Influence of oxygen on the process of formation of nanostructured films of indium-tin oxide

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In this work, the impact of oxygen presence in the working gas mixture on the formation of indium tin oxide films obtained by magnetron sputtering at high temperatures was studied. The addition of oxygen to the working mixture changes the film growth mechanism. The films grown in an oxygen-free plasma are an array of nanowires, while the films grown in an oxygen-containing medium have a weakly structured surface. According to the X-ray diffraction analysis, the films differ in preferential crystallographic orientation and its degree. The paper also compares the optical characteristics of the films under study.

Keywords: nanostructured films, ITO, transparent conducting oxides, magnetron sputtering, X-ray phase analysis.

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1. Introduction

In most modern opto- and photoelectronic devices the indium tin oxide (ITO) films are used as transparent conductive contacts and conductive coatings. The structure of such films may vary depending on the purpose and conditions of their use. As a rule, dense films produced by vacuum deposition methods are used, with a refraction index of 1.9−2.1 in the visible wavelength range. However, in some cases, nanostructured ITO films, which have a lower effective refraction index [1], can be used to change the light reflectance at the film-environment interface. Since in such films the refraction index can change gradiently along the direction of film growth, this makes it possible to create antireflection coatings based on them. In addition, such films have a high specific surface area, which allows them to be used as catalytic coatings in electro- and photochemical processes, as well as sensitive and fast-acting sensors for various gaseous and liquid substances. One of the most common methods for producing such films is the magnetron sputtering method.

It was previously shown [2] that the composition of the working gas mixture and the deposition temperature influence the process of formation of one or another type of ITO film surface during magnetron sputtering. At the substrate temperature above 150°C in the oxygen-free plasma of gas discharge the growth of nanowires can begin by the vapor-liquid-crystal (VLC) mechanism. When ITO target is sputtered, the oxide decomposes, resulting in metal droplets being deposited on the substrate if the metal's melting temperature is lower than the substrate temperature. As droplets of molten metal are saturated with oxygen from the environment, at the interface between the solid phase and droplets layers of indium-tin oxide are formed, the melting point of which is higher than the temperature of the substrate. The process of continuous formation of filamentary nanocrystals occurs, the diameter of which is determined by the size of the metal droplets [3]. Accordingly, the number of filamentary crystals per unit surface area of the film, and therefore the specific surface area of the film, will depend on the probability of the formation of molten metal droplets.

This paper studies the properties of indium-tin oxide films formed by magnetron sputtering at high temperatures, depending on the composition of the working gas mixture.

2. Experimental procedure

ITO films were grown by magnetron sputtering onto substrate heated to 550°C on a specialized unit for combined electron beam and magnetron sputtering, manufactured by Torr Int., USA, in direct current mode both in pure argon plasma and in mixture of argon and oxygen in a ratio of 0.95 : 0.05 vol.%, respectively. After this, they were annealed in a nitrogen atmosphere at the same temperature. 1.2 mm thick borosilicate glass slides with $n_d = 1.51$ and $\nu D \approx 60-62$, similar in parameters to BK7 from the Schott catalog, were used as a substrate.

To monitor the films thickness a quartz sensor was used, placed in the working chamber and measuring the weight of the applied material. The mass content of the substance in all films corresponded to its mass content in unstructured dense film 220 nm thick.

To obtain SEM images of the films JEOL JSM-7001F scanning electron microscope manufactured by JEOL Ltd., Japan was used. The transmission and reflection spectra of the samples were examined using an Optronic Laboratories OL 770 spectroradiometer. The radiation was incident onto the samples from the film side normally to the surface.

X-ray diffraction measurements were carried out on D2 Phaser powder diffractometer (Bruker AXS, Germany). Diffraction curves from the samples were recorded in a

