PAPER • **OPEN ACCESS**

Research of the photovoltaic properties of anodized films of Sn

To cite this article: D A Afanasyev *et al* 2015 *IOP Conf. Ser.: Mater. Sci. Eng.* **81** 012118

Research of the photovoltaic properties of anodized films of Sn

D A Afanasyev[1], N Kh Ibrayev[1], G S Omarova[1], Zh K Smagulov[1]

[1]Karaganda, 100028, Kazakhstan, Institute of Molecular Nanophotonics, E.A. Buketov Karaganda State University

E-mail: a_d_afanasyev@mail.ru

Abstract. The results of studies of photovoltaic properties of solar cells based on porous tin oxide films, sensitized with an organic dye are presented. Porous films were prepared by electrochemical anodization of tin in alkaline electrolytes based on aqueous solution of NaOH and aqueous ammonia NH_4OH. It was found that the time of anodizing of the Sn films affects on conversion efficiency of light energy into electrical energy. Increasing of the sorption time leads to an increase of the number of molecules on the surface of the porous film. For the solar cell based on tin oxide there is a strong dark current, which significantly reduces the efficiency of conversion of light energy into electrical energy.

1. Introduction

Today metal oxides such as titanium oxide, tin oxide, zinc oxide, etc., still remain in the field of view of researchers. With the rapid development of nanotechnologies and their applications are discovered new properties of these substances on the micro- and nanoscale [1-3]. Electrochemical anodization is one of the promising methods of obtaining of nanostructures. Electrochemical oxidation and electrolytic formation of the oxide film on the surface of metals, alloys and semiconductors [4, 5] occurs during anodization. The oxide film protects the product against corrosion, has insulating properties, could be used as a good base for the paint coatings used for decorative purposes. For a number of metals, under certain conditions of anodizing it`s possible to obtain a porous oxide films with predetermined dimensions of the nanopore, film thickness and porosity. Such metals include aluminum, niobium, tantalum, titanium, zirconium [6]. For each of these metals its own conditions for the anodizing process exsist. Properties of the porous films strongly depend on the properties of metal.

An integral part of modern material science is the analysis of the microstructure, which acquires special value in relation to porous structures, where the state of the object (pore size, orderliness, and others) significantly affects the complex of the physical and chemical properties [7, 8]. It is therefore important to determine the impact of technical conditions of nanomaterials on their microstructural and geometrical properties. In this paper we present the results of the investigation of microstructural properties of the tin oxide films obtained by electrochemical oxidation.

2. Methods and Results

Granular tin with 99.99 % purity was used as a starting material. Tin plates were prepared from granules. The thicknesses of plates were equal to 0.5 mm and the dimensions were 2.5×2.5 cm. Chemical polishing of tin plates was carried out before anodizing. Before anodizing the surface of the polished plate was degreased with ethanol and then was cleaned in an ultrasonic bath.

Synthesis of porous SnO_2 was performed in a two-electrode electrochemical cell using a constant current source MPS-7081. The auxiliary electrode was a titanium plate, and a working electrode was polished plate of tin. As electrolyte an aqueous solution of NaOH and aqueous ammonia solution NH_4OH was used. The electrolyte was obtained on the basis of dual water filtration and deonization with system AquaMax Basic 360. The resistivity of the water was equal to 18.2 MΩ/cm. Anodizing of the porous film of tin oxide was carried out at room temperature (25 ºC).

Voltage was kept constant (potentiostatic anodization mode) during the process of anodizing. After anodizing film was washed with distilled water and dried in an oven at a temperature of T = 50 °C.

An important step in controlling of the anodizing process is the measurement of the current density in the anodizing process. The current value allows estimating the reaction rate and the thickness of the oxide layer. Nature of the change of the current shows the step of forming of oxide film.

Figure 1 shows the current characteristics of the anodization process in an aqueous solution of NaOH. Gradual decrease in the current density with increasing time of anodizing is observed for the anodizing process. No increase of the current density anodizing and no expressed transitions between stages of formation of barrier and porous oxide layers [9].

