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Development of ITO layers for high efficiency CdTe solar cells

G.S.Khrypunov

National Technical University "Kharkiv Polytechnical Institute",
21 Frunze St., 61002 Kharkiv, Ukraine

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The high-frequency non-reactive magnetron sputtering regimes have been found providing ITO films exhibiting a necessary combination of optical and electrical parameters of those layers in ITO/CdS/CdTe solar cells.

Идентифицированы режимы высокочастотного нереактивного магнетронного распыления пленок ITO, которые обеспечивают необходимое сочетание оптических и электрических параметров этих слоев в составе солнечных элементов ITO/CdS/CdTe.

Cadmium telluride has been recognized as a promising photovoltaic material for thin-film solar cells (SC) [1]. To intensify the photoelectrical processes, the wide-band "window" effect is used in all modern film SC. This effect makes it possible to lower the surface recombination rate of non-equilibrium charge carriers due to shift of their generation region from the surface being irradiated [2]. This effect is realized by using degenerated wide-band semiconducting materials exhibiting a high transmission coefficient for solar radiation (at least 86 %) in the SC film structure. It has been shown [3] that, if the surface electric resistivity of the wide-band "window" does not exceed 12 Ω/▫ , then the presence of such a layer does not cause a decreased SC efficiency. Films of indium and tin oxides (ITO) are used as the wide-band gap "windows" in the SC with CdTe base layer.

To date, techniques have been developed to obtain transparent and conductive ITO wide-band gap "windows" on glass substrates that are used in production of CdTe thin-film SC [4, 5]. The non-reactive high-frequency magnetron sputtering is among optimal methods to obtain such layers. Nevertheless, in our opinion, the high optical and electric characteristics realized for the ITO films on glass substrates cannot still guarantee optimality of those layers in a specific use thereof in CdTe thin-film SC. This is due to the fact that the ITO formation is the first technological step in manufacturing SC on the basis of cadmium telluride, therefore, the ITO properties may change in the course of the further high-temperature treatments intended to obtain the semiconducting structure. The purpose of this work is to develop a non-reactive high-frequency magnetron sputtering technology to provide ITO layers for CdTe thin-film SC that would take into account the effect of above-mentioned heat treatments on the initial optical and electric properties of the wide-band gap "windows".

The ITO films were deposited onto glass substrates in a MRC6031 high-frequency magnetron unit. The target being sputtered consisted of compacted mechanical mixture of finely dispersed In_2O_3 (90 % wt.) and SnO_2 (10 % wt.), both of semiconductor purity grades. The initial partial pressure was 10^{-6} Torr. The magnetron specific power (P_w) was varied from 2200 to 1200 mW/cm^2, thus corresponding to the range used in production of transparent conductive ITO films [5]. The films were deposited in argon-oxygen atmosphere at

$6\cdot10^{-3}$ Torr pressure. The gas leak-in system design made it possible to vary the oxygen concentration (C_O) within limits of 0 to 3 % (vol.). The ITO film thickness, as determined by a profilometer, was varied within 0.45 to 0.63 μm range. The ITO film crystalline structure was examined by X-ray diffraction under copper anode emission. To study the film surface resistance ($R_\int$), the four-probe technique was used. The concentration (n) and mobility (μ) of the major charge carriers in the ITO films were determined using the Hall e.m.f. method. The spectral dependences of the film transmissivity were studied using two-channel method in the 200 to 1100 nm spectral range. The average transmissivity value ($T_{400-800}$) was calculated for the 400 to 800 nm range.

First, studied was the effect of the oxygen partial pressure and the magnetron sputtering specific power on the crystalline structure, optical and electrical properties of ITO films deposited onto unheated glass substrates. The magnetron specific power P_w = 2200 mW/cm^2 being constant, the oxygen concentration C_O increase in the argon-oxygen mixture from 0 to 3 % (vol.) results in the surface resistivity $R_\int$ increase from 9.1 to 15.7 Ω/∫ while the average transmissivity $T_{400-800}$ from 3.7 to 23.2 % (Fig. 1, curves 1, 2). The $T_{400-800}$ value attains 17 % already at C_O about 1 %vol. and then changes only slightly. The low transparency of the wide-band gap "windows" is due to a high concentration of oxygen vacancies in the growing layer [6]. Thus, in spite of the increasing oxygen concentration in the gas mixture, its atoms may no have time to occupy the crystal lattice sited due to the high sputtering power. At the other hand, according to [6], at a high specific power of magnetron sputtering, intrinsic point defects (oxygen vacancies) can arise in the growing oxide film.

