Structure, optical and electrical properties of ITO films on flexible polyimide substyrates

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ITO layers on industrial polyimide films intended for high efficiency flexible CdTe solar cells have been obtained for the first time. The air-annealed ITO films obtained at the magnetron power of 1500 mW/cm^2, oxygen partial pressure in the argon/oxygen mixture 3 % (vol.), and the deposition temperature 450°C show the surface resistance of 11 Ohm/□. In the photosensitivity region of the CdS/CdTe solar cells, the average transmission coefficient of the ITO/polyimide system has been found to be 72 %.

Впервые на промышленных полиамидных пленках получены слои ITO для высокоэффективных гибких солнечных элементов на основе CdTe. После изготовления солнечного элемента, пленки ITO, полученные при мощности магнетрона 1500 мВт/см^2, парциальном давлении кислорода в составе аргоно-кислородной смеси 3 об.% и температуре осаждения 450°C, имеют величину поверхностного электро-сопротивления 11 Ом/□. В области фоточувствительности солнечных элементов CdS/CdTe средний коэффициент пропускания гетеросистем ITO/polyimide составлял 72 %.

The ITO (solid solution of tin in indium oxide) layers are used widely as transparent electrodes (wide-band "windows") in CdTe film solar cells (SC) [1]. Using non-reactive magnetron sputtering, we have obtained ITO layers exhibiting the optimum optical and electric parameters in the CdTe SC [2]. Recently, the flexible CdTe solar cells are under intensive development (see, e.g., [3]). In such SC type, the mass is reduced considerably due to replacement of glass substrate by thin polyimide film whereon the device structure ITO/CdS/CdTe is then formed. This principle makes it possible to attain an electric output per unit mass exceeding by several times that obtainable in traditional SC based on silicon single crystals. The development of procedure providing the transparent conductive ITO layers on polyimide films is among important stages in creation of high efficiency flexible CdTe solar cells. Hence, this work was aimed at the study of crystalline structure, optical and electrical properties of ITO layers formed by non-reactive high-frequency magnetron sputtering on polyimide films intended for wide-band "windows" of flexible CdTe SC.

The ITO layers were deposited onto 7 to 10 μm thick polyimide films (produced by Upilex) using non-reactive high-frequency magnetron sputtering according to the procedure described in [2]. The oxygen concentration in argon/oxygen mixture was 3 % vol., the magnetron specific power was 1500 mW/cm^2. These conditions of the magnetron sputtering were identified before as those providing the deposition of ITO layers with optimum optical and electrical properties onto glass substrates [2]. The substrate temperature was varied from 20 to 450°C, the upper temperature limit being defined by the polyimide film temperature resistance.

The crystalline structure of the polyimide films and ITO layers was studied by X-ray diffraction. The samples were imaged in Cu anode emission. The predominant orientation extent of ITO layers was analyzed quantitatively by processing the experimental diffraction maxima using the texture coefficient, C_i [4]:

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

where I_i is the i-th peak intensity; I_{oi}, the i-th peak intensity according to the ASTM table; N, the number of the found diffraction maxima (the reflections corresponding to multiple indices are neglected).

To compare the predominant orientation extent of different samples, the G parameter [4] was calculated as

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

The surface resistance ($R_{\square}$) of the ITO layers was studied using the four-probe technique. The concentration (n) and mobility (μ) of major charge carriers in the ITO layers were determined by e.m.f. method. The spectral dependences of transmission coefficients were studied using two-channel technique in the 200 to 1100 nm range. Since the solar cell efficiency is influenced considerably by the number of photons attaining the basic layer, the mean transmission coefficient $T_{500\text{-}900}$ was determined in the 500–900 nm spectral range corresponding to the photosensitivity region of the CdS/CdTe SC [5].