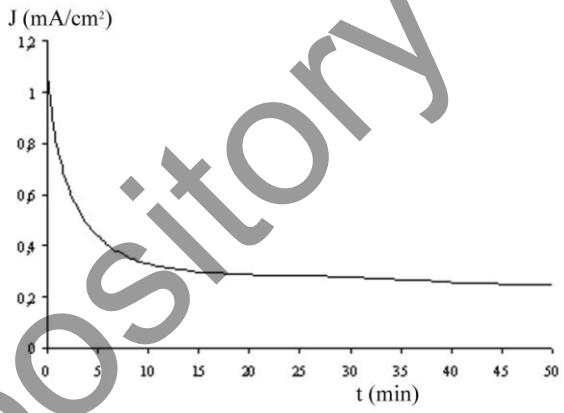

Figure. 1. Current characteristics tin anodizing process in an alkaline solution NaOH, U = 12 V.

When anodizing occurs in aqueous solution of NH_4OH the stage of increase of the current density (Figure 2) is observed. The growth of the barrier layer of tin oxide occurs at this stage. When the current density reach the maximal value it begin gradually decrease. At this stage the porous structure of the oxide film forms. However, analysis of the current characteristics and a comparison with the standard model representations, allows only predicting the probability of occurrence of an oxide film of porous type. The formation of pores in anodising tin could be confirmed with electron microscopy and probe measurements of obtained samples.

For the microstructural study of the films, anodized under various conditions of anodizing, the scanning electron microscope (SEM) JEOL JSM-5910, operating in the mode of secondary electron emission (SEI) with a permissive ability in a high vacuum of 3 nm was used. The electron energy of the probe was 20 keV, the probe current was 0,1nA, and the measurement time was 50 s. Working distance was 10 mm. All films were subjected to the control of the elemental composition. Microanalysis of quantitative elemental composition of the films was made by energy dispersive method with X-ray spectrometer where detector JXA-8200 is embedded in the SEM. Quantitative microanalysis of chemical elemental composition of the investigated films was carried out by a special

program PHI-RHO-Z by mathematical processing of the energy-dispersive spectra using a computer that came with SEM. The study of the elemental composition of the film obtained in aqueous solution of NaOH, showed the presence of the tin atoms and oxygen, indicating the formation on the surface of an tin oxide film (Figure 3). Also the energy-dispersive spectrum contains sodium atoms.

The presence of sodium atoms is a negative factor that may affect on the further application of oxide films as a porous semiconductor layer in photovoltaic solar cells. Therefore, further anodizing of tin was held in NH_4OH.

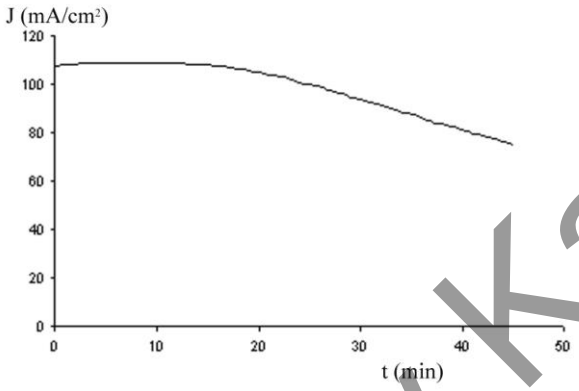

Figure 2. Current characteristics of tin anodizing process in an NH_4OH alkaline solution.

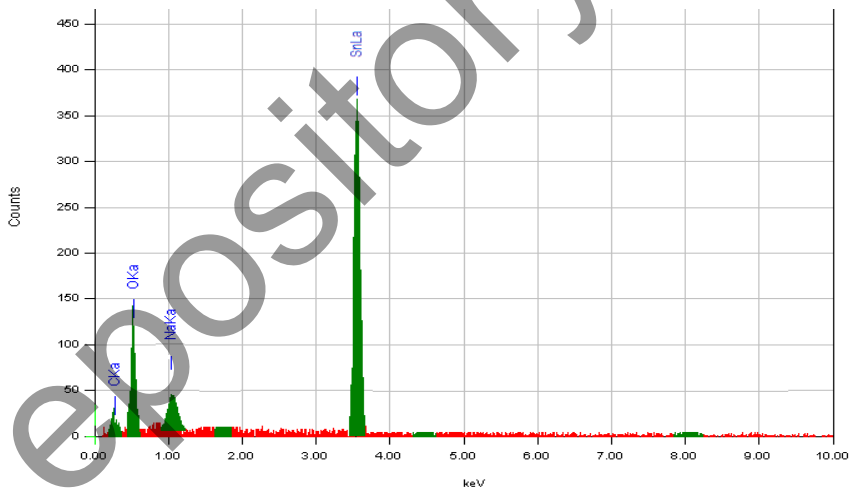

Figure 3. X-ray spectrum of the anodized surface of tin at the anodization in NaOH with the distribution of elements on the surface.

