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Structure and Optical Properties CdS and CdTe Films on Flexible Substrate Obtained by DC Magnetron Sputtering for Solar Cells

G.I. Kopach*, R.P. Mygushchenko, G.S. Khrypunov, A.I. Dobrozhan, M.M. Harchenko

National Technical University «Kharkiv Polytechnic Institute», 2, Kyrpychov Str., 61002 Kharkiv, Ukraine

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The paper describes investigate of crystal structure and optical characteristics of the CdS transparent window layers and the CdTe base layers, obtained by direct current magnetron sputtering on glass or polyimide substrate, and output parameters the flexible thin film solar cells based on them. The band gap in obtained hexagonal CdS films is E_g = 2.38-2.41 eV and optical transparency of CdS films is 80-90%. Conducting chloride treatment of CdTe layers, obtained at T < 300⁰C, promotes wurtzite-sphalerite phase transition. Cooling ITO/CdS layers to room temperature before CdTe deposition, removal of the air and subsequent heating in vacuum to the required temperature of the substrate leads to an increase of the energy conversion efficiency and open circuit voltage of the polyimide/ITO/CdS/CdTe/Cu/Ag flexible solar cell.

Keywords: Cadmium sulphide, Cadmium telluride, Direct current magnetron sputtering, Solar cell, Thin films.

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1. INTRODUCTION

Thin film solar cells based on CdS/CdTe heterostructure are prospective for an industrial production [1]. Nowadays solar cells formed on flexible polyimide films are being actively developed [2]. Such constructive and technological solution allows to install flexible solar cells on surfaces of any shape and to achieve several times higher electrical power per unit of weight than in traditional solar cells. One of the stages in the development of effective flexible solar cells is the creation of an economical industrial technology of CdS and CdTe semiconductor layers production. This is promising to use a widely applied method of non-reactive direct current magnetron sputtering (DC magnetron sputtering) as such technology. However, there are some technological problems during the deposition of semiconductor films by this method. They are caused by low conductivity of CdS and CdTe pressed powder targets and sufficiently low emission ability of these materials. In order to determine the optimal physical and technological modes of condensation by DC magnetron sputtering, the study of crystal structure and optical properties of CdS and CdTe films on glass substrates is relevant.

The condensation modes of CdS and CdTe films with optimal crystalline structure and optical properties were used for the production of laboratory samples of flexible superstrate solar cells polyimide/ITO/CdS/CdTe/Cu/Ag. The output parameters and light diode characteristics of such solar cells were determined.

2. EXPERIMENTAL DETAILS

Thin films of CdS and CdTe were obtained by DC magnetron sputtering at a pressure 0.8-1 Pa. As a working gas we used Argon, whose pressure in the vacuum chamber was regulated in manual mode.

The targets with diameter 76 mm and thickness 2-2.5 mm were made by cold pressing from cadmium telluride and cadmium sulfide powders. After this the targets were annealed in vacuum at residual pressure more than $1.3 \cdot 10^{-2}$ Pa and temperature 60-80 °C within 3 hours. The feature of used in laboratory technology of condensation CdS and CdTe films by DC magnetron sputtering magnetron design is that the cooling circuit covered only the magnetic system so there was no forced cooling of sputtered target.

The glass or polyimide substrates were installed in the substrate holder with mobile heater. For the implementation of the process of thermionic emission of electrons from the target material for plasma discharge ignition the target was preheated for 15 minutes. The target "training" process was carried out within 5 min in the mode of maximum approximation to the technological mode of obtaining films, while the current plasma discharge was to increase. After the "training" process, the target substrate with a movable substrate holder carrier was moved to the position above the target without changing the discharge electrical parameters and pressure in the chamber. The distance from the substrate to the target was 40 mm. The temperature of the substrate was monitored using a thermocouple.

The structure of the obtained CdTe and cadmium sulphide films was studied by the X ray diffractometry (XRD) methods [3]. There was conducted automatic recording of X ray spectra at θ-2θ scanning using X-ray diffractometer DRON-4 with step 0.01-0.02 degrees in K_α- radiation of cobalt anode.

To accurately determine the phase composition of the obtained CdTe films we used the "oblique" shooting method, during which in the radiation of cobalt anode in the process of θ-2θ scanning were conducted detection and registration of diffraction reflections from those sphalerite and wurtzite planes, that are not detected in the foregoing registration method because of texturing of samples.