The effect of the deposition temperature on the optical and electrical properties of the ITO/polyimide system obtained by magnetron sputtering of ITO on dielectric polyimide films was studied. The X-ray examination of the polyimide films evidences the amorphous structure thereof (Fig. 1a). The phase composition analysis of the deposited ITO layers (see, e.g., Fig. 1b, 1c) shows that within the studied range of the deposition temperature T_s (20 to 450°C), the layers

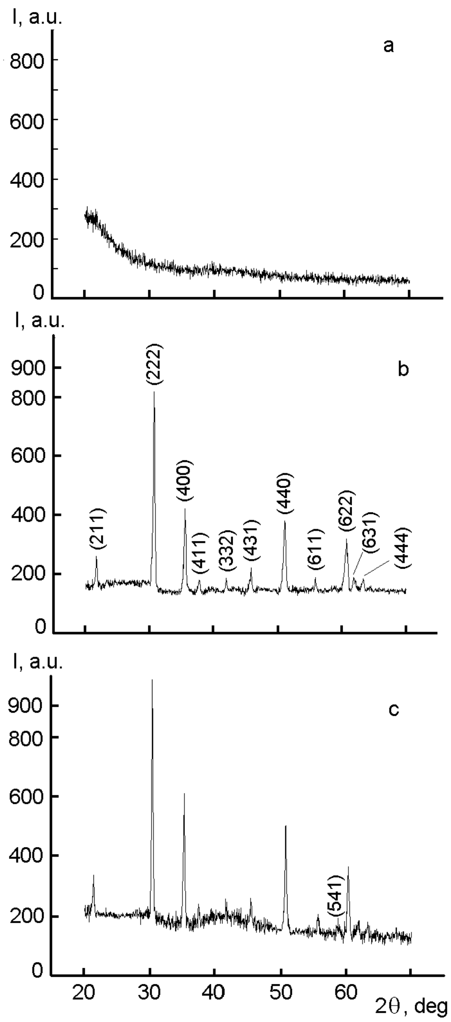

Fig. 1. Crystalline structure of ITO/polyimide heterosystems. XRD patterns of polyimide film (a); ITO layer deposited at T_s = 20°C (b) and at T_s = 450°C (c).

have cubic structure and are oriented predominantly in the (400) direction. According to [6], the predominant orientation of an ITO film is characterized by qualitative index being the $I_{(222)}/I_{(400)}$ ratio. According to In_2O_3 phase having no predominant orientation, this ratio is 3.33, according to

Table 1. Quantitative analysis of the predominant orientation extent of ITO layers

T_s, °C	C_i												σ
	(211)	(222)	(400)	(411)	(332)	(431)	(440)	(611)	(541)	(622)	(631)	(444)	
20	1.02	0.92	1.19	0.96	0.98	1.01	0.98	0.96	0.00	1.04	0.95	0.95	0.07
20*	0.95	0.75	2.22	1.09	0.80	0.84	0.97	0.81	0.90	1.06	0.81	0.81	0.37
450	0.98	0.79	1.46	0.98	0.98	0.98	0.98	0.98	1.24	0.87	0.98	0.82	0.15
450*	0.94	0.63	1.64	1.24	1.05	0.73	0.96	1.04	1.03	1.01	1.01	0.70	0.26

*after subsequent anneal in air (430°C, 25 min).

ASTM data [7]. As to the films under study, as the deposition temperature rises, this ratio decreases from 2.6 (the ITO films deposited onto unheated substrate) to 1.8 (at T_s = 450°C). The quantitative analysis shows that as the substrate temperature rises, the predominant orientation extent increases from G = 0.07 (T_s = 20°C) to G = 0.15 (T_s = 450°C) (see Table 1).

Studies of optical and electrical properties of ITO films (see Table 2) evidences that as the substrate temperature rises form 20 to 450°C, the surface electric resistance decreases monotonously from 18.1 to 4.6 Ohm/□. The Hall e.m.f. study has shown that the reduction of the ITO layer surface electric resistance is due to the increase of the major charge carrier mobility from μ = 11.7 cm^2/(V·s) (T_s = 20°C) to μ = 38.5 cm^2/(V·s) (T_s = 450°C) while the major charge carrier concentration remains essentially constant, n = (5.8 to 6.5)·10^{20} cm^{-3}. Similar dependences were observed before for ITO films on glass substrates [2]. The mobility increase at rising deposition temperature is ascribed usually to reduced carrier scattering at the grain boundary surface as the layer predominant orientation is enhanced (see, e.g., [8]) that we have observed in experiment.