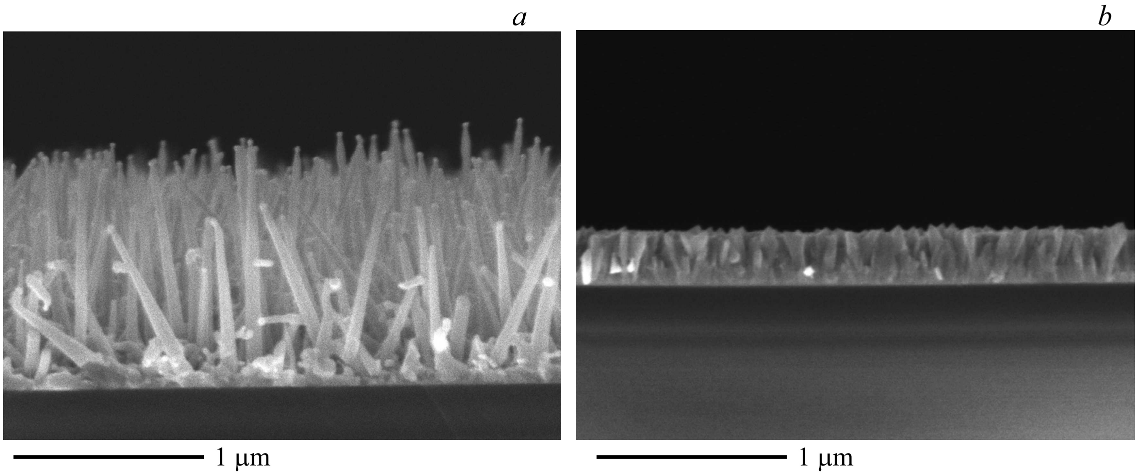

Figure 1. SEM image of ITO film grown: *a* — in oxygen-free atmosphere, *b* — in oxygen-containing atmosphere.

wide range of angles 2θ(degrees), the recording step was 0.03 degrees, the signal accumulation time at a point — 20 sec. The temperature in the unit at the time of diffraction patterns registration was 41°C. The phase composition of the films was determined using a specialized software package EVA (Bruker AXS, Germany) based on ICDD diffraction database, PDF-2, release 2014. For structural analysis of the coating features, the TOPAS-5 software package (Bruker AXS, Germany) was used. Using this software, a profile analysis (Rietveld method) of the obtained experimental diffraction curves was carried out.

3. Experimental results

Figure 1 shows SEM images of the films obtained. It can be seen that the morphology of the films is significantly different. Both films consist of a sublayer on which a structured top layer is grown. In the case of film growth in a pure argon discharge, the upper layer of the film is formed by array of filamentary crystals, oriented predominantly in the vertical direction, with filling of maximum 20% of the substance (Figure 1, *a*). Let us recall that these structures are obtained as a result of growth from nucleus droplets according to the VLC mechanism. The top layer of the film grown in oxygen-containing environment has a denser grain structure. Despite the fact that in the given SEM image of chip of the film grown in oxygen-containing environment, it is difficult to estimate the proportion of voids in the upper layer of the film, the total thickness of the film was about 290 nm, which is approximately by 30% greater than the thickness of the dense film. The presence of excess amount of oxygen in the chamber prevents the formation of droplets; accordingly, for a film obtained in oxygen-containing mixture (Figure 1, *b*), a different growth mechanism is realized. In this case, the sputtered material is saturated with oxygen before deposition on the substrate.

The Table presents the results of X-ray diffraction analysis of the samples. X-ray diffraction analysis of the obtained diffraction data showed that the coatings consist exclusively of material having a body-centered cubic lattice of space group $I2_13$, with parameters close to cubic indium oxide — In_2O_3 (PDF-2, No. 00-044-1087). However, the ratio of reflex intensities with different Miller indices differs significantly in different samples. The lattice cell parameter, the average size of the coherent scattering region (CSR) — L_{vol}, were estimated. Both samples are described in the model consisting of two phases: one of which had a weak texture in the [001] directions; the second had a bright texture in 2 directions [001] (in the sample without oxygen) and [211] (with oxygen). Moreover, for the film sputtered in oxygen-containing plasma, the parameters of the cell of phases, of which it consists, differ significantly from each other. Based on the parameters of the obtained phases: their texture, CSR sizes, as well as the mass content of phases in the film, a conclusion was made about the crrespondence of phases and the observed film layers. Note also that in our recent study [6], the proposed method for identifying phases obtained by XPA and layers observed in SEM images gives relevant results when describing similar ITO films deposited at different temperatures in oxygen-free atmosphere. In the case of film sputtering in oxygen-containing atmosphere, the mass content of the material in the layers, according to SEM images, has similar values, however, the size of the CSR of one of the phases, determined by X-ray methods, exceeds the size of CSR of the second phase by 2 times, which also makes it possible to relate phase determined in X-ray diffraction analysis with layers observed in SEM images.

According to the above considerations, the sublayer of both films studied has a very weak texture in the [001] direction; however, the degree of texturing of the upper part of the films is different and is most pronounced in the images obtained in the oxygen-free environment. An interesting feature of films obtained in oxygen-containing gas mixture is that their top layer is textured in different — [211] direction, in contrast to films deposited in oxygen-free plasma, which are oriented in [001] direction.

