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Influence of Plasma Treatment on Physical Properties of Thin SnO_2 Films Obtained from $SnCl_4$ Solutions with Additions of NH_4F and NH_4OH

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Abstract

This paper considers the effect of oxygen and hydrogen plasma on SnO_2 films synthesized from solutions of tin tetrachloride containing NH_4F and NH_4OH additives. It was found that the treatment of samples with oxygen plasma for 5 min led to a decrease in transparency by 1.11 and 1.17 times. On the transmission spectra, a decrease in the transmittance at a wavelength of 450 nm to 38.1% (1.24 times) in samples obtained from solutions with the addition of NH_4F and up to 29.9% (1.53 times) in samples obtained from solutions with the addition of NH_4OH is observed. The formation of tin oxide (II) under the influence of the reducing properties of hydrogen plasma is assumed. At the same time, the formation of metal tin from tin dioxide is not observed here. Due to the decreasing of transmission coefficient in the long-wave region of the spectrum. There is an increase in surface resistance after treatment with oxygen plasma, due to filling oxygen vacancies. Treatment of hydrogen plasma films leads to a decrease in surface resistance. Perhaps due to the increase in oxygen vacancies under the influence of hydrogen plasma. Within five minutes, the oxygen and hydrogen plasma had a more active effect on the films obtained from the solution with the addition of ammonium hydroxide, which is associated with a higher porosity of the sample. Consequently, irrespective of the time of plasma exposure with increasing the surface of contact between ionized gases and the film material, the interaction efficiency will increase.

1. Introduction

The electrical conductivity of tin dioxide is extremely sensitive to the state of the surface in the temperature range 300–800 K, at which oxidation-reduction reactions take place on its surface. Nanocrystalline films of tin dioxide are selectively sensitive to the presence of toxic gases, organic and some biological molecules in the surrounding atmosphere [1–3]. SnO_2-based films are also used as transparent conductive coatings [4], ultraviolet photodetectors [5], passivating layer in transparent heat-reflecting mirrors [6]. The synthesized tin oxide films do not always have good electrical conductivity. In order to reduce electrical resistance and increase gas sensitivity, small concentrations of impurities are added to the films. For example, fluorine ions, which are donors of free charge carriers [7, 8].

This paper considers the effect of oxygen and hydrogen plasma on SnO_2 films synthesized from solutions of tin tetrachloride containing NH_4F and NH_4OH additives.

2. Experimental

The work used substances qualification «especially clean» production of a company «Labhimprom» (Kazakhstan).

Thin films of tin oxide were obtained by sol-gel method. Solutions were prepared from anhydrous tin tetrachloride in ethanol. After maturation (more than 6 h), a fluorinating agent – NH_4F was added to the film-forming solution The ratio of tin ions to fluorine ions was 10/4. NH_4F crystals were dissolved during 2-hour stirring at a speed of 140 rpm and parallel heating – 35 °C on the orbital rotation shaker LAB-PU-01. The acidity of the final

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solution was controlled by pH-Meter pH-150M and was pH = 1.80.

Since after the addition of ammonium fluoride, the acidity of the solution changed and became close to the pH of the tin acid deposition (pH = 2.0), a solution with pH = 1.80, but containing no fluorine ions was produced. As a reagent, increase the basic properties of the solution, was selected NH_4OH because when heated it breaks down into easily removed from the film products (NH_3 + H_2O). In the matured alcoholic solution $SnCl_4$, 20% alcoholic ammonia solution was added drop by drop with constant stirring until the required pH value was reached.

The final concentration of tin ions in all solutions was 0.13 mol/l.

The solutions were applied to the surface of the preliminarily purified glass slide fixed on a specially designed table of the rotor of the central centrifuge. After that, the sample was turned at a velocity of 3800 rpm for 3–5 s, with the aim to remove the excess solution from the substrate surface. The substrate with the remaining thin layer of the solution was heated by infrared radiation up to 80 °C for 1–2 min to vaporize the solvent. The dried sample was annealed in a muffle furnace for 15 min at 400 °C. After cooling, the cycle was repeated. Fifteen layers were applied altogether.

Treatment of the samples in oxygen and hydrogen plasmas with a power of ~20 W and at an oscillation frequency of 27.12 MHz ± 0.6% was performed under a pressure of 6.5 Pa and at a temperature of ~100 °C for 5 min.