* gkopach@ukr.net

Optical studies of CdTe and CdS layers were conducted using the spectrometer SF-2000. The transmission spectrum of studied films was used to determine the thickness of the layers. The thickness of the layers was determined by the formula:

$$t = (M \lambda_1 \lambda_2) / (2(n(\lambda_1) \lambda_2 - n(\lambda_2) \lambda_1) \quad (1)$$

where λ_1, λ_2 – the wavelengths of two adjacent extremums (interferential maxima or minima of transmission spectrum) in nm; $n(\lambda_1)$, $n(\lambda_2)$ – refractive index, depending on the wavelength λ_1, λ_2.

The bandgap of thin films was determined by calculating the dependence of absorption coefficient on the wavelength $\alpha(\lambda)$ using the Beer–Lambert law:

$$T = [(1 - R)^2 e^{-\alpha t}]/[1 - R^2 e^{-2\alpha t}] \quad (2)$$

where T – transmission coefficient; R – reflection coefficient; t – film thickness.

The CdTe and CdS polycrystalline films bandgaps were determined by extrapolation of the linear portion of the $(\alpha \cdot h\nu)^2 = f(h\nu)$ curves (where h – Planck constant, ν – frequency) to the intersection with the $h\nu$ energy axis.

Measurement of light current-voltage (J-V) characteristics of the obtained solar cells polyimide/ITO/CdS/CdTe/Cu/Ag was performed in AM 1.5 simulated solar light. The output parameters and light diode characteristics of the studied solar cells were determined: short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) of J-V characteristics and, ultimately, efficiency (η) by analytical processing of light J-V characteristics [4]:

$$\eta = (J_{sc} \cdot V_{oc} \cdot FF)/P_{in}, \quad (3)$$

where $P_{in} = 10^3$ W/m^2 – the incident solar power.

According to the equivalent scheme of the solar cell [4], the quantitative characteristics of the photovoltaic processes are the light diode characteristics of the solar cell: the density of the diode saturation current J_0, the photocurrent density J_{ph}, the device ideality factor A, the serial resistance R_s and the shunt resistance R_{sh}, which are calculated per unit area of the solar cell. The connection of the efficiency of a solar cell with light diode characteristics implicitly is described by the theoretical light J-V characteristic of the solar cell [5]:

$$J = - J_{ph} + J_0\{\exp[e(V - JR_s)/(AkT)] - 1\} + (V - JR_s)/R_{sh}, \quad (4)$$

where J – current density flowing through the load, e – the charge, k – the Boltzmann constant, T – the temperature of device, V – voltage drop on load.

By approximating the experimental values of J and V according to (4), output parameters, light diode characteristics and efficiency of solar cells were theoretically calculated [6].

3. RESULTS AND DISCUSSION

CdS films were condensed by DC magnetron sputtering on a glass substrates at different physical and technological modes: substrate temperature $T_{sub} = 220$-250 °C, pressure of inert gas $P_{Ar} = 0.9$-1 Pa, magnetron discharge current density $J = 1.1$ mA/cm^2, the voltage on magnetron $V = 550$-600 V, deposition time 5-15 min.

Studying the XRD patterns of CdS layers lattice grown at deposition time 5-15 min (Fig. 1), the only one diffraction peak was observed for all of the received films at the angle $2\theta = 30.62^0$. Considering that the CdS stable structure is hexagonal [4], subsequent diffractogram data processing was done for this CdS phase. This peak corresponds to reflection (002) hexagonal phase of CdS. Low intensity of this peak is due to small thickness of the sample. For all samples the intensity of peak lies in the 220-280 imp/s range, which indicates almost the same thickness of obtained CdS layers. Estimated values of interplanar spacing lies in the 3.379-3.391 Å range, which corresponds to the value of lattice constant $c = 6.758$-6.782 Å.

