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Development of back contact for CdS/CdTe thin-film solar cells

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The peculiarities of photo-electric processes in thin film CdS/CdTe solar cells with different back electrodes (Cu/Au, ITO) has been studied. The Cu-free ITO back electrode is shown to cause the formation of a low-quality tunnel heterojunction n^+-ITO/p^+-CdTe and the negative influence of the grain surface boundary of the base layer on the diffusion and separation of non-equilibrium carriers. A new design of transparent back electrode based on Cu/ITO composition is proposed. It is shown that the use of Cu nanolayer in ITO back contact provides the degradation-resistant bifacial solar cells with efficiency exceeding 10 %.

Изучены особенности фотоэлектрических процессов в тонкопленочных солнечных элементах CdS/CdTe с различным типом тыльного электрода (Cu/Au, ITO). Показано, что отсутствие меди в солнечных элементах с тыльным электродом ITO приводит к формированию низкокачественного туннельного гетероперехода n^+-ITO/p^+-CdTe и к негативному влиянию зернограничной поверхности базового слоя на процессы диффузии и разделения неравновесных носителей заряда. Предложена новая конструкция прозрачного тыльного электрода на основе композиции Cu/ITO. Показано, что использование нанослоя Cu позволяет получить деградационно-стойкие двусторонне чувствительные солнечные элементы с КПД выше 10 %.

1. Introduction

At present, the laboratory samples of thin-film solar cells (SC) based on *n*-CdS/*p*-CdTe show maximum efficiency of 16.5 % [1]. In such SC, opaque back electrode are used. The base CdTe layer is illuminated through a thin CdS layer and transparent front electrodes made of high-doped oxides of In, Sn or Cd with n^+-type conductivity. In tandem device structures [2], several base layers with different band gap E_g values are used. In the SC with high base layer E_g, both front and back electrodes should be transparent. This allows low energy photons attain the next SC of the tandem structure having a lower base layer E_g [3, 4]. The film SC with CdTe and $CuInSe_2$ base layers is of good promise for use in tandem SC [5] ($E_{g\,CdTe}$ = 1.46 eV and $E_{g\,CuInSe2}$ = 1.10 eV).

However, the film SC on CdS/CdTe base are not used in tandem structures, since no transparent back electrodes to *p*-type layers of cadmium telluride are developed to date. When the "comb" electrodes are used, the high specific resistance of CdTe base layers limits the efficiency of such SC at the level of 1 %. The heterosystem Cu/Au is a traditional low-ohmic tunnel back contact for *p*-type CdTe [6]. When using such electrodes in SC on CdS/CdTe base, the main problem consists in diffusion of Cu from the contact to the *p-n* junction, thus causing degrada-

tion of output characteristics [7]. In [8], a layer of degenerate semiconductor consisting of indium and tin oxides (ITO) was applied as the transparent tunnel contact for *p*-CdTe layers. However the efficiency of such SC did not exceed 7.7 %. Therefore, to develop a transparent and stabile back contact for SC on CdS/CdTe base, we carried out in this work comparative investigation of photoelectric processes in such SC with ITO and Cu/Au back electrodes.

2. Experimental

The CdS/CdTe/ITO film heterosystem was prepared by thermal vacuum deposition on glass substrates coated with a SnO_x:F layer. Prior to formation of back electrodes, the standard "chloride" treatment was realized by deposition of a $CdCl_2$ film onto the CdTe surface and followed by annealing in air at 430°C. Then the CdTe base layer surface was etched in a bromine-methanol solution [9]. To form the back electrode on the glass/SnO_x:F/CdS/CdTe/ITO solar cell, the 300–350 nm thick ITO layers were deposited on the etched surface by nonreactive high-frequency magnetron sputtering at 250°C. To form the back electrode on the glass/SnO_x:F/CdS/CdTe/Cu/Au solar cell, about 10 nm thick Cu films and 50 nm thick Au films were sequentially deposited onto the etched base layer surface by thermal vacuum evaporation. Then the solar cells were annealed in air at 250°C for 25 min.

