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The effect of three-minute exposure of oxygen plasma on the properties of tin oxide films

Research devoted to the effect of three-minute exposure of oxygen plasma on the properties of tin oxide films investigation. The films were obtained by sol-gel method from five-water tin tetrachloride solution. The concentration of tin ions in the $SnCl_4$/EtOH film-forming system was 0.14 mol/l. The solution system was deposed on the glass substrate by carring out a modified dipping method. Plasma treatment was performed at a pressure of 6.5 Pa and a power of about 20 Watts. The frequency of the oscillations produced by the generator was 27.12 ± 0.6 % MHz as well. The temperature of the samples during processing did not exceed 100 ºC. As a result of the formation of tin oxide (II), the film transmittance decreased after treatment with oxygen plasma. The width of the electric forbidden zone of the obtained samples was calculated, which was 3.95 eV for glass and 3.79 eV for film. The resistance of the films was determined by 10 measurements on different parts of the samples. The film without processing has a resistance of about 4255 ± 1158 kΩ, after processing, the resistance decreased by 25 times and amounted to 167 ± 26 kΩ. A decrease in resistance indicates an increase in the concentration of charge carriers in the sample. The resulting SnO is a semiconductor that lowers the transmittance of the studied films and contributes to reducing their resistance. X-ray structural analysis of the samples was also performed. After processing in oxygen plasma, the intensity of reflection from the (110) plane have increased. It should be noted that the number of planes with (101) indexes has decreased. The study of the sample surface showed the destructive nature of three-minute exposure by oxygen plasma.

Keywords: thin films, SnO_2, sol-gel method, oxygen plasma treatment, transparency, structure, resistance, tin oxide (II).

Introduction

The study of tin oxide is associated with its multifunctional application. Tin dioxide belongs to a class of materials that combines high electrical conductivity with optical transparency and is therefore an important component for optoelectronic applications [1–3]. The lattice oxygen from the surface of the tin oxide is able to react chemically with the reagent and after the reaction to be renewed by the oxygen of the gas phase (mechanism of Mars – van Krevelen) [4]. This ability makes it possible to use SnO_2 as a catalyst for oxidative processes [5–7]. The change in the resistance of tin oxide in the presence of various gases formed the basis for use as a sensitive element in gas sensors [8–10].

Among the various methods used to improve the functional properties of metal oxide layers, plasma treatment is of particular interest [11–13]. Analysis of changes in the optical parameters and structural characteristics of tin dioxide after plasma treatment allows us to better understand the dynamics of changes in the physical properties of thin films of tin dioxide.

Experimental

To produce SnO_2 films, five-water tin tetrachloride was used as the initial reagent, and 97 % ethanol was used as the solvent. In tin tetrachloride systems, ethanol does not precipitate longer than in water-based systems. $SnCl_4$/EtOH film-forming systems with a tin ion concentration of 0.14 mol/l were prepared. Film-forming systems were applied to substrates (glass slides) by a modified dipping method. They were air-dried for 1–2 minutes and annealed on IKA C-MAG HP7 electric stoves at a temperature of 400°C in the air. In this case, tin tetrachloride interacts with water from the air to form tin hydroxide and hydrochloric acid. Hydrochloric acid and solvent are removed from the film-forming system when heated, and unstable $Sn(OH)_4$ decomposes to form water and the desired tin oxide by reaction [14, 15]:

$$Sn(OH)_4 \rightarrow SnO_2 + 2H_2O \quad (1)$$

12 layers were applied. The film thickness was determined by a microbalance [16] and amounted to 413 = 7 nm.

Treatment of SnO_2 thin films in oxygen plasma was performed in a quartz tube. Oxygen was obtained by pyrolytic decomposition of potassium permanganate:

