

Optimization of the ITO frontal electrodes for flexible CdTe thin film solar cells

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The optimization of the ITO frontal electrodes for flexible solar cells on CdTe base was carried out by annealing in air at 430°C. It has been shown, that for "superstrate" ITO/CdS/CdTe/Cu/Au solar cells, the preliminary annealing of ITO films provides the efficiency increase from 8.5 % up to 11.3 %, while for NaCl/ITO/CdS/CdTe/Cu/Au "substrate" solar cells, from 2.2 % up to 7.8 %.

Путем отжига на воздухе при температуре 430°С проведена оптимизация фронтальных электродов ITO для гибких солнечных элементов на основе теллурида кадмия. Показано, что для солнечных элементов ITO/CdS/CdTe/Cu/Au (типа "superstrate") предварительный отжиг слоев ITO обеспечивает рост эффективности от 8,5 % до 11,3 %, а для солнечных элементов NaCl/ITO/CdS/CdTe/Cu/Au (типа "substrate") от 2,2 % до 7,8 %.

Alongside with traditional thin film solar cells (SC) on the CdTe base, flexible SC are now under active development. In such SC, the glass substrate is replaced by thin polyimide film [1]. The frontal electrodes are a part of the CdTe based SC on any substrates. Usually, frontal the electrodes are prepared from layers of transparent and conducting oxides, for example, SnO_2:F and ITO (indium and tin oxides) [1]. Through such frontal electrodes, the solar radiation should attain the photoelectrical active base layer at minimal losses. The surface resistance of the frontal electrode should not contribute essentially to the SC total resistance. This is necessary to avoid the increased SC efficiency. When preparing the "superstrate" flexible SC, the device heterosystem ITO/CdS/CdTe/Cu/Au is formed on a transparent heat-resistant polyimide film. The SC is illuminated through this film [1]. When manufacturing the "substrate" SC (see, e.g., [2]), this heterojunction is deposited on a glass substrate with a NaCl sublayer. Then, a flexible polyimide film is formed at the back Au electrode surface. The flexible SC is separated from the glass substrate by dissolution of NaCl layer. As a result of "chluride" treatment [3,4] the surface resistance of ITO layers increases for both types film SC on the CdTe base.

In those works, the optimum conditions of the ITO layer deposition on various substrates have been determined. Under these conditions, the surface resistance increase did not surpass allowable value for frontal electrodes of high-efficiency SC. Nevertheless, the change of the frontal electrode crystal structure (that is possible in the course of the heterostructure formation) can influence the SC efficiency. Therefore, aiming at the increase the efficiency of SC on CdTe base, the influence of crystal structure of air-annealed and unannealed ITO layers on the efficiency of photo-electric processes was studied in various types of such device structures where the films were used as the frontal electrodes.

The crystalline structure of the CdTe base layers and ITO layers was studied by X-ray diffraction under copper anode emission. To compare the texturing extent of

ITO layers, the G parameter was calculated by processing experimental diffraction maxima [5]. The lattice period (a) of the ITO layers was determined after K_α-doublet division from the position of (622) diffraction maximum. The position was determined by the median method [6]. The lattice period of CdTe base layer was calculated for all diffraction maxima and refined using function $\cos^2\theta(1/\sin\theta + 1/\theta)$ by the Nelson and Reelly method [7].

The concentration n and mobility μ of major charge carriers in the ITO layers were determined by e.m.f. method [8]. The physical and technological regimes for deposition of the "superstrate" and "substrate" SC on the base of CdS/CdTe/Cu/Au heterosystems are described in [1, 2, 9]. The SC efficiency and output parameters (open-circuit voltage U_{oc}, the short-circuit current density J_{sc}, fill factor FF of the light current-voltage characteristics (CVC)) were determined by analytical processing of the light CVC. measured in the AM1.5 illumination mode at light flow power 100 mW/cm^2. The light diode characteristic of the SC (the saturation diode current density J_o, diode ideality coefficient A, series resistance R_s, and shunting resistance R_{sh}) were determined by fitting experimental CVC to theoretical one [10]:

$$J = -J_{ph} + J_o\{\exp[e(U - JR_s)/(AkT)] - 1\} + (U - JR_s)/R_{sh}, \quad (1)$$

where J is the load current density; J_{ph}, photocurrent density; e, electron charge; k, the Boltzmann constant; T, the SC temperature; U, the loading voltage. To specify the diode characteristics which define the SC efficiency, the quantitative influence of the light diode characteristics on the SC efficiency was simulated mathematically upon modification of the SC design and technological parameters. This will provide an essentially simplified determination of the physical mechanisms responsible for the efficiency of photoelectrical processes.