The microstructure of anodized tin oxide films in an electrolyte based on water and NH_4OH was carried out. The measurements were performed with a scanning probe microscope JSPM-5400 (JEOL) using the methods of atomic force microscopy (AFM). Results of anodizing in solution NH_4OH at room temperature are shown in Figure 4.

Reduction of temperature at the anodizing process leads to an increase of inhomogeneity of film relief. Against the background of the rough surface of the film the porous structure of the film is formed (Figure 4).

The microstructure of the surface of the anodized film of tin oxide was also investigated with a scanning electron microscope (SEM) JEOL JSM-5910 (Figure 5). Microscopic measurement of the film structure of the anodized tin was identical to AFM images of the surfaces (Figure 4). Similarly,

the AFM images, images taken with the SEM testify the formation of a developed mesoporous surface. Inside the mesopores the pores of smaller size are formed. At the same time the structure obtained by electron microscopy measurements, corresponds to images obtained by the probe microscope (Figure 5).

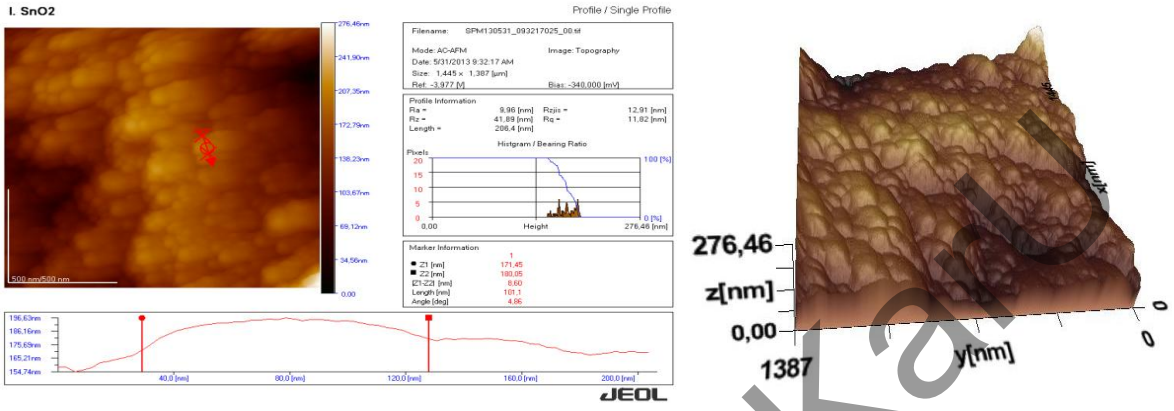

Figure 4. AFM images of a surface of a porous tin oxide obtained at room temperature in NH_4OH.

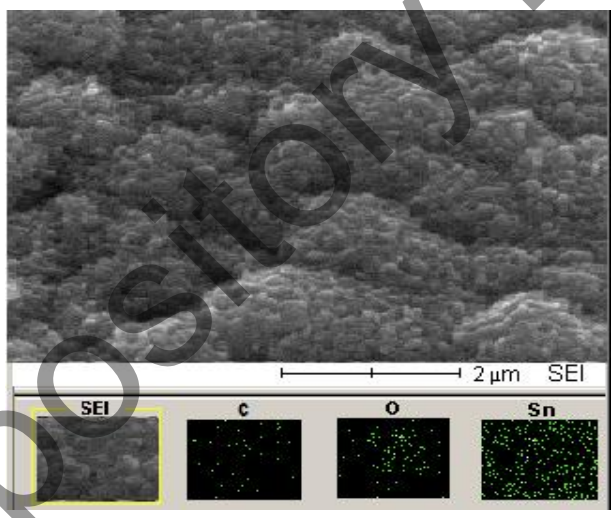

Figure 5. The microstructure of the surface of the tin oxide film.

Minor presence of carbon on the image (Figure 5) indicates the presence of organic compounds on the surface of the tin. Against the background of inhomogeneous relief of the film there is a uniformly distributed porous structure, which is evidence of the formation of the oxide layer of porous type for SnO_2. The pore size of the nanostructured tin oxide depends on the conditions of anodization. Typical pore sizes were determined from the AFM images of the films (Figure 4). The dimensions were equal to 100 nm for films obtained at room temperature.