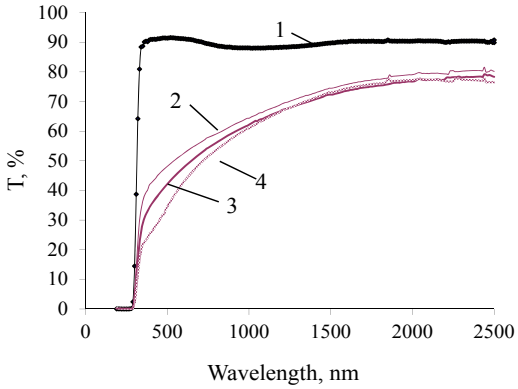
The transmittance spectra of the films were measured on SF-256 UVI (190–1100) nm and SF-256BIK (1000–2500) nm two-beam spectrophotometers. The surface resistance of the films was measured at room temperature according to four-probe method. The surface of the layers was analyzed by Atomic force microscopy (JSPM 5200, Jeol, Japan) using AFM AC technique.

3. Results and discussion

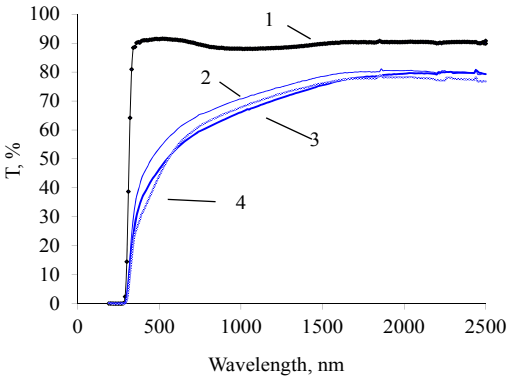
3.1. The optical properties of the films

Figure 1 shows the transmission spectra of films synthesized from solutions of tin tetrachloride containing NH_4F and NH_4OH additives and treated with hydrogen and oxygen plasma for 5 min.

The transmission spectra of films obtained from solutions of tin tetrachloride in ethanol without additives [7] demonstrate interference peaks, which



(a)



(b)

Fig. 1. The transmission spectra of SnO_2 films synthesized from tin tetrachloride solution containing NH_4F (a) and NH_4OH (b) additives and treated with plasma for 5 min: 1 – glass substrate; 2 – annealing for 15 min at t = 400 °C; 3 – after treatment with O-plasma; 4 – after treatment with H-plasma.

usually occur in the case of thin uniform plane-parallel films with a thickness multiple of the wavelength. Film, without additives, is passed 80-85% of the flow of electromagnetic radiation over the whole measured wavelength range. The transmission spectra of the films obtained from solutions with addition of NH_4F and NH_4OH show a decrease in transparency from 85 to 40–65% in the range of visible wavelengths of 300–700 nm. The transmission spectra showed no interference peaks. The transmission spectrum demonstrates interference fringes under the condition of weak absorption of radiation by a thin film, and the thickness of the transparent substrate should always be much larger than the thickness of the film. The film itself is on the substrate. With a decrease in film thickness, the interference extremes move away from each other [9]. Interference bands in the transmission spectra are not observed at all in the case of absorption and/or scattering of electromagnetic radiation from

irregularities of the film surface. Studies of the surface structure of films [10] obtained from solutions of tin tetrachloride in ethanol with the addition of NH_4F and NH_4OH showed that the absence of interference peaks is due to a greater extent to the scattering of electromagnetic radiation from surface irregularities.

Processing samples with oxygen plasma for 5 min led to a decrease in transparency of 1.11 and 1.17 times. This may be due to increased surface roughness. After treatment with hydrogen plasma, the samples acquired a brown tint. On the transmission spectra, a decrease in the transmittance at a wavelength of 450 nm to 38.1% (1.24 times) in samples obtained from solutions with the addition of NH_4F and up to 29.9% (1.53 times) in samples obtained from solutions with the addition of NH_4OH is observed. This indicates the formation of chemical compounds other than SnO_2, under the influence of the reducing properties of hydrogen plasma. Perhaps it is tin oxide (II) [11], which has a black-blue or brown-black color. Recovery of tin dioxide to metal tin is unlikely. The appearance of metal particles would lead to a decrease in the transmission coefficient in the long-wave region of the spectrum [12].

3.2. Surface resistance measurement

The surface resistance of thin SnO_2 films was determined by 5 measurements with a confidence level P = 0.95 and a Student's coefficient $t_{0.95.4} = 2.776$. The measurement results are presented in Table 1.

As can be seen from Table 1, films synthesized from a film-forming solution containing NH_4F have less resistance than films obtained from solutions that do not contain ammonium fluoride, which indicates the presence of fluorine ions as an additional source of free charge carriers in the structure of the films.