The research has shown (see Table 1) that air annealing of ITO layers deposited on the glass substrates results in increased extent of predominant orientation in the [400] direction from $G = 0.37$ to $G = 0.54$. The lattice period decreases from a = 10.202 Å to a = 10.193 Å. Angular widths $\Delta_{2\theta}$ of (211), (222), (400) diffraction maxima are reduced ($\Delta_{2\theta}$ were measured at the half of diffraction maximum intensity). According to the ASTM table, the lattice period of cubic In_2O_3 phase makes a = 10.118 Å [11]. The essential excess of the lattice period in researched ITO layers is connected with a significant tin concentration in those layers. When tin atoms having larger ion radius substitute for indium atoms in the unit sites or in interstitial positions, this results in increased lattice period [12]. According to experimental data (see Table 1), the air annealing causes a reduced concentration of major charge carriers. The n reduction can be connected with decreasing concentration of the oxygen vacancies being electrically active n-type defects [12].

However, this process does not play any essential part. The research of undoped In_2O_3 layers evidences that after air annealing, the n reduction is by one order lower. Therefore, the n reduction in ITO layers is a result of impurity oxidation. That is, oxygen transforms tin from electrically active state (indium lattice sites) into inactive one (at grain boundaries). Besides, the air annealing can also cause oxidation of tin being in inactive state in the indium lattice interstitials. Therefore, it is obvious, that after air annealing, the tin concentration decreases both in the indium sublattice sites

Table 1. The air annealing influence on the properties and structure ITO films.

Substrate	n, 10^{20} cm^{-3}	μ, cm^2/(V·s)	G, r.u.	a, Å	$\Delta 2\theta_{(211)}$, deg.	$\Delta 2\theta_{(222)}$, deg.	$\Delta 2\theta_{(400)}$, deg.
Glass	5.9	34	0.37	10.202	0.20	0.32	0.26
Glass*	2.4	36	0.54	10.193	0.22	0.26	0.17
Poli	6.5	39	0.15	10.162	0.24	0.24	0.26
Poli*	2.8	35	0.27	10.164	0.12	0.24	0.28
Glass/NaCl	5.5	20	0.07	10.173	0.32	0.26	0.30
Glass/NaCl*	2.5	18	0.02	10.177	0.47	0.30	0.36

* — after annealing in the air at the temperature 430°C within 25 min.

and in interstitials of the ITO layer lattice. As a result, the crystal lattice distortion decreases. This causes the observed reduction of *a*. It is known that the main contribution to physical width of diffraction maxima is brought by microscale strains and size of the coherent scattering areas (c.s.a.) [6]. Therefore, the $\Delta_{2\theta}$ reduction of ITO layers after air annealing testifies to c.s.a. increase and microscale strain decrease. Thus, it is possible to assume that increase of predominant orientation degree in the annealed ITO layers in the [400] direction and $\Delta 2\theta$ decrease are caused by recrystallization processes. At such recrystallization, some grains are fused together into a single grain with most thermodynamically favorable predominant orientation. Thus, a fraction of impurity leaves volume to grain boundary. This process reduces the microscale strain level.

The consideration of Table 1 shows that the air annealing results in increased predominant orientation extent in the [400] direction in the ITO layers deposited on polyimide films, too. However, the predominant orientation extent is much lower ($G = 0.15$) and increases only to $G = 0.27$. In contrast to ITO layers on the glass substrates, the annealing of ITO layers on the polyimide film results in the lattice period increase from $a = 10.162$ Å to $a = 10.164$ Å. At the annealing, the decrease of $\Delta 2\theta_{211}$ is observed. The $\Delta 2\theta_{222}$ remains unchanged while $\Delta 2\theta_{400}$ is increased. As the (221), (222), (400) reflections are observed at angles $2\theta = 21°$, $30°$, $35°$ respectively, the $\Delta 2\theta_{211}$ reduction evidences, first of all, an increased c.s.a, while increasing $2\theta_{400}$ testifies to increase of the microscale strain level. This is caused by that at small angles, the physical widening of the diffraction maximum is due mainly to c.s.a. size while at large angles, it is defined by the microscale strain level [6]. The lattice period increase in the ITO layers on polyimide film after annealing may be due to plastic straining of the flexible substrate. As a result, the lattice period change in the ITO layers is defined by two physical mechanisms: oxidation of tin in the ITO layers and stretching stresses from the polyimide film. Such stresses are due to straining of the polyimide film during high-temperature air annealing.

