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PROPERTIES OF THIN TRANSPARENT SnO_2:Sb FILMS

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We study the electrical and optical properties of tin dioxide films, produced by the spraying method of aqueous-alcoholic solution of tin tetrachloride with antimony trichloride addition. Results of the influence of the films deposition temperature and the antimony concentration on the resistance, the charge carriers mobility and their concentration, and transmission spectrums are presented.

Keywords: *THIN DIOXIDE FILM, RESISTANCE, MOBILITY, CHARGE CARRIERS CONCENTRATION, TRANSMISSION SPECTRUM.*

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1. INTRODUCTION

Repairable energy systems can fill the fast increasing energy demands without ecological disturbance [1-3]. The direct transformation of radiation energy to electric one using the photoelectric transducers is one of the fundamental ways to ecological problem solving [4-6].

One of the ways of increase the phototransducer efficiency coefficient is using the wide-gap ($E_g \approx 2,0\text{-}3,7$ eV) semiconductors, for example, In_2O_3, SnO_2, ZnO, In_2S_3, TiO_2, CdO, ITO, IFO, and others [7-13]. They have good transparency (> 80 %) in visible band of wavelengths, significant refraction coefficient ($n \approx 1,6\text{-}2,3$), small values of surface resistance ($R_{surf} \approx 10$-70 Ohm/m^2), variety of low-temperature processing techniques ($T \approx 390$-970 K) [14-18]. Properties of wide-gap semiconductors depend on methods and conditions of their production.

It is known, that the most saving and simple deposition method of transparent conducting coatings on the SnO_2 basis is spraying of $SnCl_4$ or $SnCl_2$ and $SbCl_3$ [19-24] solutions. Spraying is the process of chemical deposition, during which the fine drops of solution substance are going towards the surface of heated plate, where they react with continuous coating formation [25-29]. Properties of SnO_2:Sb films depend on such factors as process temperature and solution concentration. The balance of these parameters allows to obtain the films with pre-controllable properties, from the point of view of their effective application in solar cells.

The aim of the present work was the study of surface temperature influence during spraying and concentration of alloying component on such parameters as surface resistance, resistivity, carrier concentration, mobility, and optical transmission.

2. EXPERIMENTAL TECHNIQUE

SnO_2:Sb films production was performed with experimental device, which consists of three elements: spraying system, heater, and ventilating system.

The spraying system is following: compressor, manometers, pipelines, solution-delivery system, quartz reaction chamber, sprayer, and sprayer mobility system. The heater consists of: thermostat, heating element, chromel-alumel thermo-couple, and temperature controller. The ventilating of reaction chamber was realized using the pipeline system and ventilator.

The main parameters of films deposition process are the following: the accuracy of temperature measuring was not less than ± 5%; the oxygen pressure on carboy output was 0,1 MPa; solution-flow velocity during spraying was kept at 7-10 ml/min.; the distance between the sprayer nozzle and the plate surface was determined experimentally and equals 23 cm; the nozzle internal diameter, from which the solution is spraying, did not exceed 0,5 mm. The oxygen was used as carrier gas and delivered discontinuously in 3-4 sec for prevention of the plate surface cooling. The spraying process was lasted 25-40 sec. The film deposition took place at the temperatures 320°C, 380°C, and 440°C on the surface of glass (4 cm×4 cm) and silicon (76 mm) plates. The thickness of studied films was 500 nm.

Firstly for glass surface cleaning the plate boiling in solution of chromic mixture, which was 100 g of $K_2Cr_2O_7$ per 1 l of H_2SO_4, was used, and then – rinsing in distilled water. For depletion of glass surface layer from cations of alkaline metals the plates were dipped in 0,5 N of nitric acid solution for three hours. Then they were washed in flowing distilled water and dried off.

The preparation of solution was done by dissolving of 75 g of $SnCl_4$ $5H_2O$ (0,26 M) in 1 l of ethanol, and by tin trichloride ($SbCl_3$) adding for providing the necessary antimony concentration. The antimony concentration was varied from 0 to 6 weight percents.

The thickness (d) of made SnO_2 films was measured using the profilograph-profilometer Tencor P-10. Films transmission spectrums were registered with the help of spectrophotometer Hitachi U-4100 UV-VIS-NIR in the wavelength range from 500 to 2500 nm. The film structure was investigated using the X-ray diffractometer Bruker D8 Advance at the room temperature with monochromator CuK_α ($\lambda = 1{,}54\cdot 10^{-10}$ m). Accelerator operating conditions were 40 kV/35 mA. Film surface resistance (R) was measured using the four-probe method, and the resistivity was determined as $\rho = R\cdot d$ [30]. The charge carrier mobility and the concentration were found by the Hall method [31].

