VOL. 12, NO. 10, MAY 2017 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences
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www.arpnjournals.com

RESEARCH OF ITO AND ITO/SNO_2 FRONT ELECTRODES FOR FLEXIBLE PHOTOELECTRIC CONVERTERS BASED ON SULPHIDE AND CADMIUM TELLURIDE

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ABSTRACT

In order to optimize the front electrodes of flexible photoelectric converters based on sulphide and cadmium telluride, they studied the effect of annealing on air at 430 °C for 25 minutes on a crystal structure, the optical and electrical properties of ITO films obtained by non-reactive magnetron sputtering method on a polyimide substrate. It was found that the annealing in air leads to the decrease of ITO film preferential orientation degree in <100> direction, which indicates the oxygen concentration increase in these layers. There is also a significant increase in surface electrical resistance from 6.5 Ω to 30.4 Ω after the annealing in air, which is caused by the main charge carriers concentration decrease from 9.8 10^{20} cm^{-3} to 2.2 10^{20} cm^{-3} and leads to the film quality factor decrease from $\Phi = 8.7 \cdot 10^{-3}$ Ω^{-1} to $\Phi = 3.1 \cdot 10^{-3}$ Ω^{-1}. It was shown experimentally that the application of an unalloyed tin dioxide layer with the thickness of 40 nm allows to limit the decrease the quality factor of the ITO/ZnO heterosystems after the annealing in air to $\Phi = 5.2 \cdot 10^{-3}$ Ω^{-1}.

Keywords: film electrodes of indium and tin oxides, surface electrical resistance, transmission ratio, quality factor, preferential orientation degree, concentration of main charge carriers.

1. INTRODUCTION

The rapid development of micro- and nanoelectronics, related with the production of liquid crystal displays, plasma and sensor panels, organic light-emitting diodes, gas sensors, electromagnetic converters, photoelectric converters (FEC) and photodetectors, requires the improvement of technologies for the production of film transparent electrodes [1 - 6]. The films of wide-gap degenerate semiconductors of n-type conductivity are used as such layers: ZnO: Al, ITO (indium and tin oxides), SnO_2:F, SnO_2:Sb, Cd_2SnO_4, $CdIn_2O_4$. ITO films have a better combination of surface resistivity and transparency coefficient than SnO_2:F films among wide-gap degenerate semiconductors of n-type, a greater thermal stability than ZnO:Al films and lower deposition temperatures than Cd_2SnO_4 and $CdIn_2O_4$ films [6]. Therefore, IT films are widely used in micro- and nanoelectronics nowadays.

Traditionally, the deposition of ITO films is carried out on glass substrates using magnetron sputtering methods. However, new types of flexible substrates have appeared in recent years - thermostable and transparent polyimide films, which have improved functionality for the use in high-tech products of microelectronics - photoelectric converters based on sulfide and cadmium telluride [7, 8]. The features of flexible substrate physical and mechanical properties cause the need to optimize the technology of ITO film layer production using these substrates. Besides, the technology for the development of ITO films must be adapted to the features of production technology concerning previous and subsequent mating layers of FEC. Therefore, the optimization of the design and technological solutions concerning the film front electrodes of ITO for flexible FEC based on CdS/CdTe should be considered an urgent research task of great practical importance.

2. EXPERIMENT TECHNIQUE

In this work the layers of ITO were deposited by the method of non-reactive magnetron sputtering at a constant current in an industrial device UVN-71. The sputtering target was a compacted mechanical mixture of indium and tin oxide finely dispersed powders of semiconductor purity with the content of 90 wt. % In_2O_3 and 10 wt. % SnO_2. The magnetron sputtering of a target consisting of only tin oxide with semiconductor purity was also carried out for a number of experiments. The magnetron with the diameter of 40 mm and the magnetic induction of 0.1 TL was used for the production of ITO and SnO_2 films. The length of the discharge gap, which is the gap between the magnetron and the substrate, was 70 mm. The specific power of the magnetron was 0.2 W/cm^2. Upilex polyimide films with the thickness of 7 μm were used as flexible substrates. The substrate temperature during the deposition of ITO layers was 300 °C, which, according to the published data (see, for example, [9]), corresponds to the optimum deposition temperature range at non-reactive magnetron sputtering at the constant current of ITO films. The working pressure of the argon-air mixture during the spraying process was maintained within the range of $(2.1 - 2.6) \cdot 10^{-2}$ Torr.