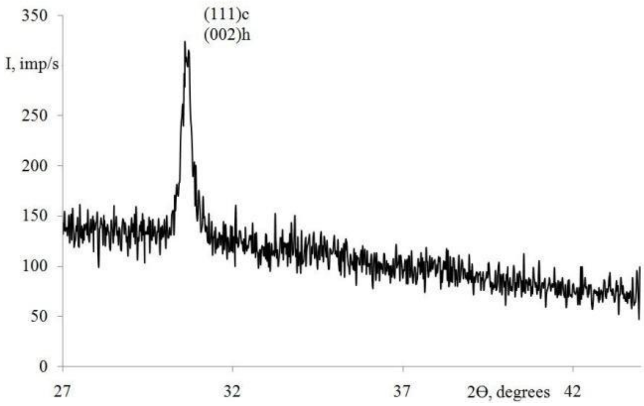

Fig. 1 – XRD pattern of obtained CdS sample layer

Table 1 – Technological modes of obtaining CdTe films

№	T_{sub} at start, °C	T_{sub} at finish, °C	τ, min	P_{Ar}, Pa	V, V	I, mA	t, μm
1	330	315	15	0.8-1	600	60	0.3
2	300	300	15	0.8-1	600	40	0.39
3	295	292	25	0.8-1	600	40	1.03
4	300	300	25	0.8-1	600	60	2.36
5	270	315	15	0.9-1	600	80	2.12
6, 8, 9	312	295	25	0.9-1	650	80	4.9-5.1
7	312	297	15	0.8-0.9	650	100	> 5,5

Spectral dependences of transmission coefficient of obtained CdS layers are presented in Fig. 2.

According to results of optical studies there is a strong absorption of radiation in the wavelength range 400-500 nm, while in the visible and infrared spectral range the CdS films transparence is up to 80%. Typical thickness of the investigated CdS layers is 150-250 nm. The bandgap in obtained CdS films is $E_g = 2.38$-2.41 eV, which is close ($E_g = 2.42$-2.45 eV) to CdS monocrystals value.

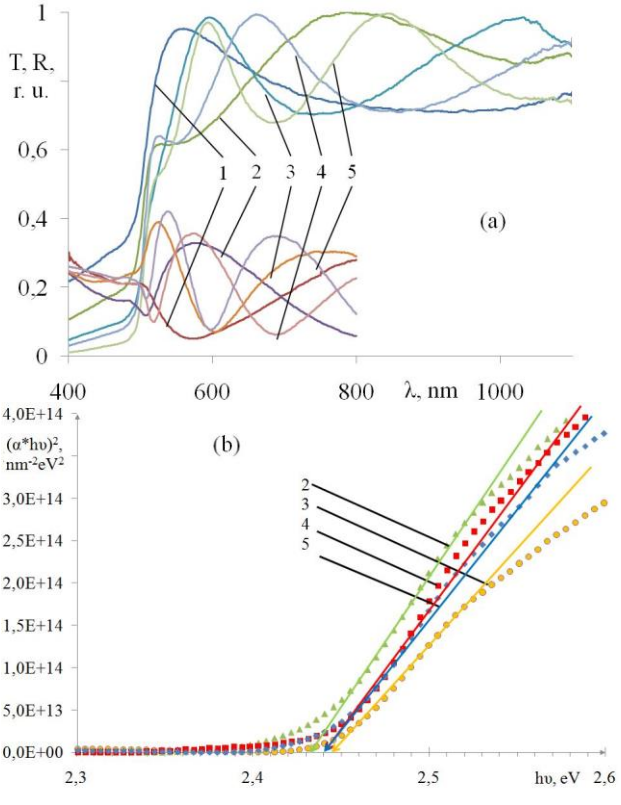

Fig. 2 – Spectral dependences of transmission and reflection coefficients (a) and dependences $(\alpha \cdot h\nu)^2 = f(h\nu)$ (b) of samples 1-5 respectively

The optical transparency of CdS films is 80-90%, which indicates the ability to use such films as a transparent window layer in solar cells based on CdS/CdTe heterostructure.

CdTe layers were obtained on glass substrates under the following conditions: T_{sub} = 295-315 °C, P_{Ar} = 0.8-1 Pa, J = 2.2-5.4 mA/cm², V = 600-650 V, deposition time 15-25 min.

The structure and optical properties of CdTe thin films grown on glass substrates using DC magnetron sputtering method at different physical and technological condensation modes were investigated (Tabl. 1).

The typical XRD pattern of CdTe sample layer obtained at different physical and technological condensation modes (samples 3, 4, 6, 7) is presented in Fig. 3 (by the example of sample 6).