In the wavelength range of 500 to 900 nm, the mean transmission coefficient of the ITO/polyimide systems obtained in the 20 to 450°C deposition temperature range was varied from 68.8 to 70.9 % (Table 2). The comparison of the spectral dependences of transmission coefficient for the ITO/glass and ITO/polyimide heterosystems (Fig. 2a, curves 1 and 2) evidence that for the ITO/polyimide system, the $T_{500\text{-}900}$ is lower. This is due to the lowered transparence of polyimide film as compared to glass. The experimental difference in the absorption edge between the ITO/glass and ITO/polyimide heterosystems is due to the

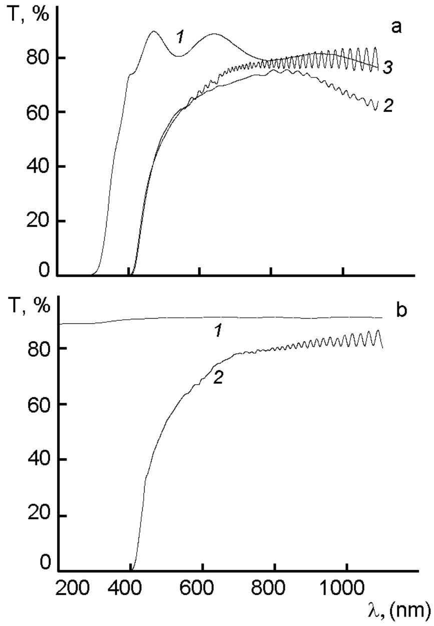

Fig. 2. Optical properties of ITO/polyimide and ITO/glass heterosystems. a) Spectral dependences of transmission coefficient for ITO/glass (*1*) and ITO/polyimide prior to (*2*) and after anneal (*3*). b) Spectral dependences of transmission coefficient for glass substrate (*1*) and polyimide film (*2*).

difference between the polyimide film and the glass substrate (Fig. 2b, curves 1 and 2).

The crystalline structure and optical/electrical properties of the ITO layer may undergo changes during the further high-temperature treatment of the ITO/CdS/CdTe SC device structure. Our investigation of ITO layers on glass substrates [2] has shown that the electrical properties of the wide-band "windows" on glass substrates are affected most considerably due to the "chloride" treatment. The treatment consists in formation of cadmium chloride film onto the basic layer surface followed by the heterosystem annealing in air at 430°C for 25 min [9]. In [2], the "chloride"

Table 2. Effect of the deposition temperature on optical and electrical properties of ITO layers

T_s, °C	t, μm	$T_{(500\text{-}900)}$	$R_\square$, Ohm/□	ρ10^4, Ohm·cm	n·10^{20}, cm^{-3}	μ, cm^2/(V·s)
20	0.51	69.5	18.1	9.2	5.8	11.7
200	0.50	70.6	12.6	6.3	5.9	16.8
250	0.54	70.3	10.4	5.6	6.0	18.6
300	0.49	70.9	8.8	4.3	5.7	25.5
350	0.52	69.1	6.2	3.2	6.1	32.0
400	0.53	69.5	6.0	3.2	5.9	33.1
450	0.54	68.8	4.6	2.5	6.5	38.5

treatment was modeled by air annealing of ITO films on glass substrates. Therefore, the similar approach was used in this work.

To study the structure, optical and electrical properties of ITO layers in the device structure of flexible CdTe SC, the ITO layers deposited at different substrate temperatures were annealed in air at 430°C for 25 min. The comparative structure examinations of annealed and unannealed films (Figs. 1, 3) evidence that the air annealing results in an increased predominant orientation of the ITO layers in the (400) direction. So, for the layers deposited on unheated substrate, the $I_{(222)}/I_{(400)}$ ratio is reduced from 2.6 to 1.1, while for those deposited at 450°C, from 1.8 to 1.3. The quantitative analysis of the predominant orientation shows that the annealing causes an increase thereof from $G = 0.08$ to $G = 0.37$ for T_s = 20°C and from $G = 0.15$ to $G = 0.27$ for T_s = 450°C (see Table 1). Thus, a more substantial post-annealing changes in the crystalline structure are typical of ITO layers obtained at lower deposition temperatures. The air heat treatment was shown to cause an insignificant increase in the transmission coefficient, while the surface electric resistance increases more considerably (see Fig. 2a and Table 3). The Hall e.m.f. studies show that the $R_?$ increase is due to a reduced concentration of the major charge carriers while the mobility thereof increases to a lesser extent. So, for ITO layers deposited onto unheated substrate, the air anneal results in a 6-times reduction in the charge carrier concentration, from $5.8 \cdot 10^{20}$ to $1.0 \cdot 10^{20}$ cm^{-3}, while the mobility thereof increases thrice, from 11.7 (at T_s = 20°C) to 29.6 cm^2/(V·s). A qualitatively similar dependence was observed before [2] for ITO layers on glass substrates. We suppose that the reduction of the major charge carrier concentration is due to oxidation of the doping impurity and the increase of the mobility thereof is associated with the experimentally found increased extent of the predominant orientation of the annealed ITO layers in the (400) direction. Only the ITO layers deposited at 450°C, when annealed in air, have been found to have electrical characteristics suitable for the use thereof in high efficiency CdTe SC (the surface resistance being 11 Ohm/□). The mean transmission coefficient of the ITO/polyimide heterosystems in the wavelength range corresponding the CdTe SC photosensitivity region amounts 72 %.