The deposition of ITO films was carried out simultaneously on four flexible polyimide with 2 cm x 2 cm substrates. Then, nanoscale layers of tin oxide of different thickness were deposited on three substrates. After that, the crystal structure, optical and electrical properties of film heterosystems were studied. Then, all the samples obtained were annealed in air at 430 °C for 25 minutes and the studies were repeated.

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The structural studies of the obtained ITO films and ITO/SnO_2 film heterosystems were performed by X-ray diffractometry. The samples were taken using DRON-4 X-ray machine with the automatic record of the diffraction spectrum using the recorder at a continuous 2θ scanning within the angle interval of 2θ = 20° - 90° with Bragg-Brentano focusing (θ-2θ) in cobalt (Co) anode radiation. The rotation speed of the goniometer was 0.5 deg/min. A special computer program was used that made it possible to determine the position of the diffraction maximum ($2\theta^0$) and their intensity (I) for the analytical processing of experimental X-ray diffractograms. The standard processing of diffraction maxima was carried out at first for this purpose using this program. The processing consisted in smoothing out, the separation of the background and the doublet isolation.

The preferential orientation of ITO layers was determined by the analytical processing of the experimental diffraction maxima intensity in terms of the texture coefficient C_i value, which characterizes the fraction of crystallites for which the normal to the (hkl) plane coincides with the normal to the sample surface [10]:

$$C_i = \frac{I_i / I_{0i}}{(1/N) \cdot \sum_{i=1}^{N} I_i / I_{0i}} \quad (1)$$

where I_i – the intensity of revealed i peak;

I_{0i} - the intensity of i peak, according to ASTM table;

N – the number of diffraction maxima detected during the analysis (the reflections corresponding to divisible indices are not taken into account).

The parameter G was calculated in order to compare the samples by the degree of a preferential orientation:

$$G = \sqrt{\frac{\sum_{i=1}^{N} (C_i - 1)^2}{N}} \quad (2)$$

The surface electrical resistance ($R_□$) of ITO layers was determined by Van der Pau method, which eliminates the errors related to the size and the shape of the contact. The concentration (n) and mobility (μ) determination of the main charge carriers in ITO films were determined according to the value of Hall voltage at a constant current and a constant magnetic field.

The study of spectral dependences concerning ITO film and ITO/SnO_2 heterosystem transmission coefficient were studied by optical spectroscopy using SF-2000 spectrophotometer.

Since the front electrodes of a photoelectric converter should have not only a low surface electrical resistance, but also a high average transmittance coefficient T, then the film quality factor (F) was calculated in the work [11]:

$$\Phi = T^{10}/R_□ \quad (3)$$

Since the range of FEC pholosensibility based on CdS/CdTe, determined by the edge of the cadmium sulfide and cadmium telluride absorption band, makes (500-900) nm, then we calculated the average transmission coefficient of ITO films and ITO/SnO_2 film heterosystems in this spectral range during the analytical processing of the transmission spectra. The optical properties of polyimide films, which consist in the oscillation of the transmission coefficient value, do not allow to distinguish the transmission spectrum for ITO films and ITO/SnO_2 film heterosystems by the method of two-channel optical spectroscopy. Therefore, the average transmittance factor values of the ITO/polyimide heterosystem (ITO/Poli HS) and ITO/SnO_2/polyimide heterosystem (ITO/SnO_2/Poli HS) were determined. The expediency of optical property evaluation for the frontal contacts of flexible FEC based on CdS/CdTe is justified by the fact that the generation of nonequilibrium charge carriers whose efficiency controls the short-circuit current in the base layer of cadmium telluride occurs when photons are absorbed with the wavelength from the spectral range of 500 nm - 900 nm.

3. RESULTS AND THEIR DISCUSSION

a) The effect of annealing in air on the crystal structure, the electrical and optical properties of ITO films

During the use of ITO films as the front electrodes on the basis of flexible CdS/CdTe FEC, these film layers should provide a high quality factor not only in the initial state but also in the instrument structure after the performance of all high-temperature technological operations capable of leading to the degradation of the original optical and electrical properties. During the production of CdTe/CdS based photoelectric converters, the most high-temperature technological operation is "chloride" treatment [12]. During "chloride" treatment after the application of cadmium chloride layer on the surface of a base layer, the annealing is carried out in the air at 430 °C for 30 minutes [12]. Without such processing, it is impossible to obtain high-efficiency film FEC based on CdTe/CdS [13].