In all diffractograms of studied CdTe films there are two distinct peaks at the angles 2θ 27.05° and 91.05°. According to table ASTM 15-0770 they can belong both to hexagonal and cubic structure of CdTe: wurtzite reflections (002) and (006) and sphalerite reflections (111) and (333) respectively. Also reflections (103) and (105) of hexagonal phase CdTe are observed in diffractograms. Using of «oblique» shooting method of diffractometry at the angles 2θ 72-85° allowed to determine the exact phase composition of grown CdTe layers when rotating the sample on an angle of 20.5°. In all diffractograms only reflection (105) of hexagonal phase was observed (Fig. 3b). Thus, all studied CdTe films obtained at different physical and technological condensation modes by DC magnetron sputtering method contain only metastable hexagonal structure. The annealing of samples in vacuum at T = 400 °C for 20 min does not change the CdTe layers phase.

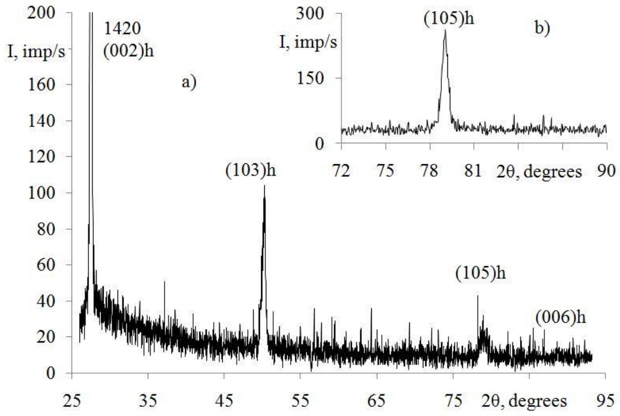

Fig. 3 – Typical XRD patterns of obtained CdTe films: (a) sample 6, (b) sample 6, by using «oblique» shooting method

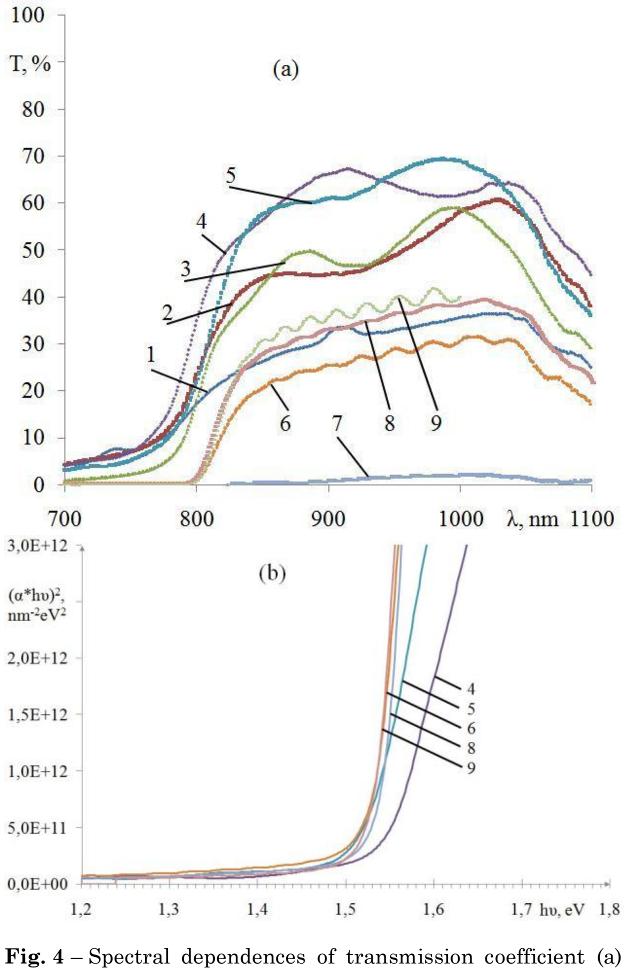

Fig. 4 – Spectral dependences of transmission coefficient (a) and dependences $(\alpha \cdot h\nu)^2 = f(h\nu)$ (b) of samples CdTe 1-9

Spectral dependences of transmission coefficient of CdTe films samples 1-9 are shown in Fig. 4 (Tabl. 1). For all samples the transparence is 5% in the visible wavelength range and about 60% in the infrared spectral range. The CdTe bandgap in obtained thin films with different thickness is 1.52-1.54 eV and established according to the same procedure, as in cases of CdS films.

