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Smooth transparent amorphous layers based on a zinc-tin-oxide composite system

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Smooth amorphous oxide thin films were obtained by using rf magnetron sputtering of ceramic targets based on a mixture of zinc and tin oxides (ZTO). The influence of the target composition, oxygen content in the working gas, and film thickness on the morphology, structure, and optical characteristics of low-temperature deposited ZTO films has been studied. The minimum relief is observed in films obtained by sputtering a target with equal molar contents of zinc and tin oxides. When using this target, some polishing effect is found when the surface roughness of the Si substrate with an ultrathin ZTO layer (up to 15 mm of thickness) is less than that of the original Si substrate..

Keywords: Zinc Oxide, Tin Oxide, Thin Film, Magnetron Sputtering, Growth.

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Thin transparent layers based on zinc-tin-oxide (ZTO) compositions, which are *n*-type semiconductors with a large band gap (more than 3.2 eV) and are characterized by a high chemical stability of parameters, are being used widely in various fields of micro- and optoelectronics. Specifically, low-temperature amorphous ZTO layers are used as channel and passivation layers in thin-film transistors of display systems for data visualization [1,2], as an active material for gas sensors [3,4], and as a buffer layer in thin-film solar cells [5,6]. Crystalline ZTO layers are also regarded as an alternative material for inexpensive transparent electrodes [7], but their resistances are still significantly higher than the values achieved in traditional In_2O_3:Sn, ZnO:Ga, and ZnO:Al layers. The main problem here is the clustering tendency of tin, which makes it difficult to obtain a highly oriented crystalline state in ZTO layers [8].

In the present study, the morphology and optical characteristics of ultrathin low-temperature ZTO layers are investigated in the context of their possible application as smoothing sublayers in transparent thin-film multilayer structures. The following parameters were examined: surface roughness and transparency in the visible region (400−700 nm). ZTO sputtering targets 51 mm in diameter and 4 mm in thickness were produced by spark plasma sintering of powder mixtures of zinc and tin oxides in the following molar ratios ν_{ZnO}/ν_{SnO_2}: ZTO1 — 0.97/0.03; ZTO2 — 0.66/0.34; ZTO3 — 0.50/0.50; ZTO4 — 0.34/0.66; and ZTO5 — 0.03/0.97. A drum-type assembly was used for layer deposition [9]. The targets were sputtered in a high-frequency discharge with a power of 100 W in an atmosphere of ultra-pure argon (99.999%) and a 9/1 Ar/O_2 gas mixture at a pressure of 0.3 Pa in the chamber. A $25 \times 26 \times 1.1$ mm borosilicate glass plate, which was then used for optical and X-ray diffraction studies, and a $25 \times 10 \times 0.5$ mm silicon plate with a thermally oxidized surface for subsequent measurements of the thickness, surface morphology, and cleavage structure by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) were mounted on the holder as substrates. No heating of the substrates was performed. The drum rotation speed was 10 rpm, the minimum distance from the target to the substrate was 100 mm, the deposition duration was 240 min. Ultrathin layers were deposited in a pure argon atmosphere under the same process conditions as thick layers; the only parameter varied was the deposition duration.

The influence of the ratio of components in the sputtered targets and the working gas composition on the structure, morphology, and optical characteristics of layers deposited within 240 min was investigated first. X-ray diffraction studies (XRD X'PERT PRO PANalytical, Netherlands) of this series of samples revealed that only the layers deposited using the ZTO1 target were characterized by the presence of a nanocrystalline ZnO phase with a wurtzite structure, while the remaining films were in an X-ray amorphous state. AFM data (AFM NTEGRA Spectra, Russia) on the average height of irregularities and optical spectroscopy data (UV-3600 Shimadzu, Japan) on transparency in the visible range for ZTO layers produced with various compositions of the sputtered target and the working gas are summarized in Table 1.

The optical transmittance of layers obtained by sputtering in an Ar atmosphere decreases with an increase

in concentration of tin oxide in the targets, while layers produced in an argon–oxygen atmosphere have high optical transmittance $T_{av} \geqslant 85\%$ regardless of the composition of the sputtered target. The ZTO3 layer obtained by sputtering a target with equal molar fractions of zinc and tin oxides in an Ar atmosphere has the smoothest surface morphology ($R_h = 2.455$ nm).

Figure 1 shows a SEM image (SEM Leo-1450, Germany) of the cross-sectional cleavage region and a TEM image (TEM Tecnai Osiris FEI, United States) of the cross section of the ZTO3 layer deposited in an Ar atmosphere. It can be seen that the ZTO3 layer has a dense uniform structure throughout its entire thickness with minimum relief on the outer surface, which is typical of multicomponent oxide systems with low mutual solubility of their components. The lack of a transition layer (characteristic of low-temperature layers based on zinc oxide [10]) at the boundary with the substrate is indicative of early coalescence of nuclei with the formation of a continuous layer in the system with equal molar fractions of zinc and tin oxides.