A high electrical conductivity of ITO n-type layers is provided by the replacement of indium with tin, and also due to the presence of electrically active intrinsic point defects of the donor type oxygen vacancies. It is quite possible that high-temperature annealing in air initiates a grain-boundary and volumetric diffusion of oxygen into an indium-tin oxide film. The volumetric diffusion of oxygen can cause the oxygen vacancy concentration decrease, and the grain boundary diffusion can cause the development of tin oxide on the grain boundary surface, which leads to the decrease of tin vacancy concentration in the indium sublattice sites where they are located in the electrically active state. The physical processes described above can lead to the increase of their surface electric resistance as the result of

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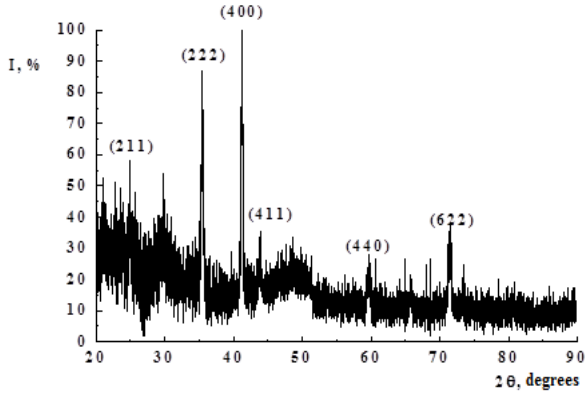
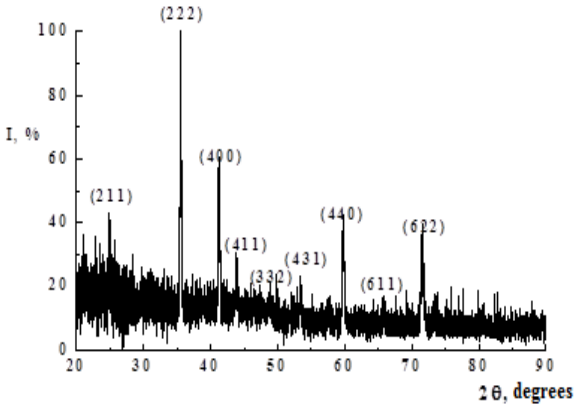
free charge carrier concentration decrease when ITO films are annealed in air. The growth of the surface front electrode electrical resistivity causes the growth of the sequential FEC resistance in a regular way, which leads to its efficiency decrease, as the result of filling factor decrease concerning the light volt-ampere characteristic of the instrument structure. Therefore, in order to optimize the constructive-technological solution of the frontal electrode for flexible FEC based on sulfide and cadmium telluride, the effect of high-temperature annealing in air on the crystal structure, the optical and electrical properties of ITO layers were studied.

The analysis of the experimental X-ray diffractograms concerning ITO films formed on polyimide substrates before and after annealing (Figure-1) showed that they have the crystalline structure of a stable cubic modification In_20_3 [16], which is uniquely confirmed by the presence of reflections from the planes (221), (222), (400), (411), (332), (431), (440), (611), (622).



(a)



(b)

Figure-1. X-ray diffractogram of the ITO/Poli heterosystem before (a) and after (b) annealing in air at 430 °C for 25 minutes.

The analysis of Table-1 shows that for ITO films before the annealing in air the maximum value of C_i corresponds to C_{400}. Therefore, unannealed ITO films are mainly oriented in <100> direction. At that, the parameter G is 0.72. After the annealing in air, the maximum value of C_i corresponds to C_{400}. Therefore, annealed ITO films are also predominantly oriented in <100> direction. However, the parameter G is 0.36. Thus, the annealed ITO films in the air lead to the preferential orientation degree decrease in <100> direction. According to literature data [14], the development of ITO films in <100> direction occurs with an oxygen deficit, and in the direction of <111> it occurs with its excess, which is conditioned by the ratio between the oxygen and indium atoms in the crystallographic planes corresponding to these directions. Thus, the annealing in the air leads to oxygen deficiency decrease in films. This process, which also increases the degree of film structural perfection, is indirectly evidenced by the analysis of the diffraction maximum half-widths (222) $W_{1/2(222)}$ and (400) $W_{1/2(400)}$ before and after the annealing of films in the air. It was found experimentally that the annealing in the air reduces the half-widths of both diffraction maxima from $W_{1/2(222)} = 0.32$ to $W_{1/2(222)} = 0.21$ and from $W_{1/2(400)} = 0.28$ to $W_{1/2(400)} = 0.23$.