To investigate the efficiency of the charge carrier generation and separation processes in SC, the spectral dependence of quantum efficiency coefficient $Q(\lambda)$ [10] was studied. To that purpose, the short-circuit current J_{sc} was measured as a function of the radiation wavelength λ. The measuring system provided an opportunity to apply a constant voltage V across the heterosystem to be studied in the course of measurements. This allowed to change the sizes of space charge regions (SCR) in the *n*-CdS/*p*-CdTe heterojunction and at the boundary *p*-CdTe/back electrode interface. The photocurrent polarity in CdS/CdTe/Cu/Au heterosystem at $V = 0$ was adopted as positive, while the opposite, as negative. For a comparative analysis of different SC, the absolute values of $Q(\lambda)$ were normalized to the maximum value of the quantum efficiency coefficient measured for the CdS/CdTe/Cu/Au SC at $V = 0$. The output parameters and light diode characteristics of SC were found by

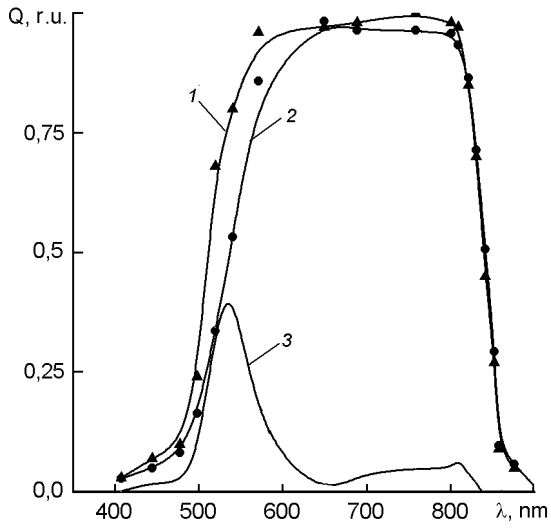

Fig. 1. Quantum efficiency coefficient $Q(\lambda)$ for CdS/CdTe/Cu/Au SC at $V = 0$ (curve *1*) and CS CdS/CdTe/ITO at $V = 0$ (curve *2*); quantum efficiency difference $Q_{Cu/Au} - Q_{ITO}$ at $V = 0$ (curve *3*).

processing of light current voltage (*IV*) characteristics measured using an automated 4145A Semiconductor Analyzer (Hewlett Packard) at the light flux power 100 mW/cm^2.

3. Results and discussion

At first studies of the $Q(\lambda)$ dependences for CdS/CdTe/Cu/Au and CdS/CdTe/ITO SCs, those were illuminated from the frontal side (from the glass substrate side) at $V = 0$. The corresponding $Q(\lambda)$ dependence for CdS/CdTe/Cu/Au SC, has shown higher values in the whole spectral range of photosensitivity as compared to that for the CdS/CdTe/ITO (Fig. 1). The largest difference between the $Q(\lambda)$ values of the investigated SC was 0.4 at the wavelength $\lambda = 550$ nm (Fig. 1, curve 3). The absorption band edge of this substance is situated at 520–540 nm, so that, when the studied heterosystems were illuminated from the CdS side, the 550 nm photons had the highest energy among those that were not absorbed substantially in the cadmium sulfide layer and reached the cadmium telluride base layer. In this case, in accordance with the energy of photons, the absorption region thereof was located near the CdS/CdTe interface. Thus, the revealed difference between the corresponding $Q(\lambda)$ values of the investigated SC evidences that the recombination losses near CdS/CdTe interface of

the CdS/CdTe/Cu/Au SC were lower than those in the CdS/CdTe/ITO SC itself.

The authors [11] believe that copper atoms diffusing over the grain boundaries passivate the grain-boundary surface near the CdS/CdTe interface in the course of the Au/Cu back contact formation. This reduces the recombination rate in that layer and results in an increase of $Q(\lambda)$ for the CdS/CdTe/Cu/Au SC. Thus, we have shown that, to enhance the quantum efficiency coefficient $Q(\lambda)$ of the CdS/CdTe/ITO heterosystem, it is necessary to reduce the negative influence of the developed grain-boundary surface of the base layer on the processes of diffusion and distribution of non-equilibrium current carriers generated near the CdS/CdTe interface under the action of photons from the short-wave range of the visible spectrum.

