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Study of functional properties stability of SnO_2 films on the duration thermal exposure and temperature changes

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Thin films of tin oxide and composite systems based on them have found the greatest applications in solar energy. The properties of oxides depend on the obtaining technology and following processes. The choice of the optimal solution maturation time influences the functional properties of the films. In this research, solutions with the adding different volume of concentrated aqueous solution of ammonia (NH4OH) per 100 ml of the system were prepared: 0.8 ml (pH=1.40), (pH=1.46) and 1.6 ml (pH=1.49). This enabled the study of the properties of films obtained from solutions of different acidity. The resistance of the films was measured in the 10 different parts of the films. In addition, the effect of the isothermal annealing time at 2500C on the structural and optical properties of the samples was investigated. As a result of this study, there was found the correlation between an increase in the duration of annealing and a decrease in the transparency of films obtained from the SnCl4/EtOH. The annealing at temperature 2500C within 6 hours led to a change in transparency of films from 93% (λ=550nm) to 88%. The further increase of the annealing duration up to 9 hours does not affect the transparency of films.

Keywords: sol-gel, tin dioxide, surface resistance, thermal exposure, transmission spectra.
PACS numbers: 61.43. Dq, 39.30. +w

1 Introduction

The dual valency of Sn provides the reversible transformation of the stoichiometric surface with Sn4+ surface cations into a reduced surface with Sn2+ surface cations. This reaction depends on oxygen chemical potential of the system. As a result of the surface reduction, Sn 5s derived surface state forms. This surface state lowers the work function and located inside of the band gap. This property provides sensorial characteristics for materials.

Thin films of tin oxide and composite systems based on them have found the greatest applications as active layers in gas analytical equipment [1–4]. Films based on tin dioxide are of great importance for intensively developing solar energy [5–7]. Tin dioxide films are also used as transparent electrodes, catalysts, anti-reflective coatings. [8-13].

Tin oxide films have good adhesion to the glass surface, high electrical conductivity, transparency, mechanical strength and chemical resistance. These properties allow them to be used as transparent conductive coatings [14-16].

Tin dioxide is transparent in the visible and near ultraviolet regions. The properties of oxides depend on the manufacturing technology and subsequent processing [17]. Currently, several methods have been developed for producing a thin film of tin dioxide based on sol-gel technology [18-20]. In particular, the choice of the optimal solution maturation time affects the properties of the resulting films. Thus, in [21], it was found that 12 hours is the optimal time for the maturation of the solution for the manufacture of films with high transparency, and 8 hours for the manufacture of films with low resistance. It should be noticed that the change in color and viscosity of the film-forming solution indicates the gel formation. The gel formation in [21] begins 10 hours after the preparation of the solution.

This paper presents studies of changes in the resistance of films upon repeated annealing. Films obtained from solutions of SnCl4 dissolved in ethyl alcohol with a concentration of tin ions of 0.16 mol/l were used for analysis.

2 Materials and Methods

During operation, the films may be subjected to thermal stress. Therefore, along with studies of the properties of the obtained films, the question also arises of maintaining the stability of the functional properties of the films.

To study the properties of films obtained from solutions of different acidity, a series of solutions were prepared with the addition of 0.8 ml (pH=1.40), (pH=1.46) and 1.6 ml (pH=1.49) of a concentrated aqueous solution of ammonia (NH_4OH) per 100 ml of the system.

Film-forming systems were deposited on a glass substrate by dropping and flowing at an angle of 45^0. The resulting samples were dried at room temperature for 30 minutes and then annealed in a muffle furnace for 15 minutes. After cooling the sample at room temperature, its resistance was measured (the distance between the contacts was 1 mm).

3 Results and Discussion

The resistance of the films was determined by 10 measurements in different parts of the samples. Student's coefficient for 10 measurements with a reliability of 0.95 = 2.262. The error was calculated by the formula:

$$\Delta\bar{A} = t_{\gamma,n-1}\frac{\sqrt{\frac{\sum_{i=1}^{n}(A_i-\bar{A})^2}{n-1}}}{\sqrt{n}}$$

where, $\Delta\bar{A}$ – the absolute measurement error, $\Delta\bar{A}$ – the Student's coefficient, A_i – is the value of the i-th measurement, $\bar{A}$ – the arithmetic mean, n – the number of measurements.

The measurement results are presented in Table 1.

Table 1 – Resistance of samples obtained from solutions of $SnCl_4$ of different acidity, after a single annealing

pH	1.40	1.46	1.49
R, MOhm	0.755± 0.132	2.805± 0.383	11.02± 4.61

To study the preservation of the stability of the functional properties of the films under thermal exposure, the samples were reannealed at a temperature of 2000C and 4000C for 15 minutes. The measurement results are presented in Table 2.