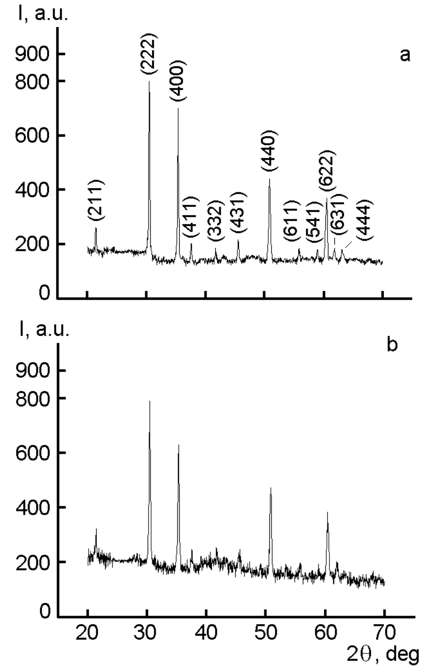

Fig. 3. Effect of the air anneal on crystalline structure of ITO layers deposited at different substrate temperatures (°C): 20 (a) and 450 (b).

Thus, transparent and conducting ITO layers have been obtained on at most 10 μm thick Upilex polyimide films using the non-

Table 3. Effect of the air anneal on optical and electrical properties of ITO layers deposited at different substrate temperatures

T_s, °C	t, μm	$T_{(500\text{-}900)}$	$R_\square$, Ohm/□	$\rho \cdot 10^4$, Ohm·cm	$n \cdot 10^{20}$, cm^{-3}	μ, cm^2/(V·s)
20	0.51	71.5	41.4	21.1	1.0	29.6
200	0.50	72.2	38.3	19.1	1.1	29.7
250	0.54	71.8	31.1	16.8	1.2	31.0
300	0.49	72.3	23.7	11.6	1.7	31.7
350	0.52	71.1	18.5	9.6	1.9	34.3
400	0.53	70.9	15.5	8.2	2.2	34.6
450	0.54	72.0	11.1	6.0	2.8	37.2

reactive high-frequency magnetron sputtering. The ITO films deposited at the magnetron power of 1500 mW/cm^2, oxygen partial pressure in the argon/oxygen mixture 3 % (vol.), and the deposition temperature 450°C show the minimum surface resistance of 4.6 Ohm/□. The transmission coefficient of the ITO/polyimide heterosystems in the 500 to 900 wavelength range corresponding the CdTe SC photosensitivity region amounts 68.8 %. After annealing in air at 430°C for 25 min, that models the effect of the "chloride" treatment (obligatory for producing the high efficiency SC) on the ITO layer properties, the lauer surface resistance rises up to 11 Ohm/□ and the transmission coefficient up to 72 %. Such electrical/optical characteristics of the ITO layer provide its suitability to be used as a wide-band "window" in the high-efficient flexible CdTe-based SC.

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Структура, оптичні та електричні властивості плівок ITO на гнучких поліамідних підкладках

Г.С.Хрипунов

Вперше на промислових поліамідних плівках отримані шари ITO для високоефективних гнучких солнячних елементів на основі CdTe. Після виготовлення сонячного елемента плівки ITO, що отримані при потужності магнетрона 1500 мВт/см^2, парциальному тиску кисню в складі аргоно-кислородной суміші 3 об.% і температурі осадження 450°C, мають поверхневий опір 11 Ом/□. У області фоточутливості сонячних елементів середній коефіцієнт пропускання гетеросистем ITO/polyimide складав 72 %.