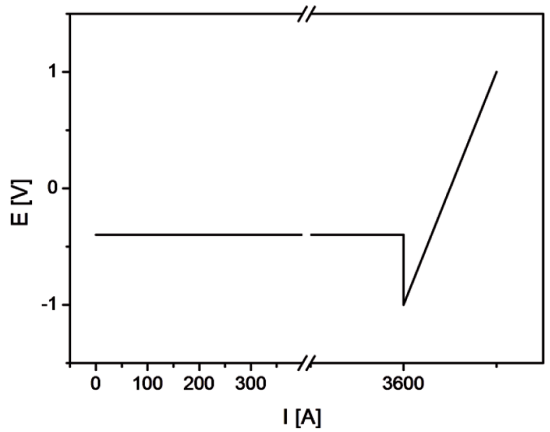
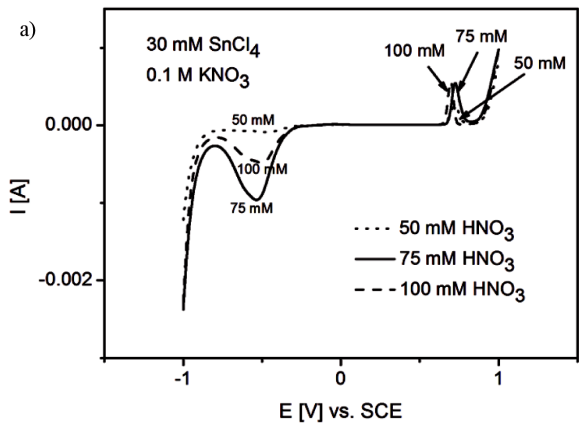


Fig. 4. The potential changes during the anodic stripping voltammetry



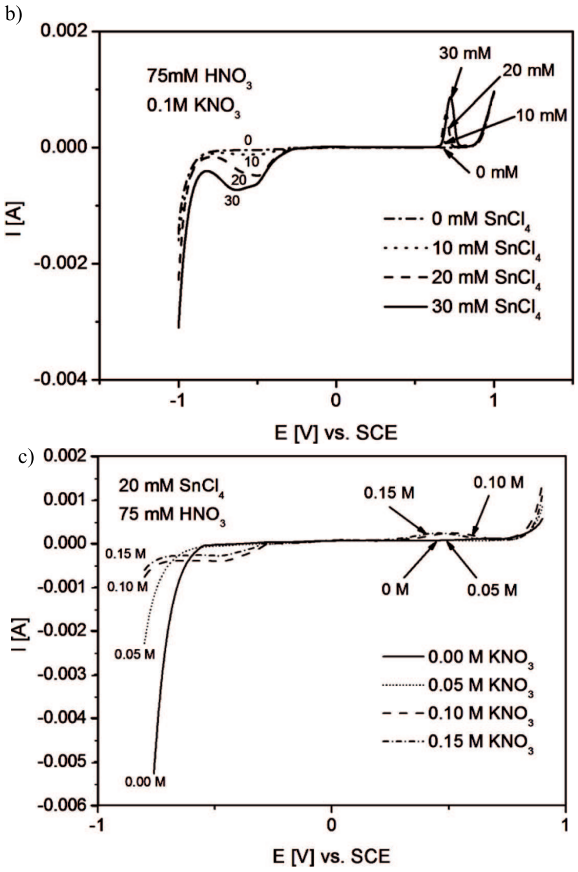
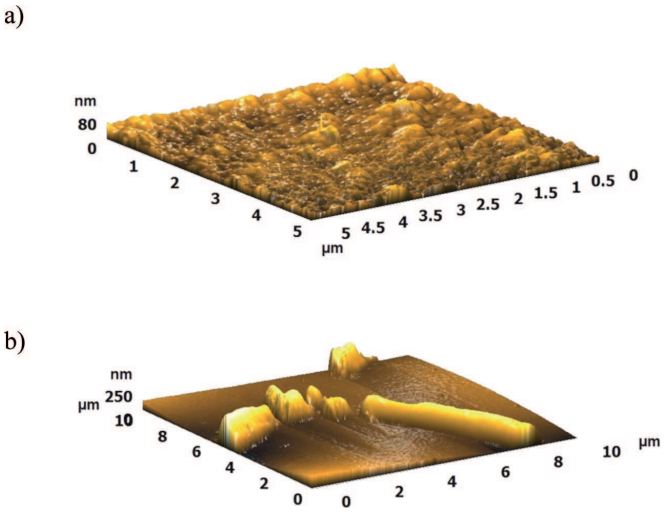