The sorption capacity of porous films of anodized tin was studied. For this purpose sorption of dye molecules was performed from a solution. Dye D149 was chosen as adsorbate.

The choice of this dye due to the fact that its energy states are best suited to energy levels of tin oxide. Therefore, the solar cells on the basis of anodized oxide films of Sn and D149 should have high rates of conversion of light energy into electrical energy.

The electronic absorption spectra were measured with spectrophotometer Specol 1500. Absorption spectra of the dye D149 before adsorption and after adsorption of molecules on the surface of the nanoporous film of Sn oxide are shown on the figure 6.

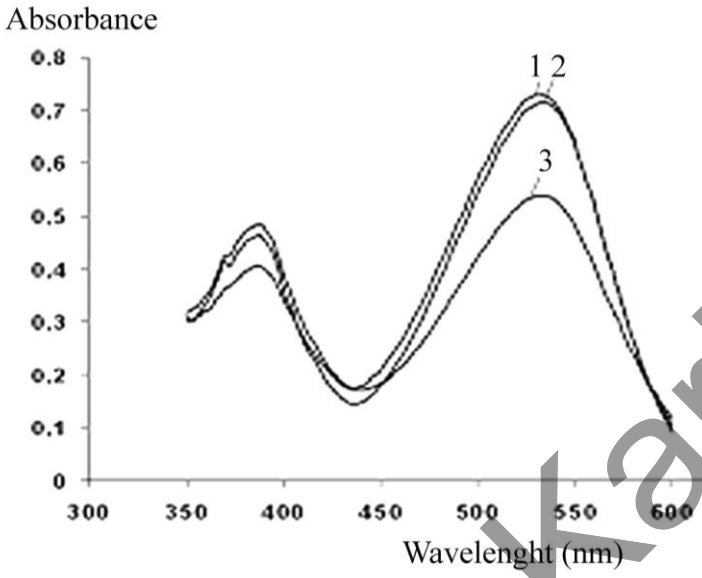

Figure 6. The absorption spectra of the D149 dye before and after sorption: 1 – before sorption 2 - 30 min sorption 3 - 40 min.

It is evidence that the process of sorption of molecules does not lead to a distortion of the absorption spectra. After sorption the optical density of the solution is reduced, which shows the decrease in the concentration of molecules in solution and the flow of physical adsorption of molecules on the surface of the anodized film tin oxide.

Increasing of the time of sorption leads to an increase in the number of molecules on the surface of the porous film (Figure 7). The concentration of molecules adsorbed on the 1 surface of the tin oxide during the 45 minutes was determined and it was $8{,}4 \cdot 10^{16}$ 1/cm^2.

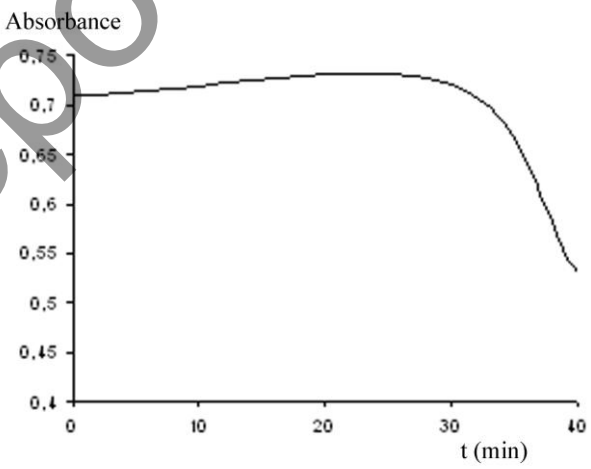

Figure 7. The dependence of the optical density of D149 dye versus sorption time into anodized Sn.

To test photovoltaic properties of the obtained films of nanoporous tin oxide solar was assembled cell according to the method closest to the methodology used by Grätzel.

The measurements were carried out in the photovoltaic mode at room temperature. Lighting of the cell surface was performed from the transparent ITO electrode, on the surface of which by method of irrigation from solution and annealing at a temperature of T=450 ^{0}C transparent thin platinum film was obtained. The power of xenon lamp was equal to 50 mW/cm^2. Photocurrent and photovoltage was not registered for films that were anodized in the electrolyte on the basis of NaOH. This can be explained by the presence of Na on the surface, which adversely affects on the photoconductive properties of tin oxide.