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2 \quad (2)$$

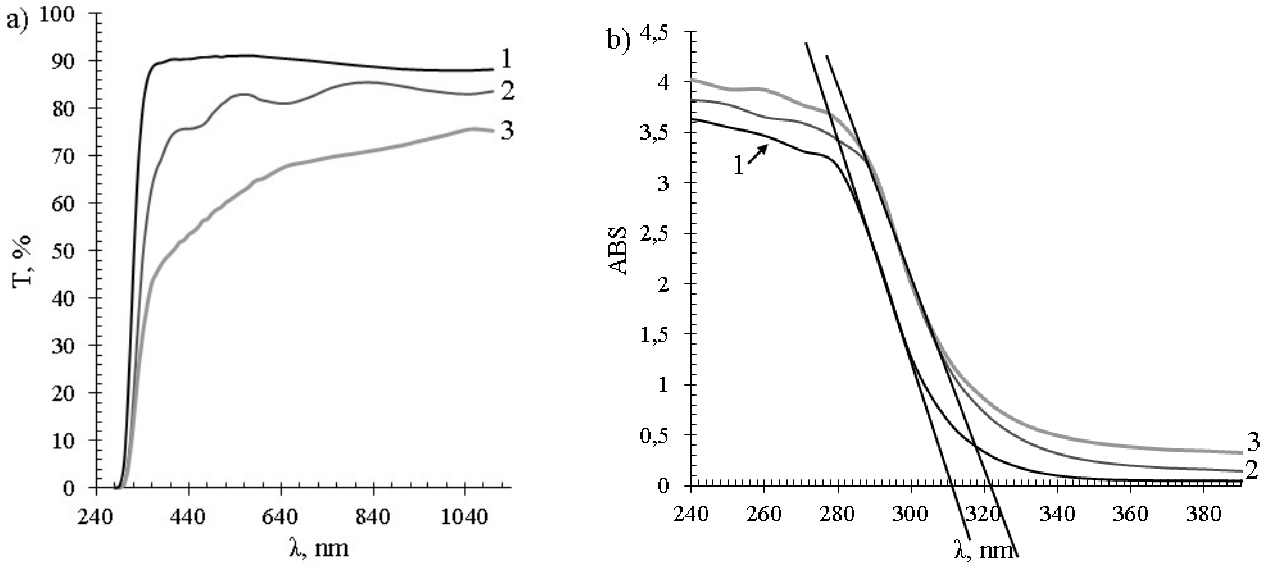
Plasma treatment was performed at a pressure of 6.5 Pa and a power of about 20 Watts. The frequency of the oscillations produced by the generator was 27.12 ± 0.6 % MHz as well. The temperature of the samples during processing did not exceed 100 ºC. The processing time was 3 minutes.

Transmission and absorption spectra were measured using a UNICO SpectroQuest 2800 spectrophotometer. The structure of the films was studied using a scanning electron microscope JSM-6490LA, JEOL and an optical microscope MPE-11. To output data to a personal computer, a television camera for a vec-535 microscope was used. The composition of the films was determined using x-ray diffraction analysis on a DRON-6 diffractometer. The resistance of the films was determined using a UT70B multimeter. The distance between the contacts was 1 mm.

Results and Discussion

Optical property

Figure 1 shows the transmission and absorption spectra of tin oxide thin films before and after oxygen plasma treatment.



1 — glass substrate; *2* — film after application; *3* — film after plasma treatment

Figure 1. *a* — transmission spectra of films; *b* — absorption spectra of films

Figure 1*a* shows that after treatment with oxygen plasma (Fig. 1*a* curve 3) the film transmittance has decreased compared to the film transmittance without processing (Fig. 1*a* nodding 2). The decrease in the transmission coefficient may be caused by the formation of compounds that are opaque in the visible region of the spectrum [17, 18]. The formation of tin oxide (II) is most likely. The mechanism of formation of SnO in SnO_2 films under the influence of oxygen-rich plasma in a chemically active (ionized) form requires further development. One of the assumptions, according to the» activated complex theory», is the formation of a complex of ionized oxygen with film defects. The resulting complex can decay to form SnO + O_2 or supplement the crystal structure to stoichiometric SnO_2.

At the edge of the fundamental absorption (Fig. 1*b*) λ_{cr} were determined for the glass substrate and film before and after treatment with oxygen plasma. For the glass substrate λ_{cr} = 311nm, for the film without processing and after processing, the edge of the fundamental absorption coincided and λ_{cr} was 322 nm. Using a well-known formula:

$$Eg = (hc)/\lambda_{cr},$$

where h is the Planck constant in eV; c is the speed of light, and λ_{cr} is the long-wave boundary of its own absorption.

The width of the electric forbidden zone of the glass — 3.95 eV and the film — 3.79 eV were calculated.