3. EXPERIMENTAL RESULTS

The films obtained with developed modes had smooth surface without spots, extraneous particles, and cavities. The concentration dependences of the surface resistance and the resistivity at three different deposition temperatures are presented in Fig. 1 and Fig. 2, respectively. Aside from the plate surface temperature the identical curve behavior is observed both in Fig. 1 and Fig. 2, namely, the strong decrease at small antimony concentrations, minimum achievement, and then the slow growth. It is known, that antimony has two oxidation levels: + 5 and + 3 [32], so in SnO_2 films it can exist in two states: Sb^{5+} and Sb^{3+}. The introduction of small concentrations of Sb^{5+} into SnO_2 grating is accompanied by replacement of Sn^{4+} in sites and by increase in a number of free carriers (electrons). Therefore the surface resistance decreases to the defined level (minimum). Then under increase of the antimony concentration and achievement of Sb^{5+}

solubility limit in grating of tin dioxide the Sb^{3+}, which compensates the donor levels generated by Sb^{5+}, occupies vacancies. This leads to the surface resistance growth, and respectively, to the resistivity increase. The surface resistance and resistivity possess the minimal values when the antimony concentration is 1,9-2,0 weight percents for three temperature values.

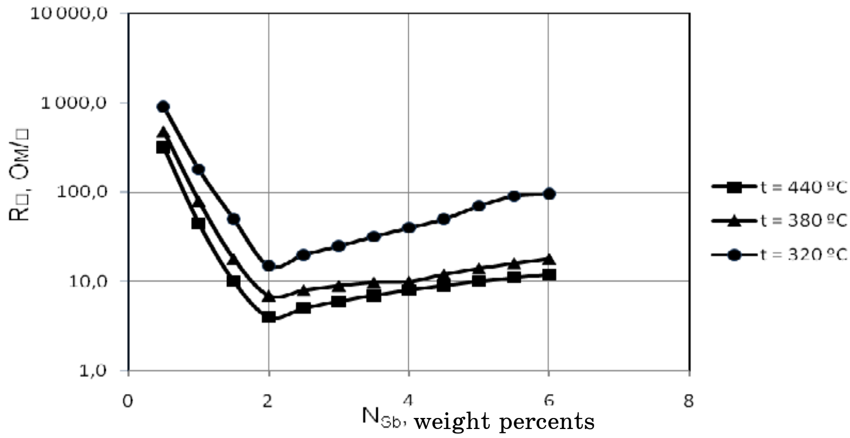

***Fig. 1** – Dependences of the surface resistance versus the antimony concentration at different deposition temperatures and SnO_2:Sb film thickness d* = 500 *nm*

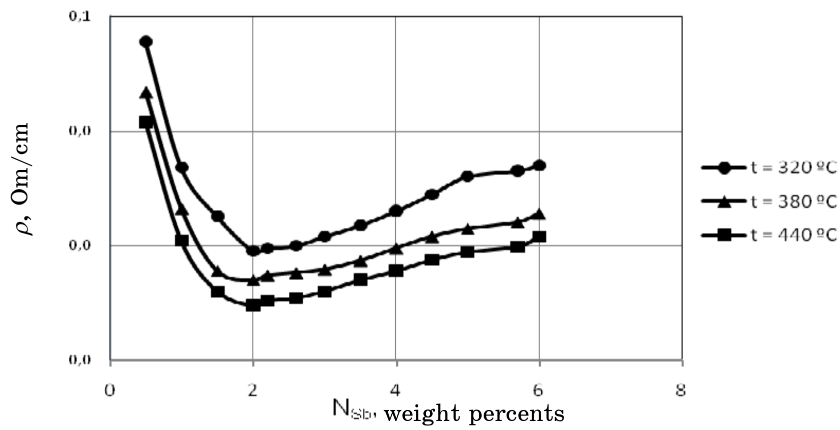

***Fig. 2** – Dependences of the resistivity versus the antimony concentration at different deposition temperatures and SnO_2:Sb film thickness d* = 500 *nm*

Dependences of the charge carrier mobility (μ) and the concentration (n) of SnO_2:Sb films with the thickness of 500 nm versus the antimony amount in solution (N_{Sb}) and process temperature are presented in Fig. 3 and Fig. 4.