Proceeding from the above considerations, the magnetron sputtering power in further experiments was decreased at the constant oxygen concentration of 3 % (vol.) in order to increase the ITO film transmissivity. The Pw decrease from 2200 to 1500 mW/cm^2 results in the transparency increase up to $T_{400-800}$ = 88.2 % (Fig. 1, curve 3), while the surface resistivity increases only slightly from 15.7 to 20 Ω/∫. The X-ray phase analyze of the layers obtained in various regimes has shown that the ITO films are of cubic modification and oriented mainly along the (400) direction.

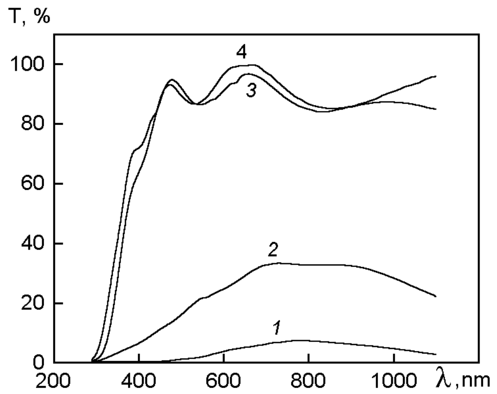

Fig. 1. Effect of magnetron sputtering regime on optical properties of ITO films deposited onto unheated substrates:

P_w = 2200 mW/cm^2, C_O = 0, $T_{400-800}$ = 3.7 %, $R_\int$ = 9.1 Ω/∫ (*1*); P_w = 2200 mW/cm^2,

C_O = 3%(vol.), $T_{400-800}$ = 23.2 %, $R_\int$ = 15.3 Ω/∫ (*2*); P_w = 1500 mW/cm^2, C_O = 3% (vol.), $T_{400-800}$ = 88.1 %, $R_\int$ = 20.0 Ω/∫ (*3*); P_w = 1200 mW/cm^2, C_O = 3 % (vol.), $T_{400-800}$ = 88.8 %, $R_\int$ = 475.0 Ω/∫ (*4*).

According to [7], the qualitative index characterizing the predominant orientation of ITO films is the ratio of two most intense diffraction maxima, $I_{(222)}/I_{(400)}$. For the In_2O_3 phase having no predominant orientation, this ratio amounts 3.33, according to ASTM data [8]. As to the ITO films under study obtained on unheated substrates at P_w = 1500 mW/cm^2, this ratio is 1.6 (Fig. 2a).

The further decrease of the magnetron power from 1500 to 1200 mW/cm^2 results in a dramatic $R_\int$ increase from 20 to 475 Ω/∫. The transmissivity increases insignificantly from 88.2 to 88.8 % (Fig. 1, curves 3, 4). The $R_\int$ increase is due to dropping concentration of major charge carriers, n, from $5.9\cdot10^{20}$ down to $2.8\cdot10^{19}$ cm^{-3} while their mobility, μ, increases slightly from 11 up to 14 cm^2/(V·s). In our opinion, the decreasing concentration of major charge carriers at the decreasing magnetron power is due to decreasing growth rate that may be accompanied by increasing oxygen concentration in the growing film. This increase in the oxygen concentration results, at the one hand, in decreasing concentration of electrically active intrinsic point defects (oxygen vacancies) of the n conductivity type. At the other hand, the excess oxygen atoms may bind tin atoms and thus transform this impurity out of the electrically active state into electrically inactive one by formation of oxide phases.

The results obtained evidence that for the ITO films grown on unheated substrates, the optimum combination of optical and electrical properties is attained at the magnetron power $P_w = 1500$ mW/cm^2 if the oxygen concentration in the argon-oxygen atmosphere is 3 % (vol.). The surface resistivity $R_ʃ = 12$ Ω/ʃ required for high-efficiency SC, however, is impossible to be provided at the attained optimum transmissivity of $T_{400-800} = 88.2$ %. Comparative analysis if literature data [3, 4] indicated that the drawback is due to insufficient mobility of electrons $\mu = 11$ cm^2/(V·s) in ITO films deposited onto unheated substrates. Since the mobility depends heavily on the crystal perfection of the layer and the elevated deposition temperature is among the most common methods to improve the ITO layer crystal structure [9], the further experiments were aimed at examination of the deposition temperature effect on the crystalline structure, optical and electrical properties of ITO films grown in optimum regime of the magnetron sputtering.