Table 2 – Resistance of samples obtained from solutions of $SnCl_4$ of different acidity, after secondary annealing at temperatures t=200^0C and 400^0C

pH	1.40	1.46	1.49
R, MOhm (t=200^0C)	0.798± 0.223	2.861± 0.103	11.2± 2.2
R, MOhm (t=400^0C)	0.532± 0.094	0.742± 0.123	6.32± 2.52

A comparative analysis of tables 1 and 2 shows that repeated annealing at 200^0C (15 minutes) does not lead to a significant change in resistance. At the same time, after repeated annealing at a temperature of 400^0C, the resistance decreases by about 1.5 times for the initial sample (without the addition of ammonium hydroxide) with pH = 1.40 and by 2-4 times for films obtained from solutions with a higher pH value.

With an increase in the annealing temperature, the sizes of SnO_2 crystallites increase due to the crystallization of the amorphous phase and the association of crystallites as a result of partial or complete destruction of defective crystallites during annealing with the addition of their atoms to more advanced crystallites. An increase in the size of crystallites and their perfection contributes to a decrease in the resistance of the films.

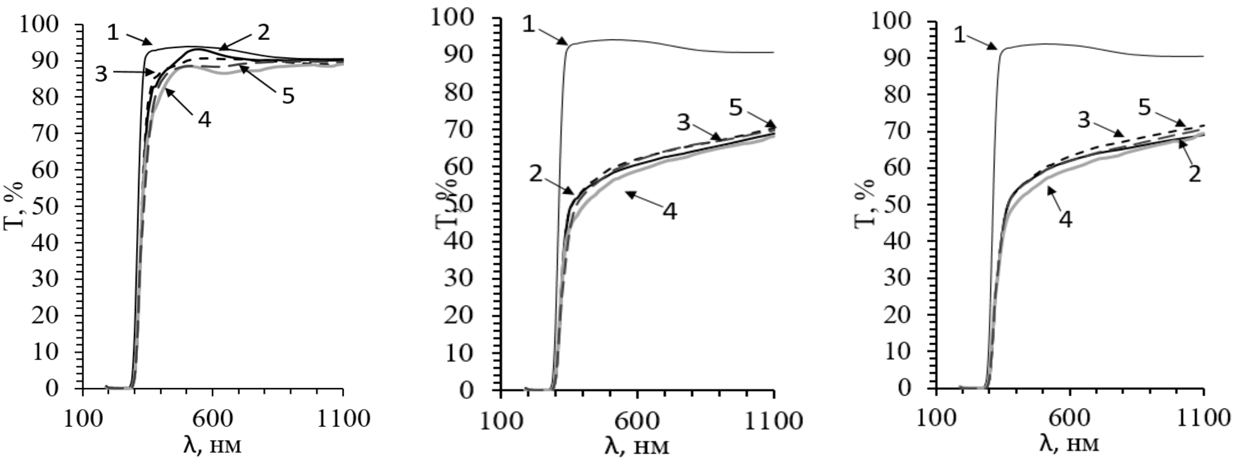
Thus, annealing for 15 minutes is insufficient to form a complete structure with stable functional properties.

The practical application of films is often associated with their heating. The "working mode", in many cases, means the presence of films, for a long time, in a heated state. In connection with the foregoing, the question arises about the stability of the properties of the films under prolonged thermal exposure.

In this section, the influence of the duration of isothermal annealing at 250^0C on the structure and optical properties of the obtained films is considered.

Figure 1 shows the transmission spectra of thin SnO_2 films obtained from a film-forming system with pH=1.40; 1.46 and 1.49.

As can be seen from Figure 1a, the transmittance decreases for films obtained from the $SnCl_4$/EtOH system with a tin ion concentration of 0.16 mol/l (pH=1.40) with an increase in the annealing time. The transmittance varies from 93% (λ=550nm) to 88% with an annealing time of 6 hours at 250^0C. Increasing the annealing time to 9 hours does not lead to a further decrease in the transmittance.