Table-1. Quantitative analysis of preferential orientation degree among ITO films.

C_i	(211)	(222)	(400)	(411)	(332)	(431)	(521)	(440)	(611)	(622)	G
Before annealing	1,0	0,6	2,7	1,4	-	0,3	-	0,8	0,8	1,0	0,72
After annealing	1,5	0,8	1,7	1,2	0,4	0,9	1,1	0,3	0,6	1,1	0,36

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The structural studies of annealed and unannealed ITO films were supplemented by the studies of their optical and electrical properties (Table-2).

Table-2. The effect of annealing in the air on the optical and electrical properties of ITO films.

Characteristics	Before annealing	After annealing
t_o, mc	0,26	0,26
$R_□$, Ω /□	6,5	30,4
$\rho \cdot 10^{-4}$, Ω·cm	1,7	7,9
$n \cdot 10^{20}$, cm^{-3}	9,8	2,2
μ, $cm^2/(V \cdot s)$	37	36
T, %	0,75	0,79
$F \cdot 10^{-3}$, Ω^{-1}	8,7	3,1

The analysis of Table-2 shows that annealing leads to a significant increase of the surface electrical resistance from $R_□$ = 6.5 Ω to $R_□$ = 30.4 Ω , which is caused by the decrease of the main charge carrier concentration from $n = 9.8 \cdot 10^{20}$ cm^{-3} to $n = 2.2 \cdot 10^{20}$ cm^{-3} at practically constant mobility of the main charge carriers at the level of 36-37 $cm^2/(V \cdot s)$ according to the studies of Hall effect.

The studies of the optical properties (Figure-2) indicate that the annealing in air leads to the mean value increase of ITO/Poli transmission coefficient in the spectral range (500-900) nm, from T = 0.75 to T = 0.79 (see Table-2).

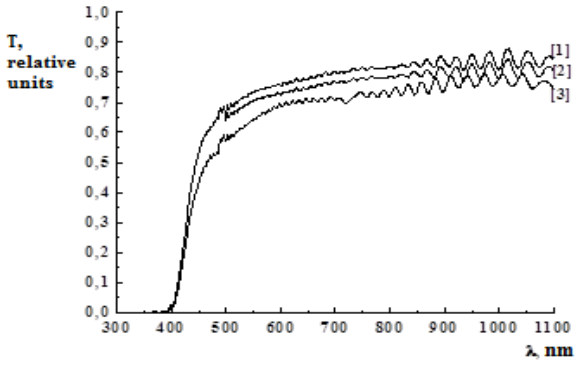

Figure-2. Spectral dependences of the transmittance ratio (T) of ITO/Poli and SnO_2/ITO/Poli heterosystems: [1] - t_{SnO2} = 0 nm (after annealing), [2] - t_{SnO2} = 0 nm (before annealing), [3] - t_{SnO2} = 60 nm (after annealing).

According to the literature data [15], oxygen vacancies are scattering centers. Therefore, the decrease in the concentration of oxygen vacancies during the annealing in the air causes the increase in the average value of the transmittance ratio.

Despite the increase in the mean value of annealed ITO films transmission coefficient, a more significant increase in the surface electrical resistance leads to the quality factor decrease by almost three times: from $F = 8.7 \cdot 10^{-3}$ Ω-1 to $F = 3.1 \cdot 10^{-4}$ Ω^{-1}. This limits the effectiveness of flexible FEC based on sulphide and cadmium telluride during the design of which resulting ITO films will be used as front film electrodes.

b) Effect of annealing in the air on electrical and optical properties of ITO/SnO2 films

In order to reduce the negative effect of high-temperature annealing in the air on the electrical properties of ITO films, it was proposed to deposit nano-sized tin oxide layers on the surface of these films, which can be a diffusion barrier for high-temperature oxygen diffusion during heat treatment. Therefore, we carried out the transmission spectra and surface resistivity study of ITO/SnO_2 film heterosystems with different thicknesses of a nanoscale tin oxide layer before and after the annealing in the air at 430 °C for 25 minutes. The results of the conducted studies concerning the influence of tin dioxide (tSnO2) nano-sized interlayer thickness on T, R□ and F are presented in Table-3.