The structure studies have shown that as the deposition temperature is elevated up to 450°C, the extent of the ITO film predominant orientation along the (400) direction increase ($I_{(222)}/I_{(400)} = 0.7$) (Fig. 2b). The substrate temperature increase above 250°C has been shown to result in the surface resistivity decrease down to $R_ʃ = 12$ Ω/ʃ (Fig. 3a, curve 1) that is caused by the increased mobility (Fig. 4b, curve 1) at the essentially constant concentration of major charge carriers (Fig. 4a, curve 1). The film transmissivity value exceeds 88 % within the whole studied range og the substrate temperature (Fig. 3b, curve 1). Thus, from the standpoint of the combination of optical and electrical properties in the initial state, the ITO films obtained on glass substrates at deposition temperatures ranging from 250 to 450°C can be used to design high-efficiency SC.

When studying the effect of ITO/CdS/CdTe SC manufacturing process on the initial properties of ITO films, the "chloride" treatment was found to cause an appreciable increase of the surface resistivity of the wide-band "window". This standard heat treatment is used to diminish the grain boundary surface and to lower the basic layer resistivity as well as to form an efficient separating barrier [11]. The "chloride" treatment is performed by applying a $CdCl_2$ film onto the basic CdTe layer surface followed by the air annealing the system at 430°C for 25 min. According to literature data, oxygen atoms diffusing across the semiconductor towards the CdS/ITO interface play an important part in the "chloride" treatment [12]. No diffusion interaction between CdS and ITO layers was observed [11]. Thus, it is obvious that the "chloride" treatment effect on the ITO film properties is associated with the oxidation process occurring during the treatment. Therefore, the ITO layers obtained at sub-

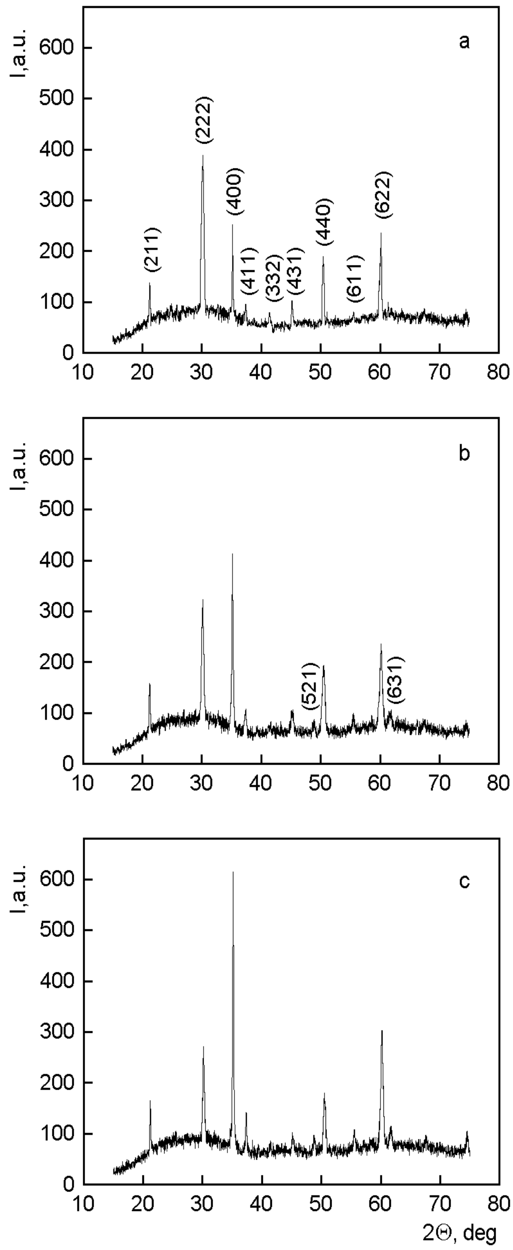

Fig. 2. Crystalline structure of ITO films obtained at $P_w = 1500$ mW/cm^2, $C_O = 3$ % (vol.) and substrate temperature (°C): 20 (a), 450 (b), 450, after air annealing (c).