Fig. 5. Linear voltammrograms for film deposited in the same time (30 min) using different electrolytes (a, b, c) (V = 20 mV/s)

The films studied by AFM were deposited using potential – 0.4 V from the electrolytes contained 0.1 M KNO_3, 75 mM HNO_3 and 30 mM $SnCl_4$. Topography of grains was taken at different stages of their growth (Fig. 6). The shape is the characteristics feature of all grains. We suppose that the texture of sputtered gold has the largest influence on the nucleation. Every grain comes into being as the result of the connection of a few smaller grains.



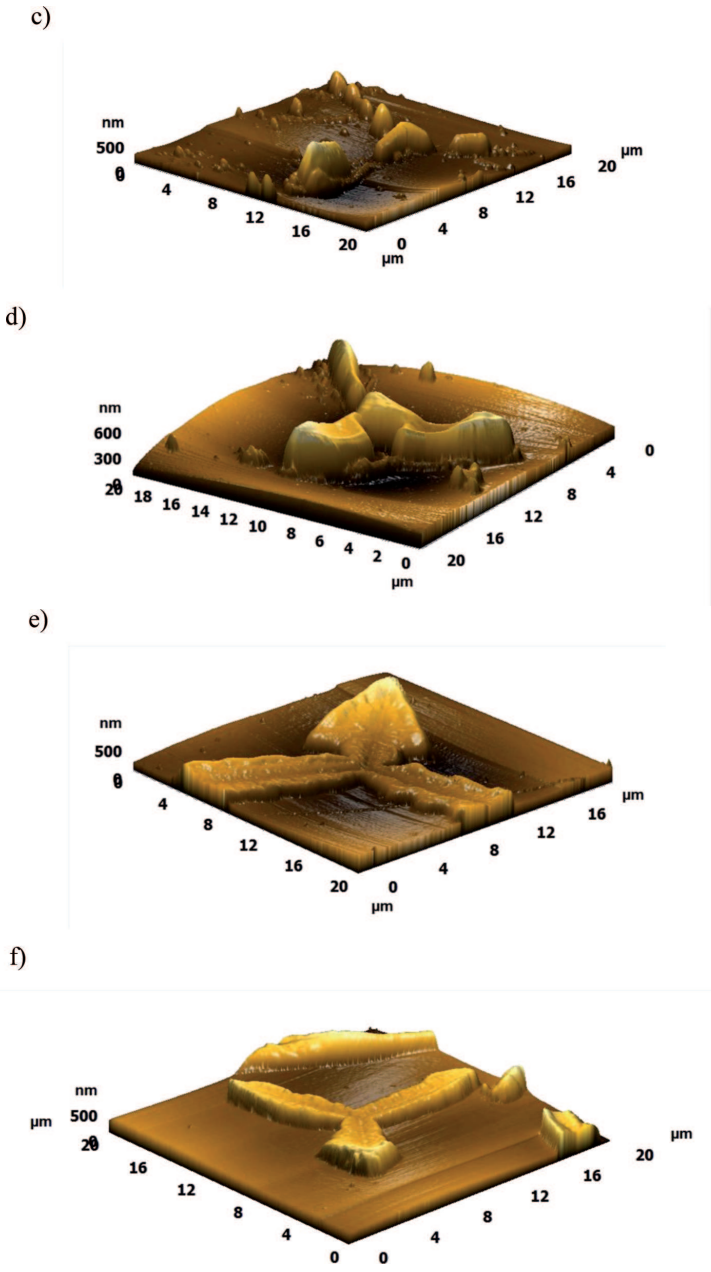


Fig. 6. Topographies of sputtered gold (a) and grains of SnO_2 deposited using E = – 0.4 V in 3600 s in different stage of growth (b , c, d, e, f)