The resistance of the films

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

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

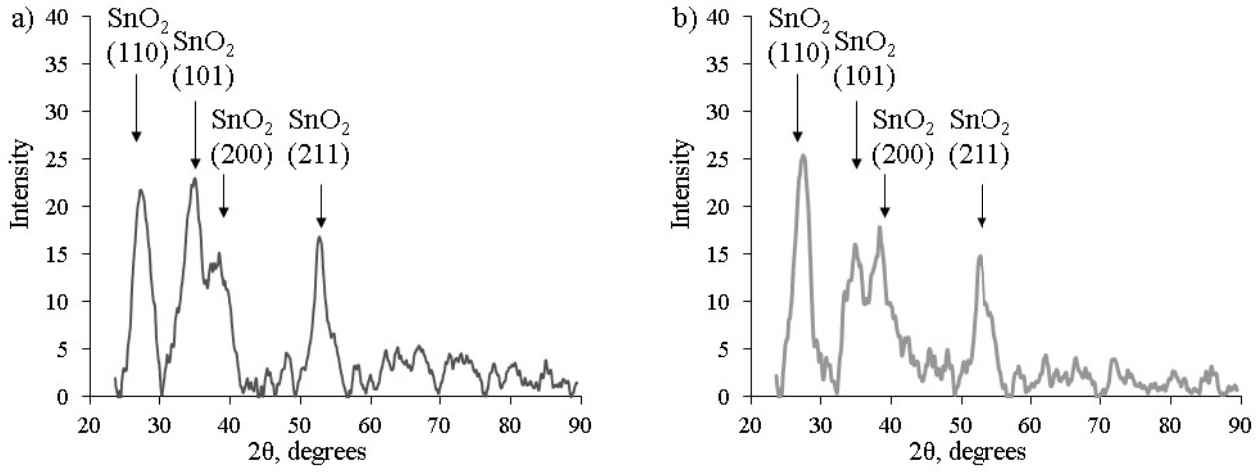
where $\Delta\overline{A}$ — is the absolute measurement error; $t_{\gamma,n-1}$ — is the Student's coefficient; A_i — is the value of the i-th measurement; $\overline{A}$ — is the arithmetic mean; n — is the number of measurements.

Despite the fact that the width of the band gap of the film, calculated from the absorption spectra, did not change after processing, the resistance of the film significantly decreased. The film without processing has a resistance of 4255 ± 1158 kΩ, after processing, the resistance decreased by 25 times and amounted to 167 ± 26 kΩ.

The conductivity of tin dioxide is associated with the presence of intrinsic defects — oxygen vacancies that form small donor levels [19]. These levels can also be formed by impurities. A decrease in resistance indicates an increase in the concentration of charge carriers. The resulting SnO, which reduces the transmittance, is a semiconductor and can also contribute to reducing the resistance.

Diffraction analysis

The source signal from thin films on a glass substrate has a high noise level. Using the method of increasing the signal-to-noise ratio [20, 21], the following data were obtained and analyzed. Figure 2 shows the results of signal selection.



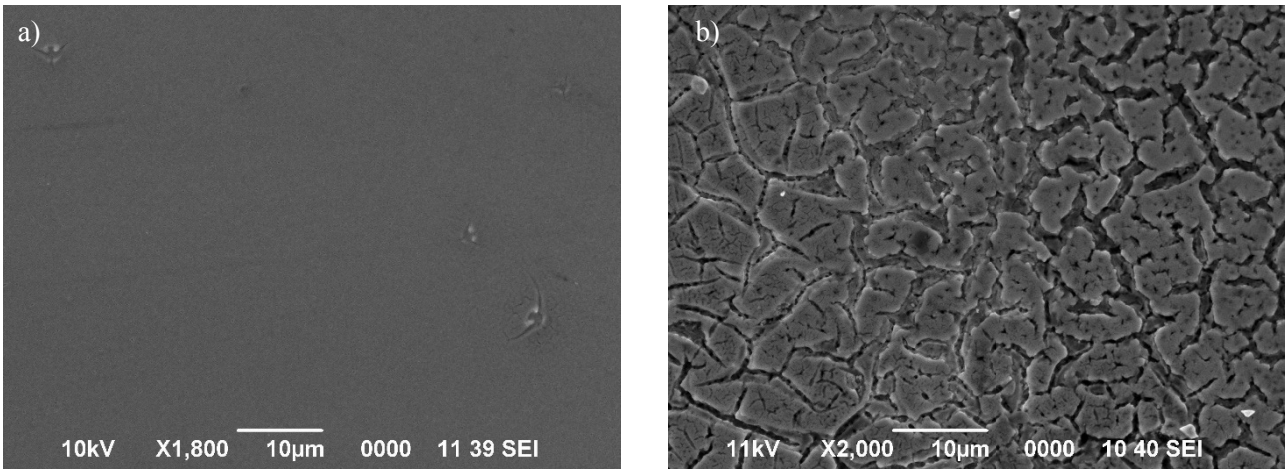
a — after application; *b* — after plasma treatment