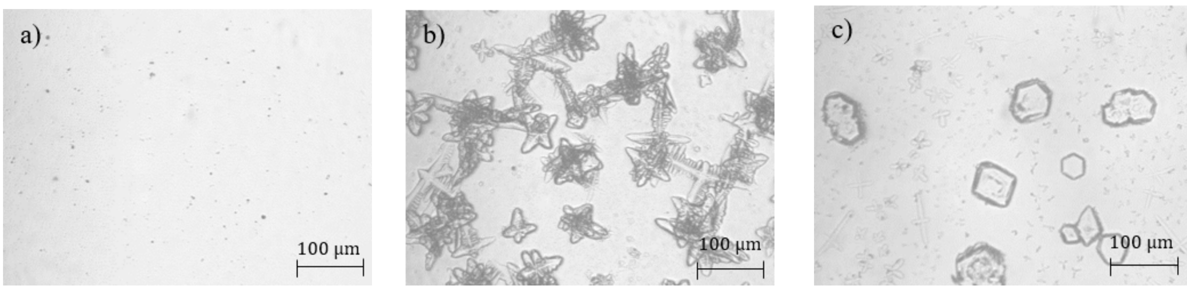


a) solution with acidity pH=1.40 b) solution with acidity pH=1.46 c) solution with acidity pH=1.49
1) glass substrate; 2) upon receipt; 3) annealing 3 hours; 4) annealing 6 hours; 5) annealing 9 hours
Figure 1 – Transmission spectra of thin SnO_2 films

The transmittance (Figure 1b, c) of samples obtained from the $SnCl_4$/EtOH system with pH = 1.46 and 1.49, with an increase in the duration of annealing up to 9 hours at 250^{0}C, changes by 1-2%.

Films, to study the stability of properties from the duration of thermal exposure, were prepared from the same film-forming systems as the films studied in the first section of this report. However, the application of the films was after three months of aging of the film-forming systems.

Figure 2 presents the surface structure of thin SnO_2 films obtained from the $SnCl_4$/EtOH film-forming system with a tin ion concentration of 0.16 mol/l.



a) solution with acidity pH=1.40 b) solution with acidity pH=1.46 c) solution with acidity pH=1.49
Figure 2 – The structure of the surface of the films after production

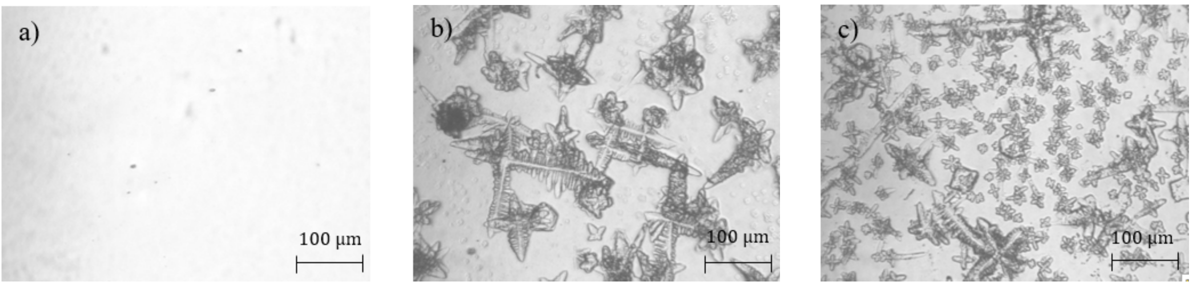
Figure 2 shows that at pH 1.40 the film-forming system has a relatively even surface (Figure 2a). At a pH of the film-forming system of 1.46, cruciform structures are formed (Figure 2b). At a system pH of 1.49, pronounced crystals of the cubic syngony formed (Figure 2c). Since HCl and an aqueous solution of ammonia are present in the film-forming system, these are presumably NH4Cl crystals. The interaction goes according to the reaction:

$$NH_4OH + HCl \;\; NH_4Cl + H_2O \quad (1)$$

Weak structural elements in the form of small cruciform structures, presumably composed of tin hydroxide and/or dioxide. Tin hydroxide, at the time of formation, has an amorphous structure. Tin dioxide is formed from tin hydroxide by the reaction:

$$Sn(OH)_4 \overset{heating}{\;\;} SnO_2 + 2H_2O \quad (2)$$

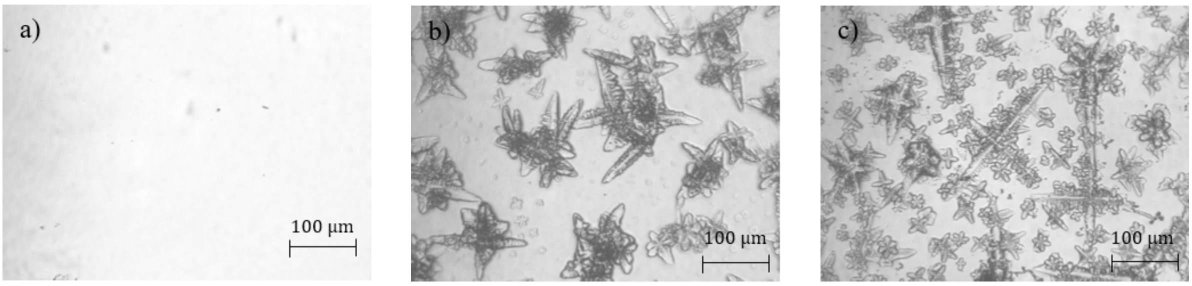
Figure 3 shows the surface structure of the films after annealing at 250^{0}C for 3 hours.