It follows from Fig. 1 that the ZTO3 layer thickness is 480 nm, which corresponds to an average deposition rate of 2 nm/min. This rate was then set in the process of deposition of a series of ultrathin ZTO3 layers used to examine the dependence of surface roughness of layers on their thickness. The ZTO3-1, ZTO3-2, and ZTO3-3 layers with design thicknesses of 30, 15, and 5 nm, respectively, were produced under the same process conditions by reducing successively the duration of sputtering of a target with equal molar fractions of zinc and tin oxides in an Ar atmosphere.

Optical spectrometry studies of ZTO3 series layers (Fig. 2) revealed that the light transmittance of the substrate with a layer deposited onto it grows rapidly with

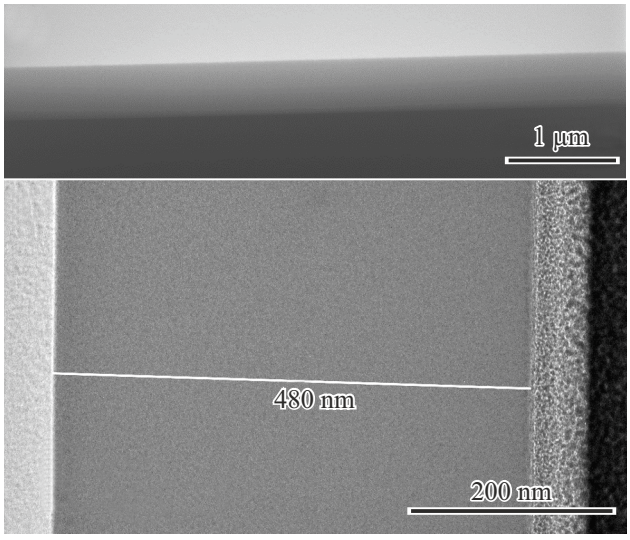

Figure 1. *a* — SEM image of the cross-sectional cleavage region of the ZTO3 sample (the sample inclination is 60°) on a silicon substrate; *b* — TEM image of a thin cross section of the ZTO3 layer.

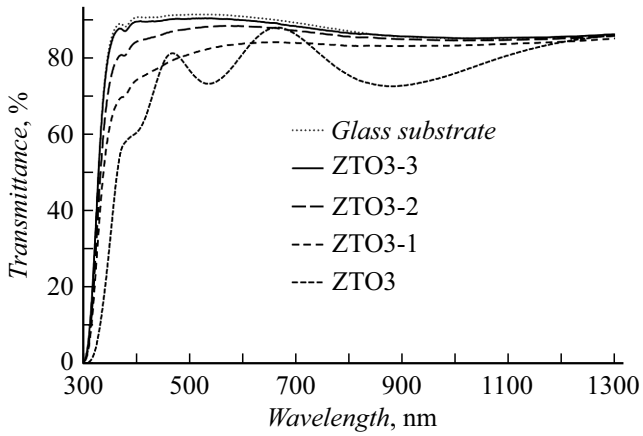

Figure 2. Optical transmittance spectra of a series of ZTO3 layers of various thickness deposited onto borosilicate glass substrates.

Table 1. Average height of surface irregularities R_h and average optical transmittance T_{av} of ZTO layers in the visible spectral range

Compound of the target	Sputtering in Ar		Sputtering in a mixture of Ar+O_2	
	R_h, nm	T_{av},%	R_h, nm	T_{av},%
ZTO1	28.334	85.2	26.275	86.3
ZTO2	4.110	77.2	6.243	85.1
ZTO3	2.455	72.8	4.678	86.1
ZTO4	3.604	70.7	3.015	86.5
ZTO5	9.341	68.8	11.341	85.5

Table 2. Variation of average optical transmittance in the visible spectral range T_{av} and average height of surface irregularities R_h with ZTO3 layer thickness

Sample	Thickness, nm	T_{av}, %	R_h, nm
ZTO3	480	72.8	2.455
ZTO3-1	30	81.5	1.829
ZTO3-2	15	87.3	0.757
ZTO3-3	5	89.7	0.760

decreasing ZTO3 thickness and that the increase in average transmittance T_{av} in the visible range is attributable mostly to an enhancement of transparency in the short-wave visible region.

As the thickness decreases from 480 to 5 nm, the average transmittance of the ZTO3 layer in the visible region increases from 72.8 to 89.7% (Table. 2). We believe that this dependence of transparency on thickness is attributable to the high probability of formation of a non-stoichiometric state with oxygen deficiency in ZTO3 layers, which is related to the vacuum growth process in an inert atmosphere. The nonstoichiometry of ZTO3 layers translates into a fairly high absorption coefficient with an accompanying exponential reduction in light transmittance with increasing layer thickness.