Results of X-ray diffraction analysis

Composition of working gases	Ar		$Ar+O_2$	
Phase	Bottom underlayer	Top underlayer	Bottom underlayer	Top underlayer
Parameter of cell a, A	10.140	10.149	10.233	10.146
Average value L_{vol}, nm	60	100	40	80
Direction of prevailing orientation	[001]	[001]	[001]	[211]
Degree of prevailing orientation (texture)	0.1	0.9	0.1	0.4
Microstresses, ε_0	$1.80 \cdot 10^{-3}$	–	–	$2.20 \cdot 10^{-3}$
Content, %	7	93	45	55
Model reliability factor, Rwp	3.25		2.88	

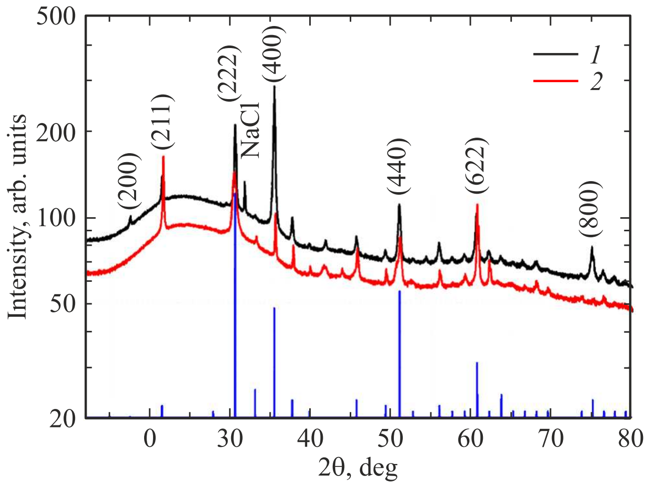

Figure 2. Diffraction curves of film deposited at temperature of 550°C and obtained: *1* — in argon atmosphere, *2* — in argon and oxygen atmosphere. Blue color indicates the bar diagram of the ICDD card, PDF-2, No. 00-044-1087, release 2014.

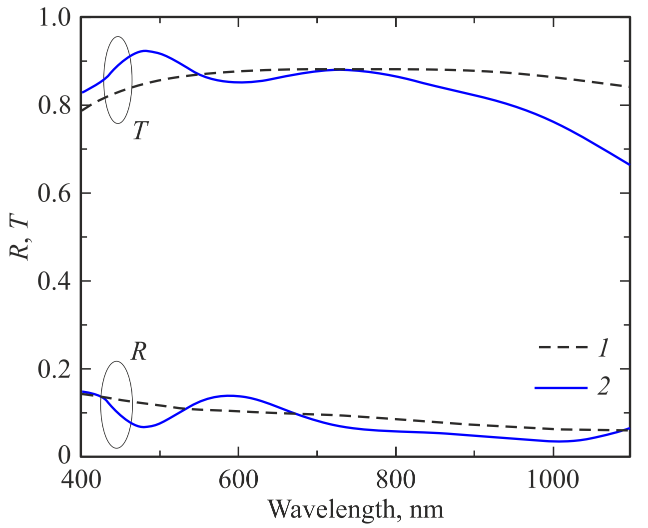

Figure 3. Reflection and transmission spectra of ITO film obtained in argon atmosphere (*1*) and ITO film obtained in oxygen-containing atmosphere (*2*).

Figure 2 shows the diffraction curves of both samples. Miller indices are noted for the most evident reflexes. The wide halo in the region of 25 degrees on the scale 2θ is caused by the glass substrate.

Differences in the crystal structure of films are not limited to texture features. In the case of film deposited in oxygen-free plasma, microstresses are recorded in the sublayer, while the structured top part is practically free of them. A film obtained in oxygen-containing environment, on the contrary, exhibits microstresses in the top layer of the film in the absence of them in the underlayer.

The results of the optical characteristics measurements of films (Figure 3) show that films grown in oxygen-containing gas mixture exhibit interference nature of the dependences of transmission and reflection, since they have sharper outer boundary. At the same time, a smooth density gradient of films deposited in oxygen-free gas discharge plasma causes smooth gradient in their effective refraction index, ensuring the absence of interference extrema in the spectra of these films.

4. Conclusion

In this paper the properties of ITO films obtained by magnetron sputtering onto the substrate heated to 550°C were investigated. It was found that the addition of even a small amount of oxygen to the composition of the working gas mixture changes the mechanism of film formation, which significantly changes the structure of the resulting films, as well as the direction and degree of preferential orientation of the grains that make up the film.

Conflict of interest

The authors declare that they have no conflict of interest.

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