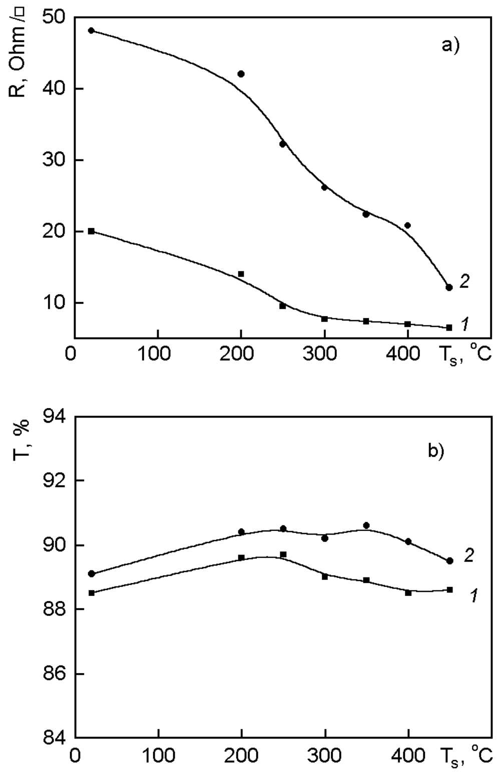

Fig. 3. Effect of substrate temperature and air annealing on $T_{400-800}$ (a) and $R_{\int}$ (b) of ITO films obtained at P_w = 1500 mW/cm^2, C_O = 3 % (vol.): prior to annealing (*1*), after annealing (*2*).

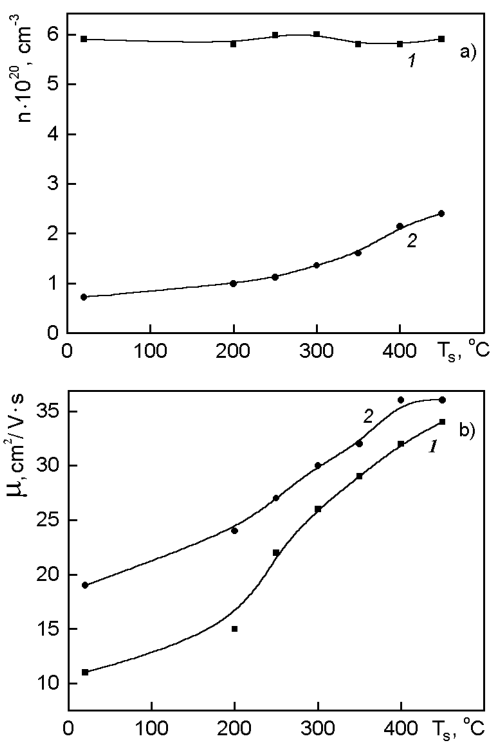

Fig. 4. Effect of substrate temperature and air annealing on n (a) and μ (b) of ITO films obtained at P_w = 1500 mW/cm^2, C_O = 3 % (vol.): prior to annealing (*1*), after annealing (*2*).

strate temperatures of 250 to 450°C were annealed in air at 430°C for 25 min in order to simulate the evolution of the wide-band "window" structure, optical and electrical properties at the "chloride" treatment of ITO/CdS/CdTe solar cells.

At all the studied deposition temperatures, the heat treatment in air has been found to cause an insignificant increase of the film transmissivity along with a considerable increase of the surface resistivity (Fig. 3a, b, curve 2). The study of Hall e.m.f. has shown that the $R_{\int}$ increase is due to decreasing concentration of major charge carriers (Fig. 4a, curve 2) accompanied by a less considerable increase in their mobility (Fig. 4b, curve 2). Thus, the air annealing causes oxidation of the doping impurity being initially in the electrically active state. Only the ITO films deposited onto substrates heated up to 450°C exhibit the optical and electrical characteristics making it possible to use the films in high-efficiency SC on the cadmium telluride basis. For those films, the transmissivity $T_{400-800}$ = 90.5 % and surface resistivity $R_{\int}$ = 12 Ω/σ. The structure studies of the mentioned films carried out prior to and after air annealing (Fig. 4b, c) evidence that the heat treatment results in increased predominant orientation of the film along the (400) direction. The $I_{(222)}/I_{(400)}$ value decreases from 0.7 down to 0.4.

To conclude, the conditions of high-frequency non-reactive magnetron sputtering have been identified that provide the required combination of optical and electrical parameters for ITO layers within the structure of solar cells on CdTe basis. When annealed in air at 430°C for 25 min, the ITO films obtained at the magnetron power 1500 mW/cm^2, oxygen partial pressure in the argon-oxygen mixture 3 % (vol.) and the deposition temperature 450°C show the surface resistivity 12 Ω/∫ and transmissivity 90.5 %. These optical and electrical parameters do not limit the photoelectrical process efficiency in solar cells on CdTe basis. The decreasing resistivity of the ITO films at the deposition temperature elevation is shown to result from increasing mobility of major charge carriers. The increased resistivity of the ITO layers after the air annealing found in experiment is due to decreased concentration of major charge carriers.

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Розробка шарів ITO для високоефективних сонячних елементів на основі CdTe

Г.С.Хрипунов

Ідентифіковано режими високочастотного нереактивного магнетронного розпилення шарів ITO, які забезпечують необхідне поєднання оптичних і електричних параметрів цих шарів у складі високоефективних сонячних елементів ITO/CdS/CdTe.