The ITO layers deposited on the NaCl/glass substrate show an insignificant predominant orientation in the [004] direction ($G = 0.07$). After air annealing of those ITO layers, the G value decreases down to 0.02. The $\Delta 2\theta_{211}$, $\Delta 2\theta_{222}$ and $\Delta 2\theta_{400}$ are increased. This evidences a reduction of the c.s.a. size and increase of microscale stresses in the ITO layers. Increase of the lattice period from $a = 10.173$ Å to $a = 10.177$ Å has been observed, too. In our opinion, the observed structural changes are caused by an intense sodium diffusion from NaCl layer to ITO ones during annealing. The latter may result in splitting of the c.s.a. and in increasing microscale stresses. The low value of the major charge carrier mobility points indirectly to reduced crystal structure perfection of the ITO layers on NaCl/glass substrates as compared to other substrates (see Table 1).

All annealed ITO layers deposited on all the investigated substrate types were annealed repeatedly in air at 430°C for 25 min. The surface electric resistance and transparency coefficient of the ITO layers were increased only by few per cent. The X-ray investigations of repeatedly annealed ITO layers show absence of any appreciable changes in the crystal structure parameters. The preliminary annealing of ITO layers has been found to result in reduction of the CdTe lattice period. So, for CdTe layers deposited on the polyimide substrates, the lattice period decreases from 6.492 Å to 6.487 Å (Fig. 1). According to ASTM, the reference lattice period value makes 6.481 Å for cubic CdTe phase [13]. Apparently, there in deposited CdTe layers are strained. These strains cause an increase of the lattice period as compared to reference value. Nevertheless, CdTe layers deposited on previously annealed ITO layers, are subjected to lower stresses.

By analytical processing of experimental light CVC (Fig. 2), the output parameters and light diode characteristics of various SC types on the ITO/CdS/CdTe base were compared. The SC were deposited on the unannealed and previously air-annealed ITO layers. The analysis shows (Table 2) that the preliminary annealing of ITO layers on glass substrate results in SC efficiency increase from 10.3 % to 11.2 %. The mathematical modeling of influence of light diode parameters on the SC efficiency testifies that the efficiency increase is caused by reduction of the diode saturation current density from $J_o = 5.7 \cdot 10^{-8}$ A/cm^2 to $J_o = 9.5 \cdot 10^{-10}$ A/cm^2 and diode ideality coefficient from $A = 2.3$ to $A = 1.8$. Preliminary annealing of ITO on the polyimide film results in the SC efficiency increase from 8.5 % to 11.3 % (Table 2). This is caused

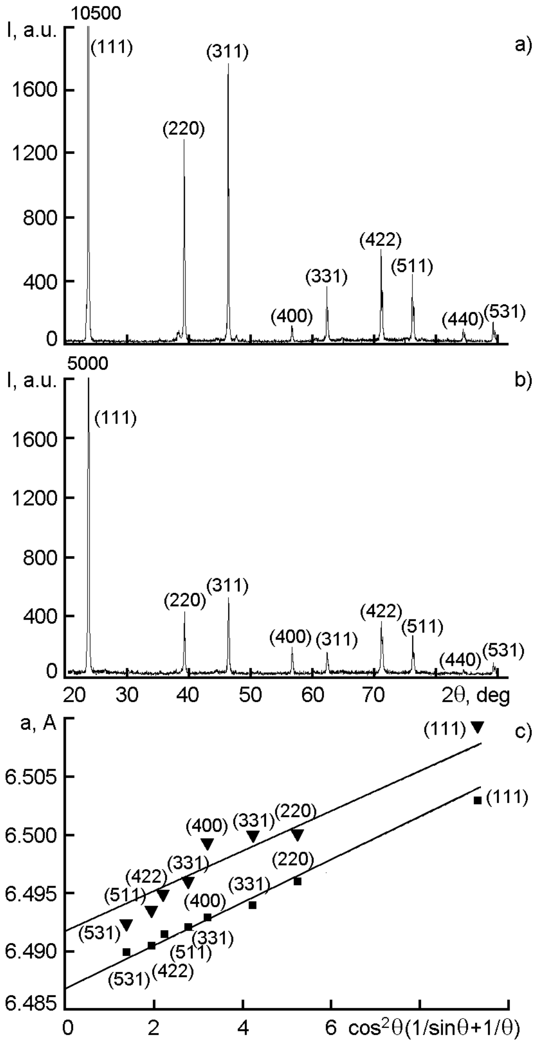

Fig. 1. Structural researches of CdTe base layers in structure the polyimide film/ITO/CdS/CdTe/Cu/Au CS: (a) XRD pattern of CdTe layer in SC structure deposited on unannealed ITO layer; (b) XRD pattern of CdTe layer in SC structure deposited on annealed ITO layer; (c) Lattice period of CdTe layers: ■ — CdTe layers in SC structure deposited on annealed ITO layer; the same on unannealed ITO layer.