For films anodized in the electrolyte on the basis of NH4OH measuring of the dark and light current-voltage characteristics was performed. Figure 8 shows the dark and light I-V characteristics of the Gretzel cell sensitized with dye D149.

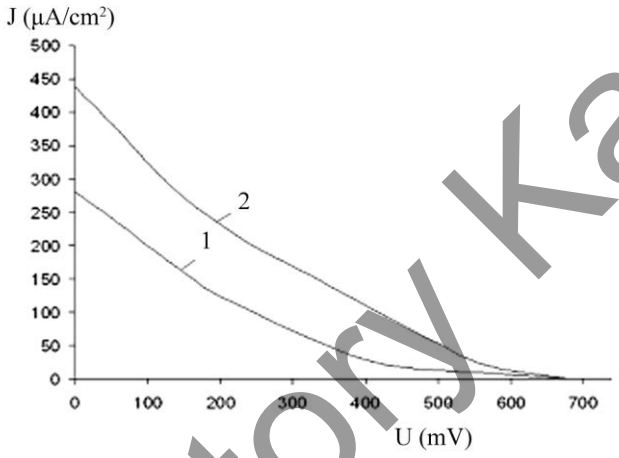

Figure 8. The current-voltage characteristics (CVC) of solar cell based on tin oxide sensitized D149 dye: 1 - the dark CVC, 2 - light CVC.

As can be seen from figure 8, curve 1, even in the absence of light exposure on the sample there is some voltage and current of the cell. Measurement of voltage and current specified by solar cell was carried out under changes of load resistence. When the light source is turned on, the voltage and current in the circuit, which includes Graetzel cell, significantly increased (curve 2). It shows that the light leads to the generation of free charge carriers in the cell and forming of photovoltage.

Analysis of obtained results showed the efficiency of solar cells based on porous films of tin oxide doped with dye molecules. The value of photovoltage and photocurrent shows a perspective of using tin oxide as a semiconductor film in dye-sensitized solar cells. However, for solar cells based on tin oxide exhibits a strong dark current, which significantly reduces the efficiency of conversion of light energy into electrical energy. To explain and eliminate this disadvantage it is necessary to perform of further study of the solar cells based on the films of tin oxide.

The results of the research can be done as number of conclusions:

1. The methodology of synthesis of porous films of Sn oxide by electrochemical anodization was elaborated.

2. The study of the elemental composition of the anodized film showed the presence of tin atoms and oxygen, which indicates the formation of tin oxide film on the surface. It was conducted the studies of the microstructure of the films of tin oxide anodized in the electrolyte on the basis of water and NaOH. Due to the presence of sodium atoms it was decided to abandon the use of this electrolyte for the preparation of porous tin oxide films.

3. The microstructure of anodized tin films obtained at different temperatures of the anodizing in NH_4OH solution was studied. For films obtained at different temperatures of anodizing different

microstructure of the porous films of tin oxide was observed. Microstructural data obtained for oxide films by scanning probe microscopy and electron microscopy correspond and complement each other.

4. Sorption capacity of tin oxide films was studied. It was found the effect of the chemical nature of the dye on the efficiency of sorption of dye in the film of anodized tin.

5. Photovoltaic properties of solar cells based on porous anodized tin oxide films, sensitized organic dye molecules D149 were studied.

References

[1] Kolmakov A, Zhang Y, Cheng G, Moskovits M 2003 *Adv. Materials.* **15**, 997

[2] Hu J, Bando Y, Liu Q, Golberg T D 2003 *Adv. Funct. Mater.* **13** 493

[3] Djurisic A B, Leung Y H. 2006 *Small*. **2** 944

[4] Belenky M A, Ivanov A F 1985 *Electrodeposition of metallic coatings, the reference* (Moscow;Metallurgy)

[5] Averianov E E 1988 *Handbook of anodizing* (Moscow: Mashinostroenie)

[6] Su Z, Zhou W 2008 *Adv. Mat.* **20** 3663

[7] Gusev A I 1991 *Physical chemistry of non-stoichiometric refractory compound* (Moscow: Nauka)

[8] Zainulin Y G, Alyamovskii SI, Gusev A I, Shveikin G P 1992 *The effect of high pressures and temperatures on the defective phase implementation* (Ekaterinburg: RISO, Ural branch of the Russian Academy of Sciences)

[9] Aitkenova G T, Afanasyev D A, Ibrayev N Kh, Khuanbai E 2014 *Bulletin of the Karaganda state University*. *Series physics*. **73** 4