Table 1
Surface resistance of SnO_2 thin films after plasma treatment

Composition of film-forming solution	Surface resistivity, kOhms/square		
	without treatment	after O-plasma treatment	after H-plasma treatment
$SnCl_4$ in ethanol with NH_4F	6.68±1.54	51.29±6.86	1.63±0.26
$SnCl_4$ in ethanol with NH_4OH	15.41±1.83	182.92±22.51	2.72±0.33

Treatment with oxygen plasma leads to an increase in the surface resistance of fluoride doped films by 7.7 times, and films obtained from a solution containing ammonium hydroxide – by 11.9 times. As is known, the conductivity of tin dioxide is due to oxygen deficiency [13]. Oxygen vacancies are donors. The energy levels have a depth (relative to the bottom of the conduction band) of 0.03 to 0.06 eV for a single, and from 0.013 to 0.21 eV for a twice ionized oxygen vacancy. Apparently, oxygen plasma treatment leads to filling of oxygen vacancies, which caused an increase in the surface resistance of the films.

Treatment of films with hydrogen plasma leads to a decrease in surface resistance. The resistance of films synthesized from a solution containing ammonium fluoride decreased by 4.1 times, and the resistance of films synthesized from a solution with the addition of ammonium hydroxide – by 5.7 times. The decrease in resistance seems to be due to the increase in oxygen vacancies under the influence of hydrogen plasma. Hydrogen, being a reducing agent and being in a chemically active (ionized) state, restored some of the SnO_2 molecules to SnO. What was already suggested when discussing the transmission spectra. And provoked the formation of additional oxygen vacancies, due to the formation of H_2O molecules.

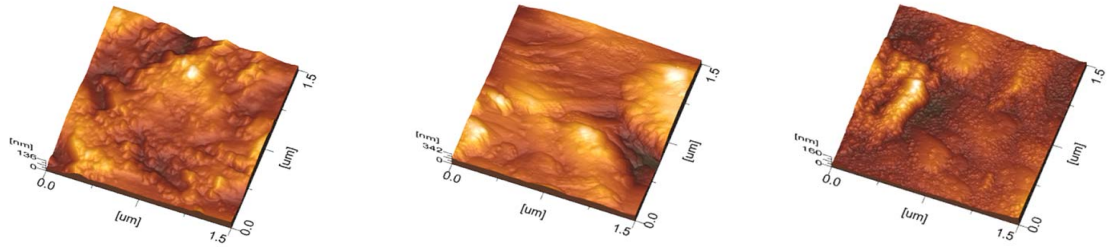
Oxygen and hydrogen plasma had a greater impact on the films obtained from the solution with the addition of ammonium hydroxide. This may be due to the greater porosity of the sample. Consequently, with the increase of the contact surface of ionized gases with the film material.

3.3. The topography of the surface of tin dioxide films

Figure 2 shows AFM images of the surface of SnO_2 films, obtained from solutions of tin tetrachloride containing NH_4F.

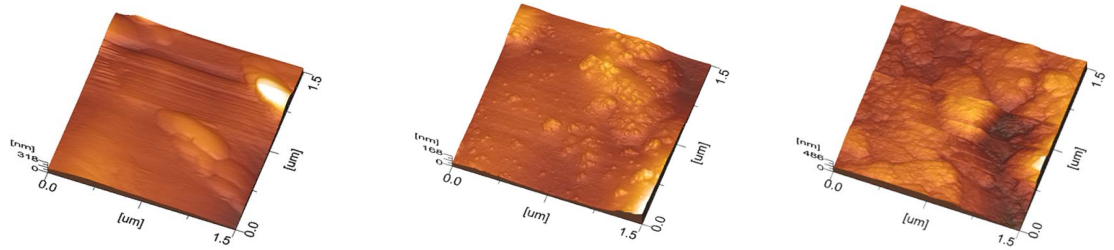
As can be seen from Fig. 2 treatment with oxygen plasma (Fig. 2b) led to the smoothing of small surface irregularities, and the treatment with hydrogen plasma (Fig. 2c), on the contrary, to the formation of small 30–50 nm dome-shaped particles. Figure 3 shows images of the surface of SnO_2 films obtained from a solution of tin tetrachloride containing NH_4OH.

From Fig. 3a it can be seen that the film obtained from a solution of tin tetrachloride with the addition of ammonium hydroxide has a smoother surface (at this increase) than the film (Fig. 2a), obtained



(a) (b) (c)

Fig. 2. Images of the surface (1.5×1.5 μm) of SnO_2 films obtained from tin tetrachloride solutions containing NH_4F: (a) – after synthesis (400° C, 15 min); (b) – after treatment with O-plasma; (c) – after treatment with H-plasma.