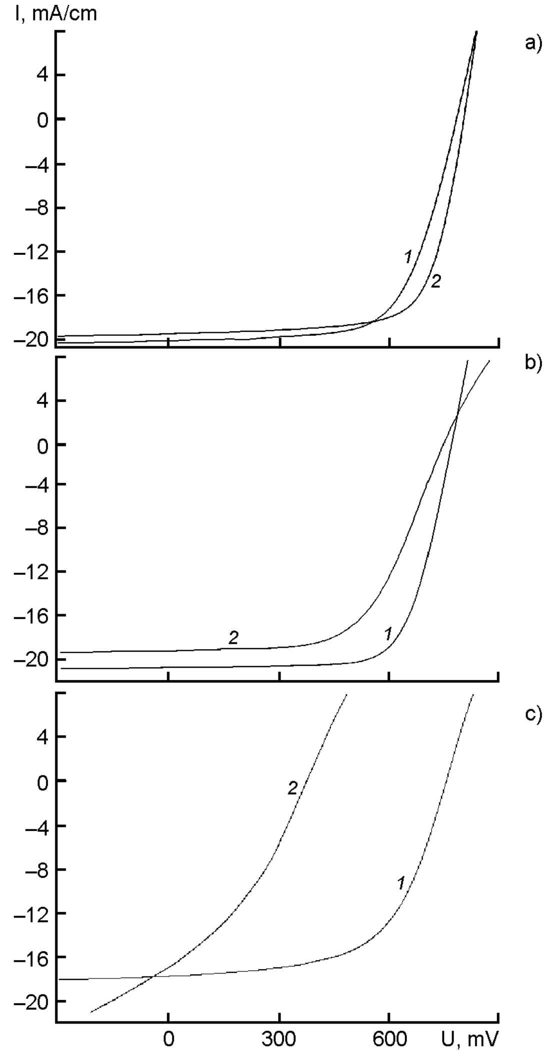

Fig. 2. Light CVC of SC on CdTe base:
(a) glass/ITO/CdS/CdTe/Cu/Au;
(b) polyimide film/ITO/CdS/CdTe/Cu/Au;
(c) glass/NaCl/ITO/CdS/CdTe/Cu/Au.
ITO layers: annealed (*1*), unannealed (*2*).

also by J_o and A reduction. In our opinion, this is connected to stability of crystal structure of the annealed ITO to "chloride" treatment of deposited SC. This, in turn, reduces the base layer strains in the CdS/CdTe device structure, the strains being possible to arise at the changes in lattice period and predominant orientation extent of the lower ITO layer. The increased base layer strain may result in a reduced SC efficiency due to many factors: adhesion deterioration, reduction of mobility charge carriers, introduction of additional structural defects, instability of electrical properties, etc. [14]. These negative processes are especially intensified if the layers are deposited on substrates with linear expansion coefficient exceeding that of the semiconductor material. Such situation is just realized experimentally at SC formation on polyimide substrate.

It has been shown, that preliminary annealing of ITO layer of NaCl/ITO/CdS/CdTe/Cu/Au SC results in the efficiency increase from 2.2 % up to 7.8 % (Table 2). According to modeling results, the increased efficiency is due to reduction of the diode current saturation density J_o from $6.0\cdot10^{-5}$ A/cm^2 to $5.6\cdot10^{-8}$ A/cm^2,

