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MORPHOLOGY AND OPTICAL PROPERTIES OF SnO_2 COATINGS, FORMED BY THE METHOD OF MAGNETRON SPLUTTERING FOLLOWED BY RADIATION ANNEALING

Vladimir Sergeevich Vaschilin, Vladimir Mikhailovich Nartsev, Valery Vladimirovich Kolesnik, Sergey Victorovich Zaitsev, Dmitriy Stanislavovich Prokhorencov, Mikhail Vitalevich Limarenco, Evgenij Ivanovich Evtushenko

Belgorod State Technological University named after V.G. Shukhov,
46, Kostyukov Street, Belgorod,308012, Russia
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Belgorod State Technological University named after V.G. Shukhov,
46,Kostyukov Street, Belgorod,308012, Russia.

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Abstract.

The effect of annealing radiation in vacuum on the structure and the properties of stannic oxide coatings formed by reactive magnetron sputtering at a working pressure of 0, 6 Pa in the chamber on the slide substrate has been studied. The results of optical and X-ray diffraction studies of SnO_2-coatings at various stages of radiation annealing at 400°C and fractographs and micrographs of the sample surface are given. It is shown that the coating of tin dioxide, deposited at 0,6 Pa, at the initial stages (the first 2-4 minutes) of the radiation annealing undergo significant restructuring: there occurs crystallization (the main peaks of cassiterite rise), the columnar structure is changed to the granular one, the thickness of coating increases and the refractive index decreases. Subsequent annealing of the radiation destroys the coating of tin dioxide.

Keywords: Magnetron sputtering, tin dioxide, vacuum radiation annealing.

Introduction. Tin dioxide SnO_2 (IV) - the compound that has a wide range of industrial application: gas sensors, transparent conductive coatings, photovoltaic panels, functional composite materials, heat-reflective coatings, etc. [1-4].

Of interest is thermal modification of such coatings, since it is one of the well-studied and used methods of management of structural, phase, electro and other properties. When heat treatment, the concentration of defects of crystal lattice is reduced, which stabilizes the physical properties of the coating and, by altering the conditions and regimes of heat treatment, one can influence the specific changes in the structure and, consequently, the properties of the crystal lattice [5]. In various sources there have been well studied and described the methods of heat treatment for coating SnO_2: muffle [6] vacuum [7], infrared [8], etc. Heat treatment by means of radiation annealing in vacuum has been little studied.

Methods. SnO_2-coatings were obtained by reactive dual magnetron sputtering on the installation QUADRA 500 TM (NPF “Alan Practitioner”) in the argon-oxygen environment (cleanliness of Ar and O_2 of at least 99,999%). The discharge current was 0,5 A, the operating pressure made 0,6 Pa, the concentration of O_2 amounted to 35 vol.%. Two tin plates (the proportion of Sn was 99.99 wt.%) were used as the targets the time of spraying the coating of tin dioxide was 185 minutes. The substrates were glass slides “MiniMed” with dimensions 76x26x1 mm and the composition of MTO (SSS 19808-86). The distance from the target to the substrate was 100 mm [9, 10].

Annealing of SnO_2-coatings was made in the photon vacuum furnace STE RTP 150 (ZAO STS SemiTeq). Before annealing, the chamber was dehumidified with flow of dry nitrogen (классификация ОЧ classification) to dew point - 40° C, the annealing temperature was monitored with a platinum thermocouple and was 400^{o}C. The samples with the obtained coatings were subjected to radiation annealing with duration of 2, 4, 8, 16 and 32 minutes, respectively, at an operating pressure of 103 Pa. The optical properties were studied in the modulation spectral ellipsometer “Uvisel 2” (Horiba Jobin Yvon). The spectral measurement range was 1,5-5,0 eV (248-827 nm) with a scanning step of 0,025 eV. Since the substrate is thin, the angle of incidence was 60º to avoid falling into the detector of ellipsometer of the rays reflected from the lower boundary the “substrate-air”.