As seen, aside from the temperature the mobility monotonically decreases, and the carrier concentration increases with the growth of alloying component amount. At the fixed Sb amount in solution the values of carrier mobility in samples, obtained with less temperature, are lower than in samples, obtained with higher temperature. For example, the mobility value 10 $cm^2/(V \cdot sec)$, which was obtained at the antimony concentration 1,5 atomic percents and temperature 320°C, can be increased up to 19 $cm^2/(V \cdot sec)$ with the same antimony amount, but at the temperature rise up to 440°C. Similarly, the value of charge carrier concentration 10^{21} cm^{-3} for SnO_2:Sb films with antimony amount in solution 1,5 atomic percents and low process temperature 320°C can be decreased almost by an order due to the process temperature increasing. The charge carrier concentration in the films, obtained at higher temperatures, is less than in the films, produced at lower temperatures. At low temperatures of film deposition (320°C) their high resistance can be conditioned by amorphous structure, and therefore by small charge carrier mobility. Temperature increase promotes the growth of crystallinity and mobility [19].

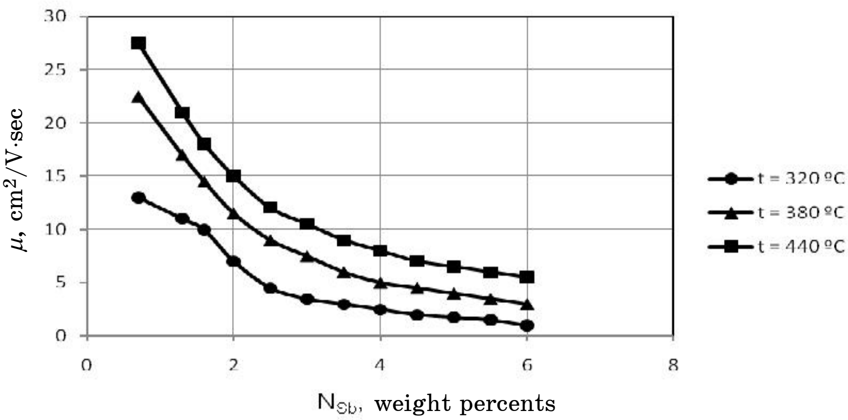

Fig. 3 *– Dependences of the charge carrier mobility versus the antimony concentration at different deposition temperatures and SnO_2:Sb film thickness d =* 500 *nm*

Transmission spectrums in wavelength range from 500 to 2500 nm of SnO_2:Sb films, produced at the temperatures 320°C, 380°C, and 440°C, are represented in Fig. 5, 6, and 7, respectively. Transmission possesses the maximal value 73% at the minimum deposition temperature (320°C) and antimony concentration (0,5 weight percents) on the wavelength 825 nm. On the same wavelength with temperature growth transmission decreases to 67% at the temperature 380°C or to 60% at the temperature 440°C. Transmission peaks move to the region of large wavelengths with temperature growth, but this displacement becomes slower with increase of antimony concentration (Fig. 5 and Fig. 6). At the antimony concentration 3,5% displacement is negligible (Fig. 6). High temperatures in the ranges of studied antimony concentrations decrease the film transmission, but increase the carrier mobility and surface resistance (Fig. 3 and Fig. 1). One more feature should be emphasized, namely, the growth of antimony concentration decreases the film transmission for all deposition temperatures. This can be conditioned by amplification of light absorption [33].

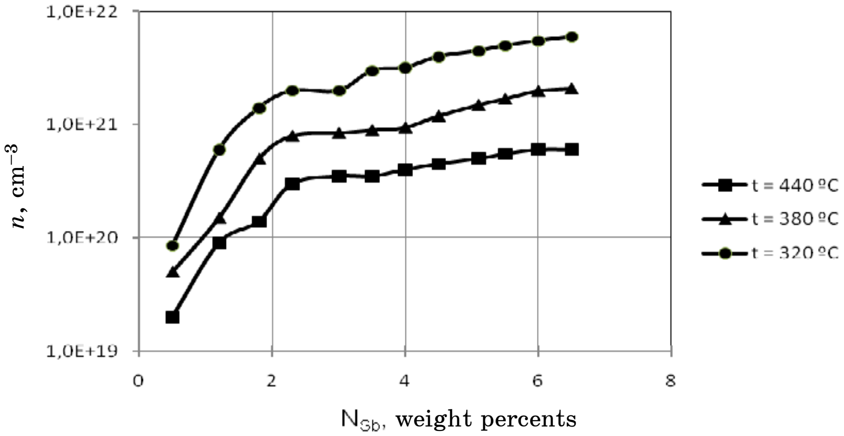

Fig. 4 – *Dependences of the charge carrier concentration versus the antimony concentration at different deposition temperatures and SnO_2:Sb film thickness d =* 500 *nm*