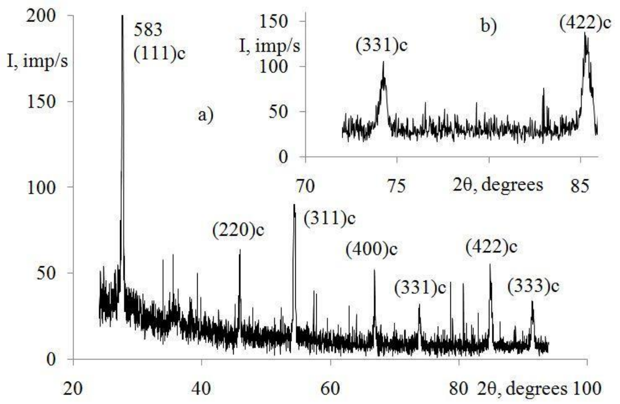

Fig. 5 – XRD pattern of sample 8 (a) after Cl treatment and annealing in air and (b) by using «oblique» shooting method

Traditional chloride treatment (Cl treatment) with subsequent annealing in air at $T = 430$ °C for 25 min [7] of studied CdTe films facilitates phase transition wurtzite-sphalerite what can be seen in XRD patterns. The typical diffractogram of sample 8 (Tabl. 1) is shown in Fig. 5a, b.

Table 2 – The output and diode parameters of flexible polyimide/ITO/CdS/CdTe/Cu/Ag solar cells with base layers of the CdTe type: Samples 1 and Samples 2

The output and diode parameters	Samples 1	Samples 2
J_{sc}, mA/cm^2	9.4	8.2
V_{oc}, mV	731	765
FF, r.u.	0.38	0.49
η, %	2.6	3.1
J_{ph}, mA/cm^2	10.1	8.4
R_s, Ω•cm^2	39.76	7.12
R_{sh}, Ω•cm^2	605.19	369,06
A, r.u.	2.2	4.3
J_o, mA/cm^2	$2.5 \cdot 10^{-5}$	$5.9 \cdot 10^{-3}$

All peaks that belong to stable cubic structure CdTe are observed. Using «oblique» shooting method at the angles 2θ 72.5-87.5° when rotating the sample on an angle of 20.5° was found, that in this area of XRD pattern only cubic structure peaks (331) and (422) can be observed, hexagonal structure peaks (105) are not presented. Thus, Cl treatment facilitates wurtzite-sphalerite phase transition, thereby studied CdTe films contain only stable cubic structure.

After Cl treatment we observed a slight decrease of FWHM values of peaks (111) and (333) compared with peaks (002) and (006) of hexagonal phase in samples before Cl treatment and annealing in air (Fig. 3 and Fig. 5). This indicates the passing of the recrystallization process and grain size increasing in the polycrystalline CdTe films. The calculated value of lattice constant in the cubic structure of CdTe films after Cl treatment is $\alpha = 6.4905$ Å. The deviation from the value α in table ASTM 15-0770 is less than 0.2%.Such CdTe films can be used as the base layer in solar cells based on CdS/CdTe heterostructure.

The influence of the technological DC magnetron sputtering modes of CdS/CdTe heterosystem deposited on flexible substrates on the output parameters of polyimide/ITO/CdS/CdTe/Cu/Ag solar cells were studied.

For the production of laboratory samples of polyimide/ITO/CdS/CdTe/Cu/Ag solar cell, ITO layers were obtained on a Upilex polyimide film (12.5 μm thick) by DC magnetron sputtering. The target contained a compressed mechanical mixture of In_2O_3 powders (90 wt. %) and SnO_2 (10 wt. %) semiconductor purity. The formation of ITO layers with a thickness of 0.3 μm was carried out in argon atmosphere at a pressure of 0.8 Pa. The electrical parameters of the plasma discharge were: the voltage at the magnetron 500 V, the discharge current density 12.6 mA/cm^2. Temperature of the substrate was $T_{sub} = 300$-350 °C. These modes of magnetron sputtering allow to obtain ITO layers on polyimide substrates with optimal electrical and optical properties [8]. After that CdS films were deposited on the ITO layers at $P_{sub} = 0.8$ Pa and $T_{sub} = 270$-280 °C (the electrical parameters of the plasma discharge were: voltage at the magnetron of 550-600 V, the density of the plasma discharge current of 2.8 mA/cm^2). The basic layers of cadmium telluride for solar cells were obtained in two ways:

1. The CdTe film was immediately condensed on polyimide/ITO/CdS heterostructure at $T_{sub} = 280$-320 °C without intermediate cooling of the substrate and vacuum violation (Samples 1);
2. The polymid/ITO/CdS heterostructure was cooled to room temperature and applied to the air. After returning to the working volume of the vacuum chamber, the polyimide/ITO/CdS heterosystem was heated to $T_{sub} = 280$-320 °C (Samples 2).