Selection of the model of layer structure of the coating, calculation of the thickness and optical properties of the layers were made applying the program "DeltaPsi2" (Horiba Jobin Yvon). Adequacy of the models of coatings was estimated according to the sum of the deviation squares between the experimental and calculated data (parameter [xi]^2):

$$\chi^2 = \sum_{i=1}^{N} \left[\left(\Psi_{\mathrm{mod},i} - \Psi_{\mathrm{exp},i} \right)^2 / \sigma^2_{\mathrm{exp},\psi i} + \left(\Delta_{\mathrm{mod},i} - \Delta_{\mathrm{exp},i} \right)^2 / \sigma^2_{\mathrm{exp},\Delta i} \right] / (NM - K), \qquad (1)$$

where N – the number of data points in the spectrum (N = 141), M - the number of spectra used to calculate (M = 2), K - the number of adjustable parameters (K = 18: 2 parameters of the thickness and 8 coefficients in the dispersion dependence of Adashi-Forouhi (S .Adachi and A.R. Forouhi) for primary and rough layer), $[PSI]_{mod,i}$, $[DELTA]_{mod,i}$, $[PSI]_{exp,i}$, $[DELTA]_{exp,i}$ - model (calculated) and experimental values of the ellipsometric angles [PSI] and [DELTA], respectively, $[sigma]_{exp, [PSI]i}$ and $[sigma]_{exp, [DELTA]i}$ – the standard deviations of the measurement of the angles [PSI] and [DELTA], and ($\sigma_{exp, [PSI]i}$ и $\sigma_{exp, [DELTA]i} \sim 0,01$), respectively.

Ellipsometric measurement shows that the transparent coatings of tin dioxide, produced at 35% O_2, consist of two layers: the base layer and the layer of roughness.

The crystal structure and the preferred orientation of the grains of thin SnO_2-coatings was studied by means of X-ray diffraction ARL X`TRA (ThermoTechno) over the range of angles 2θ from 10° to 90° with step 0,02°. To identify the phases and to index the peaks, filing cabinet JCPDF was used.

The morphology of surface and fractograph of the coatings was studied using the scanning electron microscope of high resolution TESCAN MRA 3 LMU.

The Main Part. On the diffraction patterns of the studied coatings (Fig. 1) there are the peaks of the major crystallographic planes of tin dioxide (110), (101) and (200). It should be noted that the SnO_2-coating, precipitated at the pressure of 0,6 Pa and not undergone radiation annealing, has a crystalline structure, as opposed to amorphous coatings of SnO_2, obtained at the pressure of 0,22 and 0,4 Pa [11].

Short-duration radiation annealing in vacuum (within 2-4 min) leads to the sharp increase in crystallinity of the coating of tin dioxide, which is confirmed by increasing of the intensity of all reflexes and narrowing of the peak (110). Further modification of the coatings of radiation annealing reduces the height of the peaks due to disorientation, amorphization and destruction of the structure of coatings.

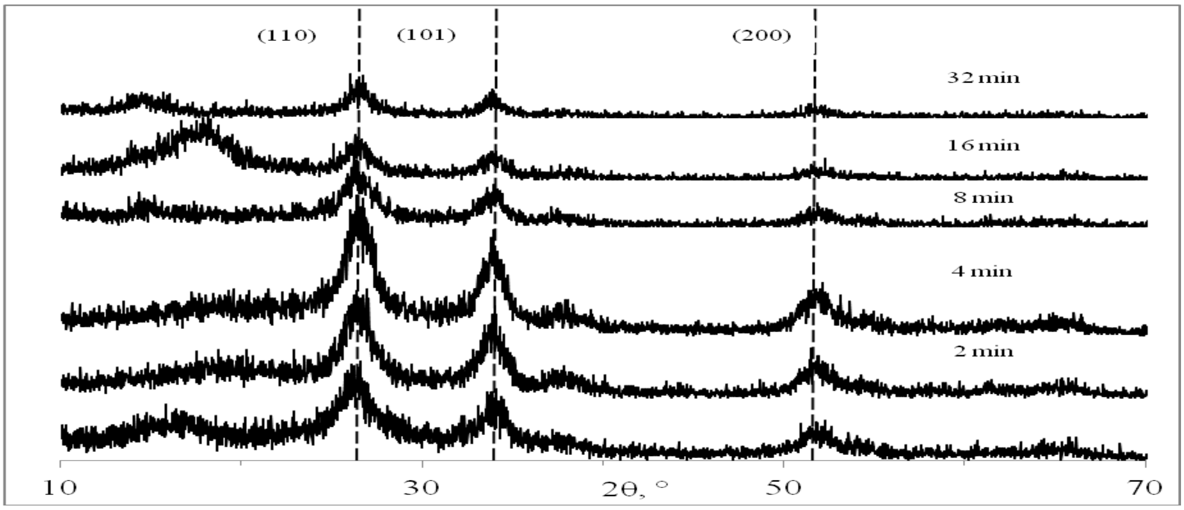

Fig. 1. Diffraction patterns of coatings depending on the duration of photon annealing SnO_2 for the samples deposited by magnetron sputtering at the pressure of 0,6 Pa.