Figure 2. X-ray diagram of tin oxide films

On X-ray diagrams (Fig. 2 *a*, *b*) peaks of reflections from the SnO_2 planes are observed. Peaks from other tin oxides are not observed. This indicates the absence of SnO in the crystalline form, and does not cancel the possibility of its existence in an amorphous state. It can be also noticed that the intensity of reflection from the (110) plane, after processing in oxygen plasma, increased. This indicates an increase in the number of planes with these Miller indexes. And the number of planes with indexes (101) has decreased. The destruction of crystallites along the planes (101) and (200) is associated with the transformation of the polycrystalline structure into a sub-nanometric cluster structure after plasma exposure [22, 23].

Surface structure

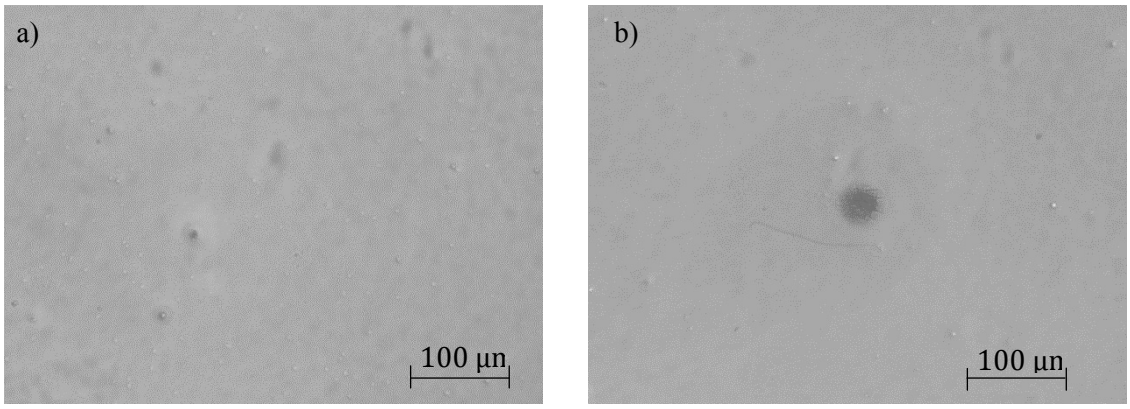
The surface structure depends on many parameters: the method of application, the concentration of the initial reagents, alloying impurities, etc. The dominant mechanism for the formation of spatial structures may be the phenomenon of self-organization [24]. Figure 3 shows images of the film surface after application and after plasma treatment.



a — after application; *b* — after plasma treatment

Figure 3. SEM images of the surface of tin oxide films

Figure 3*a* and *b* show that three-minute oxygen plasma treatment is destructive. The surface of the film was cracked. Figure 4 shows photos of the surface taken with an optical microscope with a smaller magnification.



a — after application; *b* — after plasma treatment

Figure 4. Surface of tin oxide films obtained using an optical microscope

Figure 4*a* shows that on the surface of the film after its application, there are rare, chaotically located hills — blisters [25]. They are formed by heating a wet gel. The reaction by-products and the solvent evaporate here. In places where the process of gelation has already begun, but evaporation has not yet occurred, the formation of blisters occurs. Figure 4*b* shows that the highest and most exposed blisters have darkened. Probably, in these places that SnO is formed, and it reduces the transparency of the films.

Conclusions

It was found that treatment of a glow discharge with a low-temperature plasma in an oxygen-rich atmosphere for three minutes leads to a decrease in the transparency of the films. Also, as a result of this ef-

fect, the resistance of the films is sharply reduced (by 25 times). There is a destructive effect of plasma in the destruction of SnO_2 crystallites and the appearance of cracks at the micron level on the surface of the film. An increase in the conductivity of the films indicates the formation of additional charge sources. The formation of tin oxide (II) clusters in the places of large and opened blisters was revealed.