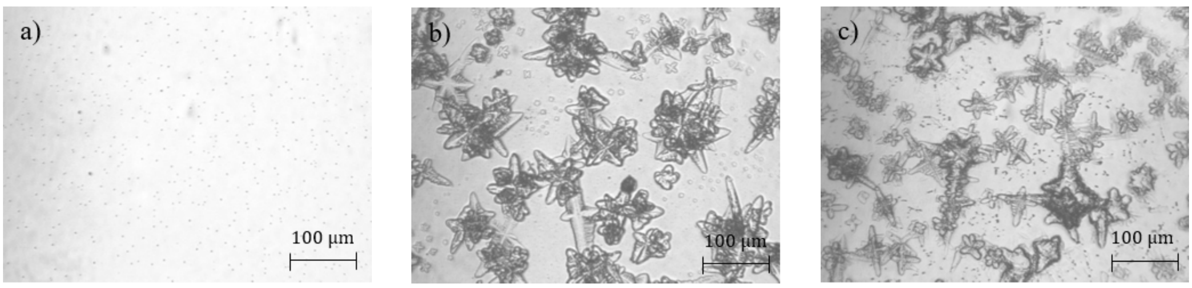
a) solution with acidity pH=1.40 b) solution with acidity pH=1.46 c) solution with acidity pH=1.49
Figure 3 – Surface structure of films after annealing at 250^{0}C for 3 hours.

As can be seen from Figure 3a, no noticeable changes are observed in the structure of the films obtained from a film-forming system with pH=1.40 after annealing at 250^{0}C for three hours. In the films obtained from a film-forming system with pH = 1.46, an increase in structural formations is observed (Figure 3b). In the films obtained from a film-forming system with pH = 1.49, both cubic syngony crystals and many large and small four- to six-petaled structures are observed (Figure 3c).

Figure 4 shows the surface structure of the films after annealing at 250^{0}C for 6 hours. Six hours of annealing at 250^{0}C did not lead to a change in the structure of the films obtained from the film-forming system with pH=1.40 (Figure 4a). In the films obtained from a film-forming system with pH=1.46 (Figure 4b), an increase in size of structural formations is observed. After six hours of annealing at 250^{0}C, no cubic crystals are observed in the structure of the films obtained from the film-forming system with pH=1.49 (Figure 4c). The four- to six- petaled structures increased in size.



a) solution with acidity pH=1.40 b) solution with acidity pH=1.46 c) solution with acidity pH=1.49
Figure 4 – Surface structure of films after annealing at 250^{0}C for 6 hours



a) solution with acidity pH=1.40 b) solution with acidity pH=1.46 c) solution with acidity pH=1.49
Figure 5 – Surface structure of films after annealing at 250^{0}C for 9 hours

Figure 5 shows the surface structure of the films after annealing for 9 hours at 250^0C. As can be seen from Figure 5a, a lot of point structural elements appeared in the film obtained from the film-forming system with pH=1.40. Nine hours of annealing at 250^0C leads to the growth of structures in films obtained from a film-forming system with pH=1.49. There are no cubic crystals.

The cubic modification of NH_4Cl is stable below 184.3^0C. Prolonged annealing at a temperature of 250^0C leads to the gradual decomposition of NH_4Cl into volatile compounds according to the reaction:

$$\begin{array}{c} T > 184{,}3^0C \\ NH_4Cl\ \ NH_3 + HCl \end{array} \qquad (3)$$

At 337.6^0C, ammonium chloride sublimes with decomposition (according to reaction 3).

4 Conclusions

A decrease in the transparency of films obtained from the SnCl4/EtOH system with a concentration of tin ions of 0.16 mol/l (pH=1.40) with an increase in the duration of annealing was found. Transparency varies from 93% (λ=550nm) to 88% with an annealing time of 6 hours at 2500C. Increasing the annealing time to 9 hours does not lead to a further decrease in transparency. The transparency of the samples obtained from the SnCl4/EtOH system with pH=1.46 and 1.49, with an increase in the duration of annealing up to 9 hours at 2500C, changes within the measurement accuracy. The surface structure of the films changes with increasing annealing time. Additional structural formations are formed.

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