The morphology of surface and the fractograph of SnO_2 coatings on glass substrates, before and after radiation heat treatment in vacuum at 400°C for 2, 4, 6, 8, 16 and 32 minutes are presented in Fig. 2 [12]. One can see from the analysis of the fractograph of fracture (Fig. 2*a*) that the SnO_2 layer on the glass has a columnar structure. The columnar structure of the coating in the obtained shot consists of a vertically oriented grains divided by prismatic open pores oriented perpendicular to the substrate.

After heat treatment (Fig. 2 *c, e, g, i, k, m*) the columnar structure of the deposited coating was transformed into a granular structure, which is consistent with the changes in the diffraction patterns. The thickness of the coating layer increases from 660 nm to 900 nm initially during annealing of two minutes. The morphology of the surfaces of SnO_2-coatings (Fig. 2 *d, f, h, j, l, n*) has a nanocrystalline surface, i.e., there occurs melting of the surface of coating with the consequent formation of microcracks that increase with the time of radiation vacuum annealing.

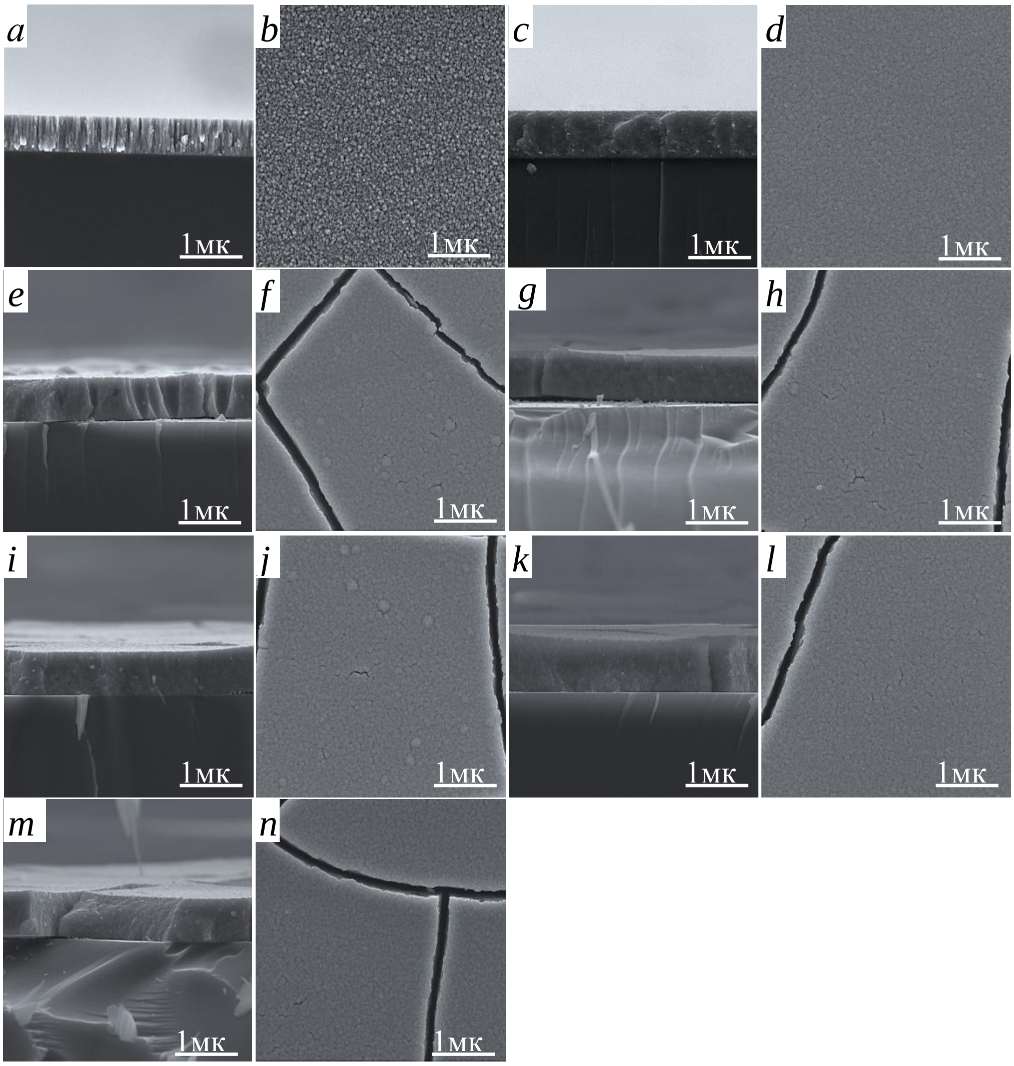

Fig. 2. The fractographs (*a*, *c*, *e*, *g*, *i*, *k*, *m*) and the morphology of the surface (*b*, *d*, *f*, *h*, *j*, *l*, *n*) of SnO_2 coatings, exposed to heat treatment at 400 °C with different delay time: *a*, *b* – without thermal annealing; *c*, *d* – 2 min; *e*, *f* – 4 min; *g*, *h* – 6 min; *i*, *j* – 8 min; *k*, *l* – 16 min;*m*, *n* – 32 min

Increasing the duration of radiation annealing leads to compaction of granular structure of the coatings and increase of its homogeneity. The analysis of the micrographs revealed that with the increase in delay time of ,thermal annealing, cracking and exfoliation of the coating from the substrate occurs.

Ellipsometric studies of tin dioxide coatings showed an increase in film thickness (Fig. 3a) and a decrease in the refractive index of the film (Fig. 3b) within the first minutes of radiation vacuum annealing, which indicates a substantial modification of the coating in the initial stages of the thermal treatment.