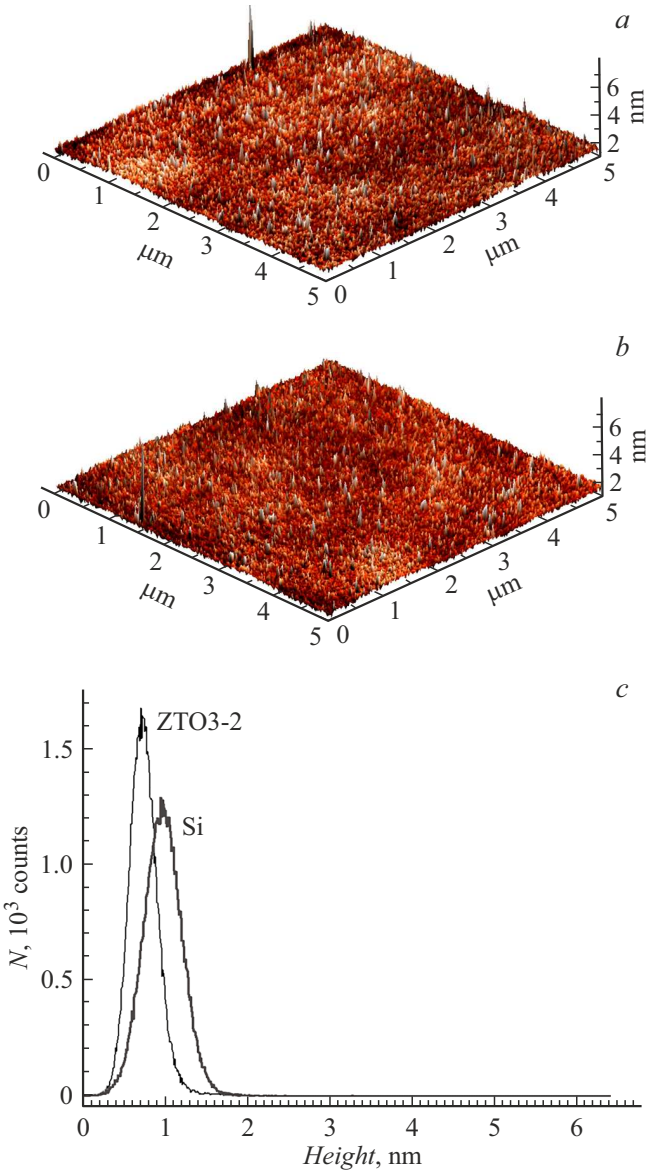

Figure 3. AFM images of the original Si substrate surface (*a*) and the ZTO3-2 layer surface on the Si substrate (*b*) and histogram of the height distribution of irregularities on the clean Si substrate and the ZTO3-2 layer (*c*).

Table 2 also presents the results of AFM evaluation of the surface relief in a series of ZTO3 layers, which are indicative of significant smoothing of the ZTO3 surface relief at layer thicknesses below 30 nm. With a reduction in thickness from 480 to 30 nm, the average height of irregularities drops to $R_h = 1.829$ nm, whereas this roughness parameter in layers up to 15 nm in thickness (ultrathin ZTO3-2 and ZTO3-3 samples) decreases further by a factor of more than 2, reaching $R_h \leqslant 0.760$ nm.

It is noteworthy that the surface roughness of ZTO3-2 and ZTO3-3 layers turned out to be less pronounced than the roughness of the silicon substrate onto which they were deposited. Figure 3 shows the AFM images of the original oxidized silicon surface (*a*) and the ZTO3-2 layer surface (*b*) and the corresponding histograms of the height distribution of irregularities (*c*). The similarity of these AFM images in terms of the nature and number of observed irregularities suggests that ZTO is deposited by a layer-by-layer mechanism with ultra-early coalescence of nuclei. Notably, according to the data from Fig. 3, *c*, the size distribution of irregularities becomes narrower when the ZTO layer is deposited, and the distribution maximum shifts toward lower irregularity height values. The so-called „polishing“ deposition effect may manifest itself here: low areas of the substrate act as potential wells for deposited particles and are filled first in the process of formation of a continuous ZTO layer; as a result, the average height of irregularities decreases from $R_h = 0.966$ nm, which is the value characterizing the quality of the substrate surface, to $R_h = 0.757$ nm.

The obtained results suggest that the following conditions must be satisfied in order to form smooth and dense transparent amorphous layers in the multicomponent ZTO oxide system:

(1) proper oxygen deficiency in the reagent composition ensuring the necessary mobility of deposited atoms on the growth surface coupled with high layer transparency;

(2) approximately equal concentrations of zinc and tin atoms in the reagent composition;

(3) minimum mutual solubility and minimum interaction of components at a given temperature on the growth surface; and

(4) adhesion to the substrate for atoms of all components exceeding the cohesion in layers.

If these conditions are met, each atom reaching the growth surface interrupts the oriented growth of crystallites and becomes a new crystallization center.

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Conflict of interest

The authors declare that they have no conflict of interest.

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