XRD patterns of resulted not-annealed films and annealed in air at 400°C for 4h are shown in Fig. 7. In the first case we can see three peaks which show the presence of tetragonal SnO_2 phase. There are also the peaks corresponding to Sn phase planes of (200), (101) [16] and Au phase planes of (200), (311), (222) [17] coming from FCC Au substrate. For annealed films peaks show on existence of tetragonal SnO_2 phase coming from planes of (110), (101), (200), (211), (220), (002), (310), (112) [18]. The difference in quantity and intensity of peaks confirm that the amorphous phase was converted to crystalline phase. XRD diffraction pattern for annealed films shows existence of Au, AuSn [19] and $AuSn_2$ [20] phase. These phases were formed in the result of reaction between the Au substrate and Sn contained in deposited films during the annealing process.

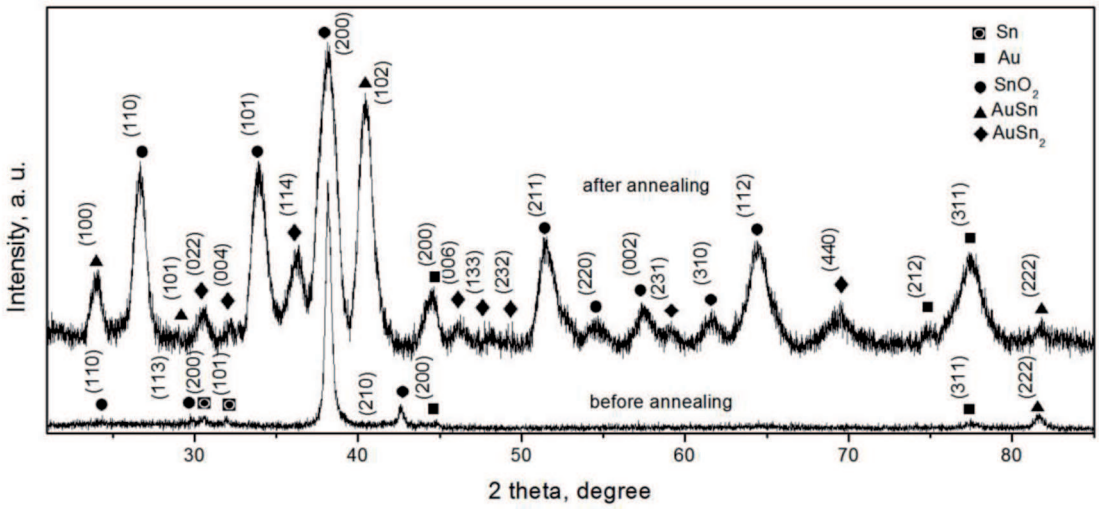


Fig. 7. XRD diffraction patterns for films deposited in 4h using potential E = – 0.4 V

4. Conclusions

The conducted studies showed that at the temperature 25 °C, the best potential for synthesis of tetragonal structures of SnO_2 is E = –0.4 V and optimum composition of the electrolyte for synthesis is: 75 mM HNO_3; 0.1 M KNO_3; 30 mM $SnCl_4$. Electrolyte for nanostructures synthesis often have the concentration of $SnCl_4$ lower than 30 mM. Then, the process of deposition will proceed more slowly, creating better conditions for the control of the morphology of the deposited SnO_2. The present work showed that the electrochemical synthesis of SnO_2 is the method which presents a lot of advantages over other methods because of its simplicity and low expenses.

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