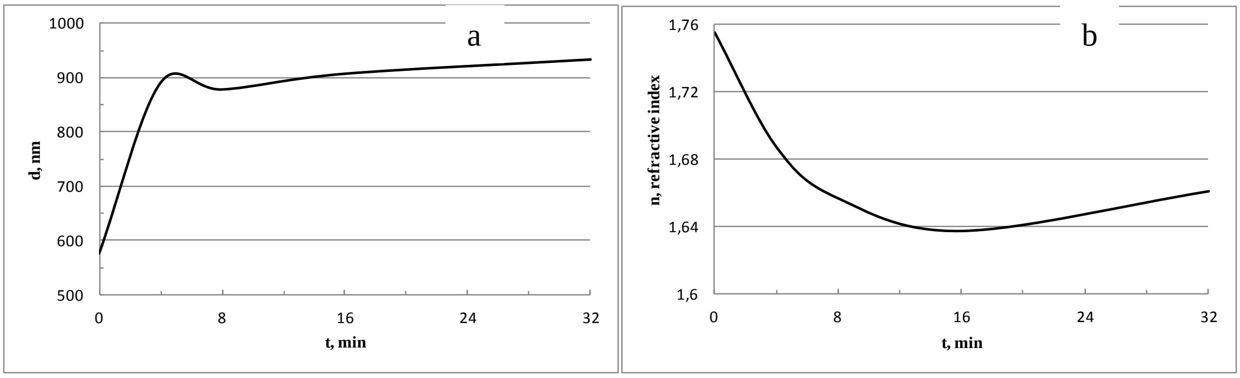

Fig. 3. a-dependence of the thickness of SnO_2 coating on the time of radiation vacuum annealing d=f(t); b-dependence of the index of refraction of SnO_2 coating on the time of radiation vacuum annealing n=f(t)

The thickness of the coating increases at the initial stage of radiation vacuum annealing at 300 nm, peaking by the fourth minute (corresponding to most of the crystallized coating of tin dioxide Fig. 1), further annealing does not lead to significant changes in the thickness of the coating of tin dioxide (Fig. 3.a). The refractive index of SnO_2 coating without annealing was n = 1,76, the minimum value of the refractive index is achieved by the sixteenth minute of the radiation and vacuum annealing was n = 1,64. This rate of decrease in the refractive index is much slower than in SnO_2coating 0,4 Pa, where minimum n = 1,74 is achieved for two minutes from the beginning of the annealing [11].

Conclusion. This paper provides the studies by the methods of spectral ellipsometry, X-ray diffraction and electron microscopy; exposes rhe effect of photon annealing on the structure tin dioxide coating formed by physical method (PVD).

Summary. After heat treatment, the columnar structure of the deposited film was transformed into a granular structure. The analysis of the micrographs revealed that with an increase in time of delay of thermal annealing there occurs cracking and exfoliation of the coating from the substrate, the process is explained by an increased pressure in the vacuum chamber by spraying the coating, since the operating pressure reduction in the vacuum chamber does not lead to fracture of the coating.

Modification of thin-film coating of tin dioxide obtained by reactive magnetron sputtering at a working pressure of 0,6 Pa occurs during the initial stages of the radiation vacuum annealing within the first 2-4 minutes at the temperature of 400°C, which is evidenced by all of the methods of investigation of the coating.

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