Table 2. Output parameters and light diode characteristics SC

Substrate		Glass	Polyimide	Glass/NaCl
Output parameters	V_{oc}, mV	793 (774)	762 (733)	751 (373)
	J_{sc}, mA/cm^2	19.4 (20.1)	20.8 (19.3)	18.0 (17.9)
	FF	0.71 (0.66)	0.71 (0.60)	0.59 (0.35)
	η, %	11.2 (10.3)	11.3 (8.5)	7.8 (2.2)
Diode characteristics	R_s, Ω·cm^2	1.7 (2.8)	2.1 (5.8)	6.0 (5.0)
	R_{sh}, Ω·cm^2	659 (954)	6400 (2300)	343 (95)
	J_o, A/cm^2	$9.5 \cdot 10^{-10}$ ($5.7 \cdot 10^{-8}$)	$1.0 \cdot 10^{-8}$ ($1.4 \cdot 10^{-7}$)	$5.6 \cdot 10^{-8}$ ($6.0 \cdot 10^{-5}$)
	A	1.8 (2.3)	2.0 (2.2)	2.3 (3.0)

* — The output parametres and light diode characteristics SC deposited on them annealing ITO layers an given in the brackets.

of the diode ideality coefficient from $A = 2.3$ to $A = 1.8$ and the shunting resistance R_{sh} increase from 95 Ohm·cm^2 up to 343 Ohm·cm^2. Secondary ion mass spectroscopy depth profiling was done for the NaCl/ITO/CdS/CdTe/Cu/Au SC. The analytical signal distribution of the sodium isotope (^{23}Na) in glass/NaCl/ITO/CdS/CdTe/Cu/Au SC (Fig. 3) shows that the preliminary air annealing of ITO reduces the sodium concentration in the CdS/CdTe heterosystems. It seems that, at the ITO layers air annealing, there are two diffusion flows opposite to one another at the grain boundaries in these layers each other: oxygen and sodium. The oxygen diffusion results in tin oxide formation at the grain boundaries. As a result, the sodium diffusion paths at the grain boundaries become blocked. This type diffusion shows as a rule a higher rate than the volume one. This results in the experimentally observed R_{sh} increase and J_o reduction in the device structures containing previously air-annealed ITO layers. At the same time, it is to note that the above-mentioned stabilization of the ITO layer crystal structure due to air annealing is among the factors influencing the reduction J_o and A.

Thus, it has been shown in experiment that for flexible "superstrate" ITO/CdS/CdTe/Cu/Au SC, the preliminary air annealing of the ITO layers 430°C for 25 min provides stabilization of the lattice period and the predominant orientation extent of such frontal electrodes prior to the subsequent formation of the device structures. As a result, a reduction of strains which cause growth of the lattice period is observed in CdTe base layers. This causes a decreased diode saturation current density, diode ideality coefficient, and thus increase

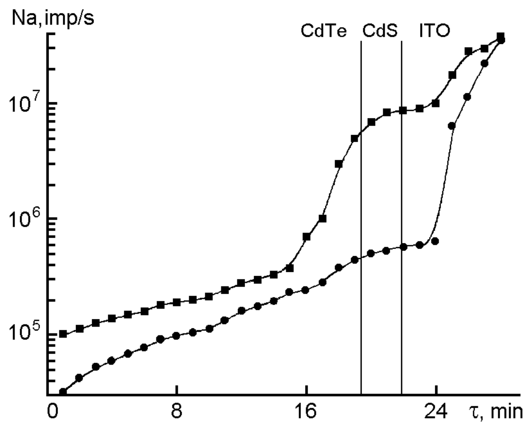

Fig. 3. Level-by-level distributions of the sodium isotope (^{23}Na) analytical signal in the glass/NaCl/ITO/CdS/CdTe/Cu/Au SC deposited on unannealed (■) and annealed (•) ITO layers.

of the device structure efficiency from 8.5 % to 11.3 %. For flexible "substrate" ITO/CdS/CdTe/Cu/Au SC, the preliminary annealing of ITO layers results in the efficiency increase from 2.2 % to 7.8 %. The preliminary annealing of frontal electrodes not only reduces of the diode saturation curr ent density and diode ideality coefficient, but increases the shunting resistance due to blocking of sodium diffusion at grain boundaries in the ITO layers.

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Оптимізація фронтальних електродів з ITO для гнучких плівкових сонячних елементів на основі CdTe

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Шляхом відпалу на повітрі при температурі 430°C виконано оптимізацію фронтального електроду ITO для гнучких плівкових сонячних елементів на основі телуриду кадмію. Показано, що для сонячних елементів ITO/CdS/CdTe/Cu/Au (типу "superstrate") попередній відпал шарів ITO забезпечує зростання ефективності від 8.5 % до 11.3 %, для сонячних елементів NaCl/ITO/CdS/CdTe/Cu/Au (типу "substrate") від 2.2 % до 7.8 %.