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Оттегі плазмасының үш минуттық қалайы оксиді қабықшаларының қасиеттеріне әсері

Оттегі плазмасының үш минуттық қалайы оксиді қабықшаларының қасиеттеріне әсері зерттелген. Қабықшалар бес текті тетрахлорид қалайының ерітіндісінен золь-гель әдісімен алынған. $SnCl_4$/EtOH қабықша түзуші жүйесіндегі қалайы иондарының концентрациясы 0,14 моль/л құрайды. Шыныдан жасалған төсенішке ерітінді батыру әдісімен жағылды. Плазма өңдеуі қысымы 6,5 Па және қуаттылығы 20 Ватт шамасында жүргізілген. Генератор жасайтын тербеліс жиілігі 27,12 ± 0,6 %-МГц-ді құрады. Өңдеу кезіндегі үлгілердің температурасы 100°С-тан артылмады. Оттегі плазмасымен өңдеуден кейін (II) валентті қалайы оксидінің пайда болуы салдарынан қабықшаның өткізу коэффициенті төмендеді. Алынған үлгілердің электрондық шекті зонасының аймағы есептелген, ол шыны төсеніш үшін — 3,95 эВ, қабықша үшін — 3,79 эВ. Қабықшалардың кедергісі үлгілердің 10 әртүрлі нүктелік аймағында өлшеніп, анықталған. Өңдеусіз қабықшаның кедергісі 4255 ± 1158 кОм-ға тең болады, өңдеуден кейін олардың кедергісі 25 есе азайды және шамасы 167 ± 26 кОм құрады. Кедергінің кемуі заряд тасымалдаушылардың концентрациясының ұлғаюын көрсеткен. Зерттеу барысында пайда болған SnO қабықшалардың өткізу коэффициентін төмендететін және олардың кедергісін азайтуға үлес қосатын жартылай өткізгіш болып табылады. Үлгілерге рентген талдауы да жүргізілген. Оттегі плазмасында өңдеуден кейін (110) жазықтықтан шағылысу интенсивтілігі артты. Бұл жерде (101) индексі бар жазықтар саны азайғанын да атап өту керек. Үлгілердің беттік зерттеуі оттегі плазмасының үш минуттық әсерінің деструктивті сипатын көрсеткен.

Кілт сөздер: жұқа қабықшалар, SnO_2, золь-гель әдісі, оттегі плазмасымен өңдеу, мөлдірлілік, қабықша құрылымы, кедергі, (II) валентті қалайы оксиді.

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Влияние трехминутного воздействия кислородной плазмой на свойства пленок оксида олова

Исследовано влияние трехминутного воздействия кислородной плазмой на свойства пленок оксида олова. Пленки были получены золь-гель методом из пятиводного тетрахлорида олова. Концентрация ионов олова в пленкообразующей системе $SnCl_4$/EtOH составляла 0,14 моль/л. Нанесение на стеклянную подложку проводилось модифицированным методом окунания. Обработка плазмой осуществлялась при давлении 6,5 Па и мощности около 20 Вт. Частота колебаний, создаваемых генератором, составляла 27,12 МГц ±0,6 %. Температура образцов при обработке не превышала 100 ºС. Вследствие образования оксида олова (II) понизился коэффициент пропускания пленки после обработки кислородной плазмой. Рассчитана ширина запрещенной зоны полученных образцов, которая для стекла составила 3,95 эВ, для пленки — 3,79 эВ. Сопротивление пленок определялось по 10 измерениям на разных участках образцов. Пленка без обработки обладает сопротивлением 4255 ± 1158 кОм, после

обработки сопротивление уменьшилось в 25 раз и составило 167 ± 26 кОм. Уменьшение сопротивления указывает на увеличение концентрации носителей заряда. Образовавшийся SnO является полупроводником, который понижает коэффициент пропускания исследуемых пленок и вносит вклад в уменьшение их сопротивления. Проведен рентгеноструктурный анализ образцов. После обработки в кислородной плазме повысилась интенсивность отражения от плоскости (110). Следует отметить, что количество плоскостей с индексами (101) уменьшилось. Исследование поверхности образцов показало деструктивный характер трехминутного воздействия кислородной плазмой.

Ключевые слова: тонкие пленки, SnO_2, золь-гель метод, обработка кислородной плазмой, прозрачность, структура, сопротивление, оксид олова (II).

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