(a) (b) (c)

Fig. 3. Images of the surface (a 1.5×1.5 μm) of SnO_2 films, obtained from solutions of tin tetrachloride containing NH_4OH: (a) – after synthesis (400 °C, 15 min); (b) – after treatment with O-plasma; (c) – after treatment with H-plasma.

from a solution of tin tetrachloride with the addition of ammonium fluoride. Oxygen plasma treatment caused the formation of separate or grouped particles of size 200–50 nm (Fig. 3b). Hydrogen plasma treatment (Fig. 3c), as in the case of a film obtained from a solution of tin tetrachloride with the addition of NH_4F, leads to the formation of small 30–50 nm particles. However, the shape of the particles is different. The films obtained from a solution of tin tetrachloride with the addition of NH_4OH particles are more flat.

Table 2 presents data on the analysis of the roughness of the films obtained from the solution of tin tetrachloride containing NH_4F and NH_4OH.

Table 2

Analysis of the surface topography of SnO_2 films obtained from a solution of the tetrachloride of tin, containing NH_4F and NH_4OH

Sample	Size images	R_a, nm	R_q, nm	R_{zjis}, nm	R_z, nm	S, mkm^2	S_{ratio}
Film obtained from a solution of tin tetrachloride containing NH_4F							
Aftersynthesis	500×500 nm 1.5×1.5 mkm	8.13 16.4	10.1 20.4	49.3 110.4	54.8 134.2	2.69 2.44	1.08 1.09
O-plasma	500×500 nm 1.5×1.5 mkm	9.20 41.5	12.0 54.8	66.9 318.4	76.7 341.1	2.82 2.82	1.13 1.25
H-plasma	500×500 nm 1.5×1.5 mkm	6.33 19.0	7.95 24.0	45.5 143.5	48.4 160.4	2.76 2.79	1.11 1.24
Film obtained from a solution of tin tetrachloride containing NH_4OH							
Aftersynthesis	500×500 nm 1.5×1.5 mkm	21.3 23.3	24.0 34.7	22.1 175.70	84.2 3071.0	2.03 2.43	1.11 1.08
O-plasma	500×500 nm 1.5×1.5 mkm	2.8 15.2	4.22 21.3	29.4 131.4	41.9 168.2	2.60 2.38	1.04 1.06
H-plasma	500×500 nm 1.5×1.5 mkm	9.94 58.3	13.5 72.6	95.8 422.3	129.6 485.7	3.08 3.82	1.23 1.70

Table 2 shows that the average height of the R_a surface points, as well as other parameters, depends on the size of the investigated area. The exception is the surface of the film obtained from a solution of tin tetrachloride with the addition of NH_4OH after synthesis. The average height of the points of the surface is 21.3 at the size of the plot 500×500 nm and 23.3 at the size of the plot 1.5×1.5 μm. However, there are rare large particles that rise 3071.0 nm from the zero point of the surface (R_z, nm).

The average height of the points of the surface is 21.3 at a section size of 500×500 nm and 23.3 at a section size of 1.5×1.5 μm. However, there are rare large particles that rise to 3071.0 nm from the zero point of the surface (R_z, nm).

Analysis of the surface topography of the films SnO_2 with the addition of NH_4F shows that the root-mean-square roughness (R_q, nm) as a result of treatment with O-plasma increases by 1.1 times, while after treatment with H-plasma decreases by 1.3 times.

Analysis of the surface topography of SnO_2 films obtained from a solution of tin tetrachloride supplemented with NH_4OH, as a result of treatment with O and H plasmas, the root-mean-square roughness decreases by 7.6 and 2.1 times.

4. Conclusions

Hydrogen, being a reducing agent and being in a chemically active (ionized) state, restored some of the SnO_2 molecules to SnO. At the same time, the formation of metal tin from tin dioxide is not observed here. Due to the decreasing of transmission coefficient in the long-wave region of the spectrum.

Surface resistance increases after treatment with oxygen plasma due to filling oxygen vacancies. Treatment of hydrogen plasma films leads to a decrease in surface resistance, due to the increase in oxygen vacancies under the influence of hydrogen plasma. Within five minutes, the oxygen and hydrogen plasma had a more active effect on the films obtained from the solution with the addition of ammonium hydroxide, which is associated with a higher porosity of the sample.

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