The following electrical parameters of the plasma discharge were used to obtain cadmium telluride layers by DC magnetron sputtering: voltage at the magnetron 650-700 V, plasma current density of 4.2 mA/cm^2.

The obtained polyimide/ITO/CdS/CdTe heterosystems were subject to Cl treatment. For this $CdCl_2$ films were applied to the CdTe layers without heating of the substrate, by thermal evaporation at a pressure of $5.3 \cdot 10^{-3}$ Pa. The obtained polymid/ITO/CdS/CdTe/$CdCl_2$ heterosystems were annealed in air at a temperature of 430^{0}C for 25 minutes. After etching of annealed heterosystems in bromomethanol solution, two-layer electrical contacts Cu-Ag were condensed on their surface by thermal evaporation. Then formed polyimide/ITO/CdS/CdTe/Cu/Ag solar cells were annealed in air at 200 °C for 20 minutes.

By analytical processing of the experimental J-V characteristics (Fig. 6), the output and diode parameters of the solar cells were determined (Tabl. 2).

The results of the study of the output parameters and the light diode characteristics of the flexible polyimide/ITO/CdS/CdTe/Cu/Ag solar cells indicate that the pre-cooling of the polyimide/ITO/CdS heterosystems, applying to the air and heating them in vacuum to a substrate temperature $T_{sub} = 300$-320 °C, contribute to the achievement of higher values of the open circuit voltage $V_{oc} = 765$ mV, the fill factor of the J-V characteristic $FF = 0.49$ r.u. and the efficiency $\eta = 3.1$% (Samples 2). At the same time, the initial parameters of Samples

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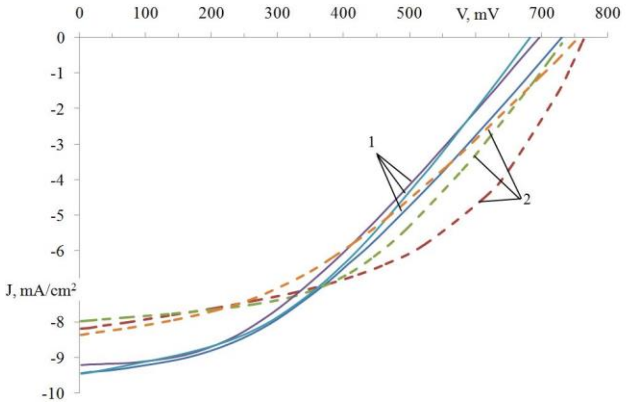

Fig. 6 – Typical light *J-V* characteristics of flexible polyimide/ITO/CdS/CdTe/Cu/Ag solar cells with base layers of the CdTe type: Samples 1 and Samples 2

which were not pre-cooled before obtaining the CdTe layer, were $V_{oc} = 731$ mV, $FF = 0.38$ r.u., $\eta = 2.6\%$. Increase of the efficiency coefficient in Samples 2 is due to an increase in the value of the open circuit voltage and the fill factor of *J-V* characteristic, as well as a significant decrease in the serial resistance. Samples 1 are characterized by higher values of short circuit current densities and photocurrent densities.

Higher values of Samples 2 efficiency may be related to the interaction of oxygen with CdS polycrystalline layer and formation of oxide compounds at grain boundaries of the semiconductor. With this heterostructure heating to temperatures of CdTe base layer deposition ($T_{sub} = 300$-320 °C) within 25-30 minutes the recrystallization process of CdS transparent window layer structure takes place. And as a result the defective crystalline layer negative impact at the interface CdS/CdTe on the crystal structure of condensed the base layer and increasing the grain size in the CdTe reduces similar [9].

4. CONCLUSIONS

The laboratory method of DC magnetron sputtering with preheating of the target for CdS and CdTe films on glass substrates was developed. The band gap in obtained hexagonal CdS films is $E_g = 2.38$-2.41 eV. Optical transparency of CdS films is 80-90%, which allows to use such films as a transparent window layer in solar cells based on heterostructure of CdS/CdTe.