The analysis of the results shows that the monotonous growth of the surface resistance from $R_□$ = 6.4 Ω at t_{SnO2} = 0 nm to R = 14.0 Ω at t_{SnO2} = 60 nm is observed for unannealed heterosystems with tin oxide layer thickness increase. A regular decrease of the surface resistivity is conditioned by the thickness of tin oxide high-resistivity layer increase within the heterosystem under study. With the thickness increase of a nanoscale tin oxide layer, a monotonic decrease in the transmittance ratio is observed from T = 0.79 at t_{SnO2} = 0 nm to T = 0.7 at t_{SnO2} = 60 nm (Table-3). From our point of view, this is due not so much by the increase of light absorption in a tin oxide layer, as by the reflection increase at SnO_2/ITO boundary.

Unlike non-annealed heterosystems, the change in the surface electrical resistance of the annealed ITO/SnO_2 film heterosystems does not occur monotonically. First, with the thickness of tin oxide increase, the surface resistance decreases from R= 30.4 Ω at t_{SnO2} = 0 nm to R = 7.1 Ω at t_{SnO2} = 40 nm. With a further increase of tin oxide thickness, the surface resistivity increases to R = 14.0 Ω at t_{SnO2} = 60 nm. The comparison of heterosystem surface electrical resistivity before and after annealing shows that the greatest difference of 24 Ω is typical for ITO films without a surface nanosized tin oxide layer, and the minimal difference is 0.1 Ω typical for the samples with a nanosized layer thickness of 60 nm. The obtained experimental results prove that a nanosized tin oxide layer prevents the growth of the surface electrical resistivity of ITO films when they are annealed in the air at 430 °C for 25 minutes. Two competing physical processes lead to the presence of an extremum concerning the dependence of the surface resistance on the thickness of tin oxide dielectric layer: the regular growth of the surface electrical

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resistance of the ITO / SnO_2 film HS with the thickness of the tin oxide layer unalloyed mating increase and, at the same time, the diffusion of oxygen reduction in ITO layer, which causes the growth of a film surface resistance of the film by reducing the concentration of oxygen vacancies and tin atoms in an electrically active state. The study of unannealed and annealed HS transmission spectra show that a noticeable increase of an average transmittance ratio is observed only for the samples without a tin oxide interlayer on the surface of ITO films (Table-3). There was not a noticeable change in the average transmittance factor for remaining heterosystems.

Table-3. The effect of annealing in the air on the optical and electrical properties of ITO/SnO2/Poli heterosystems.

SnO_2 thickness, nm	$R_{\square}$, Ω /□	T, %	$F \cdot 10^{-3}$, Ω^{-1}
0	30,4 (6,5)*	0,79 (0,75)	3,1 (8,7)
20	11,2 (6,7)	0,73 (0,74)	3,8 (7,4)
40	7,1 (6,9)	0,72 (0,72)	5,2 (5,4)
60	14,0 (13,9)	0,70 (0,70)	2,0 (2,0)

* The brackets show the values typical for unannealed heterosystems.

The described above nature of surface electrical resistance and an average transmission coefficient of annealed heterosystem change lead to the maximum development at the quality factor dependence on the thickness of the tin dioxide layer at t_{SnO2} = 40 nm (Table-3). At the same time, the maximum value of the quality factor is $5.2 \cdot 10^{-3}$ Ω^{-1}, which is significantly higher than in the annealed heterosystems where the nanosized SnO2 interlayers were not applied on the surface of the ITO films.

4. CONCLUSIONS

It was found that during the use of ITO films as the front electrodes of flexible FEC based on cadmium sulphide and cadmium telluride, one of the factors limiting the efficiency of such instrumental structures is the growth of the front electrode surface electrical resistivity during the "chloride" treatment of a base layer.

They showed experimentally that the growth of the surface electrical resistivity among the front electrodes of ITO during the process of CdTe-based FEC manufacture is conditioned by almost five time decrease of free charge carrier concentration. The application of a nano-sized tin dioxide with the thickness of 40 nm prevents the growth of the series resistance for a front electrode without a significant reduction of the average transmittance ratio in the spectral range corresponding to FEC photoelectivity based on CdS/CdTe, which allows to limit the quality factor of the annealed SnO_2/ITO/Poli heterosystems to $F = 5{,}2 \cdot 10^{-3}$ Ω^{-1}.

ACKNOWLEDGEMENTS

The article was prepared as the part of applied research and experimental development (ARED) implementation under the Agreement on the provision of subsidy No. 14.607.21.0137 issued on October 27, 2015 with the financial support of Russian Federation Ministry of Education and Science. The unique identifier of ARED is RFMEFI60715X0137.

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