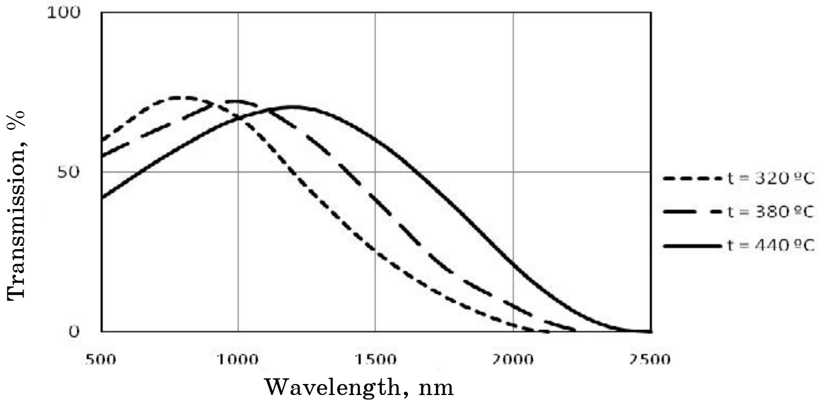

Fig. 5 – *Transmission spectrums of SnO_2:Sb films, obtained with antimony concentration* 0,5 *weight percents at different temperatures*

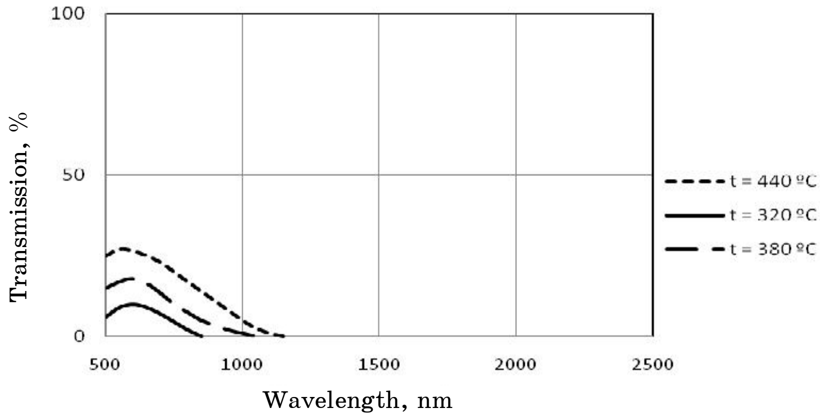

Fig. 6 *– Transmission spectrums of SnO_2:Sb films, obtained with antimony concentration* 1,8 *weight percents at different temperatures*

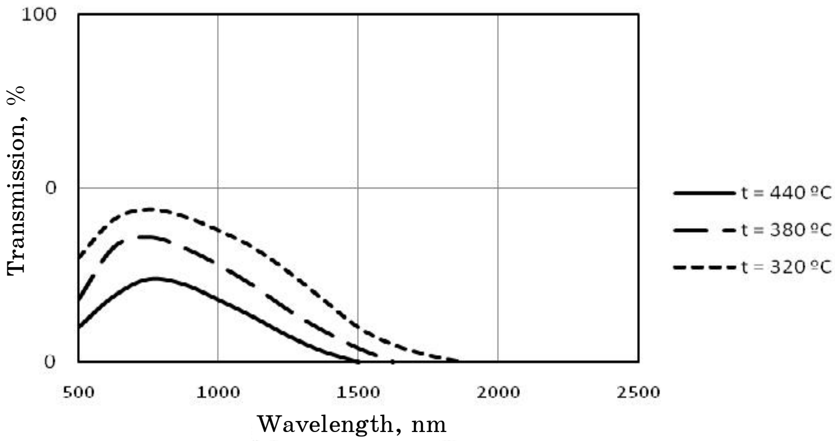

Fig. 7 *– Transmission spectrums of SnO_2:Sb films, obtained with antimony concentration* 3,5 *weight percents at different temperatures*

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