If the CdS/CdTe/ITO SC was illuminated from the frontal side and the applied electric bias was positive, the growth of electric voltage resulted in a reduction of $Q(\lambda)$ values in the whole spectral photosensitivity range (Fig. 2, curves *1*–*4*). The $Q(\lambda)$ decrease at λ increasing from 650 to 820 nm becomes more essential. An increase of the direct bias resulted in a reduction of the electric field in the space-charge region of the frontal heterojunction. This stimulated the increasing recombination losses of non-equilibrium current carriers in the SCR. The increasing direct bias also resulted in a narrowing of the SCR, which caused an increasing recombination losses of generated current carriers in the bulk when λ increased. When measuring $J_{sc}(\lambda)$ for CdS/CdTe/ITO SC at $V > 0.8$ V, a change of the photocurrent polarity from positive to negative was registered. The relevant dependences $Q(\lambda)$ are presented in Fig. 2 (curves *5*–*7*). The photocurrent polarity change was caused by the existence of two heterojunctions in the CdS/CdTe/ITO heterosystem being in the opposite connection [12], namely, the n-CdS/p-CdTe and p^+-CdTe/n^+-ITO ones. The electric resistance of the n-CdS/p-CdTe heterojunction decreased as the direct bias grew, so that a greater part of the voltage began to drop across the p^+-CdTe/n^+-ITO one, for which such a voltage polarity caused a reverse bias. As a result, the SCR dimensions of the p^+-CdTe/n^+-ITO heterojunction started to grow, which led to an effective redistribution of non-equilibrium current carriers by its potential barrier.

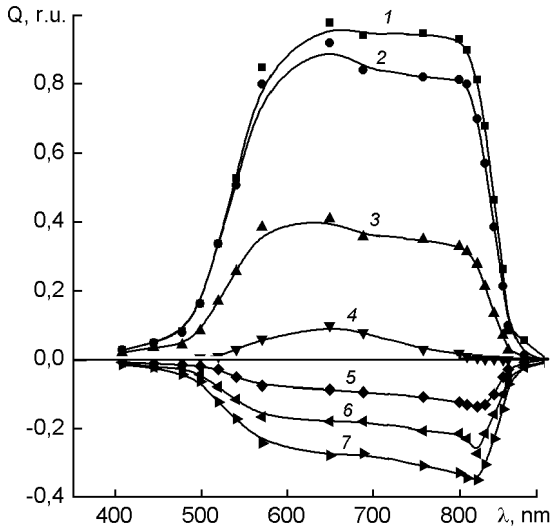

Fig. 2. Quantum efficiency coefficient $Q(\lambda)$ for CdS/CdTe/ITO SC at the frontal illumination and different voltage: $V = 0$ (curve *1*), 0.4 V (curve *2*), 0.6 V (curve *3*), 0.7 V (curve *4*6), 0.8 V (curve *5*), 0.9 (curve *6*) and 1.2 V (curve *7*).

In such a structure, most effectively separated were the current carriers generated near the SCR of the p^+-CdTe/n^+-ITO heterojunction when the SC was illuminated from its back side with photons from the long-wave spectral range. The heterojunction p^+-CdTe/n^+-ITO was studied by us before [12] It has been shown that the height of the CdTe/ITO potential barrier is 2.2 eV whereas for contact CdTe/Cu/Au, it is less than 0.3 eV. Thus, the film electrode n^+-ITO and base layer p^+-CdTe form a low-quality tunnel contact. It is the main reason restricting the efficiency of SC with ITO contact in contrast to SC with the Cu/Au back contact.

The investigation of quantum efficiency allows to assume that it is just the Cu/ITO back contact that is the optimum for use. In this contact, the thickness of Cu should be minimized to not restrict its transparence. The SCs with the new back contact type glass/SnO_x:F/CdS/CdTe/Cu/ITO were prepared using the technology described above. The difference was that prior to deposition of ITO layer by vacuum evaporation, nanosized Cu films (less than 1 nm thick) were deposited onto the CdTe layer surface.