When plasma discharge current density is 2.2-5.4 mA/cm^2 and the deposition rate is 200 nm/min., CdTe layers with hexagonal structure up to 5 μm thick were obtained. The transmittance of CdTe films with hexagonal structure in the wavelength range of the visible spectrum is up to 5%, and in the infrared spectral range is about 60%. The band gap in obtained CdTe layers of different thickness is 1.52-1.54 eV. After the Cl treatment with subsequent annealing in air at $T = 430$ °C for 25 min. (as a result of the wurtzite-sphalerite phase transition) investigated CdTe films contain only the stable cubic structure. Value of lattice constant is $a = 6.4905$ Å, that is less than by 0.2% deviate from the tabular value. Such CdTe films can be used as a base layer of solar cells based on heterostructure of CdS/CdTe.

The influence of the technological DC magnetron sputtering modes of CdS/CdTe heterosystem deposited on flexible substrates on the output parameters of solar cells is studied. It is shown that the pre-cooling of the CdS layer and its transfer to the air before deposition of the CdTe layer leads to an increasing the open circuit voltage and the fill-factor of the illuminated *J-V* characteristic and decreasing the series resistance of the solar cell. As a result, the efficiency of ITO/CdS/CdTe/Cu/Ag flexible solar cell on the CdTe base layer increases from 2.6% to 3.1%.

Структура та оптичні властивості тонких плівок CdS та CdTe для сонячних елементів на гнучких підкладках, отриманих магнетронним розпиленням на постійному струмі

Г.І. Копач, Р.П. Мигущенко, Г.С. Хрипунов, А.І. Доброжан, М.М. Харченко

Національний Технічний Університет «Харківський Політехнічний Інститут», вул. Кирпичова, 2, 61002 Харків, Україна

Досліджено кристалічну структуру та оптичні характеристики шарів широкозонного вікна CdS та базових шарів CdTe, отриманих за допомогою магнетронного розпилення на постійному струмі на скляних або поліімідних підкладках, а також вихідні параметрі гнучких тонкоплівкових сонячних елементів на їх основі. Ширина забороненої зони матеріалу у отриманих плівках CdS гексагональної модифікації становить $E_g = 2{,}38$-$2{,}41$ еВ, а оптична прозорість плівок CdS становить 80-90%. Проведення хлоридної обробки шарів CdTe, отриманих при $T < 300$ °C, сприяє фазовому переходу вюртцит-сфалерит. Охолодження шарів ITO/CdS до кімнатної температури доперед конденсацією базового шару CdTe, винесення на повітря та послідуючий нагрів у вакуумі до необхідної температури підкладки призводить до збільшення коефіцієнту корисної дії та напруги холостого ходу гнучкого тонкоплівкового сонячного елемента поліімід/ITO/CdS/CdTe/Cu/Ag.

Ключові слова: Сульфід кадмію, Телурид кадмію, Магнетронне розпилення на постійному струмі, Сонячний елемент, Тонкі плівки.

Структура и оптические свойства тонких пленок CdS и CdTe для солнечных элементов на гибких подложках, полученных магнетронным распылением на постоянном токе

Г.И. Копач, Р.П. Мигущенко, Г.С. Хрипунов, А.И. Доброжан, Н.М. Харченко

Национальный технический университет «Харьковский политехнический институт», ул. Кирпичова, 2, 61002 Харьков, Украина

Исследовано кристаллическую структуру и оптические характеристики слоев широкозонного окна CdS и базовых слоев CdTe, полученных с помощью магнетронного распыления на постоянном токе на стеклянных или полиимидной подложках, а также выходные параметре гибких тонкопленочных солнечных батарей на их основе. Ширина запрещенной зоны материала в полученных пленках CdS гексагональной модификации составляет E_g = 2,38-2,41 эВ, а оптическая прозрачность пленок CdS составляет 80-90%. Проведение хлоридной обработки слоев CdTe, полученных при T < 300 °C, способствует фазовому переходу вюртцит-сфалерит. Охлаждение слоев ITO/CdS до комнатной температуры перед конденсацией базового слоя CdTe, вынесения на воздух и последующий нагрев в вакууме до необходимой температуры подложки приводит к увеличению коэффициента полезного действия и напряжения холостого хода гибкого тонкопленочного солнечного элемента полиимид/ITO/CdS/CdTe/Cu/Ag.

Ключевые слова: Сульфид кадмия, Теллурид кадмия, Магнетронное распыление на постоянном токе, Солнечный элемент, Тонкие пленки.

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