The light *IV* characteristics of SC glass/SnO_x:F/CdS/CdTe/ITO, glass/SnO_x:F/CdS/CdTe/Cu/ITO, and glass/SnO_x:F/CdS/CdTe/Cu/Au were explored. Their output characteristics and diode parameters in initial state are given in Table. The lower

Table. Output parameters and light diode characteristics of SC with different type back contacts in initial state

Output parameters and light diode characteristics	Type of back contact		
	Cu/Au	ITO	Cu/ITO
V_{oc}, mV	788	692	741
J_{sc}, mA/cm^2	19.7	18.5	19.5
FF	0.67	0.60	0.683
η, %	10.4	7.7	9.86/10.3*
R_s, Ω·cm^2	2.0	9.0	2.22
R_{sh}, Ω·cm^2	890	1990	848
J_0, A/cm^2	$3{\cdot}10^{-8}$	$2.2{\cdot}10^{-5}$	$1.5{\cdot}10^{-8}$
A	1.8	3.9	2.06
J_{ph}, mA/cm^2	20.0	19.0	19.5

efficiency of SC with the ITO contact is connected with high values of the diode saturation current density J_0 and series resistance R_s (see Table), in contrast to SC with the Cu/Au back contact. Thus, the use of a copper film in the back contact structure causes a decreased diode saturation current and series resistance, and, as a result, an increased SC efficiency.

The stability studies of SC characteristics have shown that the least stable is SC with Cu/Au back contact (Fig. 3, curves *1*). The decreased efficiency of these SC is due mainly to decrease of shunting resistance by 3 times (from 900 up to 300 Ω·cm^2) and increase of the diode saturation current density by 4 times (from 30 up to 130 nA/cm^2). That, as is known [13], is connected with copper diffusion to the *n*-CdS/*p*-CdTe heterojunction area. On the contrary, SC with ITO and Cu/ITO back contacts demonstrate a rather high stability and even improvement of all characteristics at the initial service stage as compared to initial state (see Fig. 3, curves *2* and *3*). For example, the efficiency of SC with Cu/ITO back contact increases from 9.8 % to 10.3 % during the first six months of service and remains higher than 10 % after six-year service. This increasing efficiency is due to lowering diode saturation current density and series resistance, which at reaching of a peak efficiency receive values $J_0 = 1$ μA/cm^2, $R_s = 5$ Ohm·cm^2 for ITO back contact and $J_0 = 0.84$ nA/cm^2, $R_s = 0.5$ Ω·cm^2 for Cu/ITO back contact. The series resistance prolongs to decrease during the whole service period. This decrease is from 2 down to 1.1 Ω·cm^2 for SC with Cu/Au back contact, from 9 down to 3.7 Ω· for SC with ITO back contact, and from 2.2 down to <0.5 Ω·cm^2 for SC with Cu/ITO back contact.

The observed R_s lowering for all investigated solar sells cannot be explained only by copper diffusion from the back contact. Copper is present only in two explored SC types; further, for copper-free ITO back contact, the decrease of R_s is even more than for Cu/Au one. The crystallization of a thin (~2 nm) amorphous tellurium layer formed after etching of CdTe surface in bromine/methanol is hardly probable to cause the R_s lowering. In solar cells with copper layer in the back contacts, after the Cu deposition and deposition of the following layer (Au or ITO) the whole amorphous tellurium layer is spent for formation of $Cu_{2-x}Te$ compound which provides a lower R_s than that of tellurium layer. In SC with ITO contact, the substrate temperature during the ITO layer deposition exceeds 250°C and the deposition time is about 40 min, that is enough for full crystallization of amorphous tellurium. The absence of amorphous tellurium layer is confirmed also by a rather high quality of the ITO back contact already in the initial state that would be impossible in the presence of an amorphous tellurium layer.

As was shown in [14], two type of defect complexes, namely, electrically active Cl_{Te}–V_{Cd} and electrically inactive $2Cl_{Te}$–V_{Cd} ones, may be formed in the base layer after the "chloride" treatment. Therefore, it is possible to assume that the main cause of decreasing R_s is the photo-stimulated decomposition of electrically inactive $2Cl_{Te}$–V_{Cd}

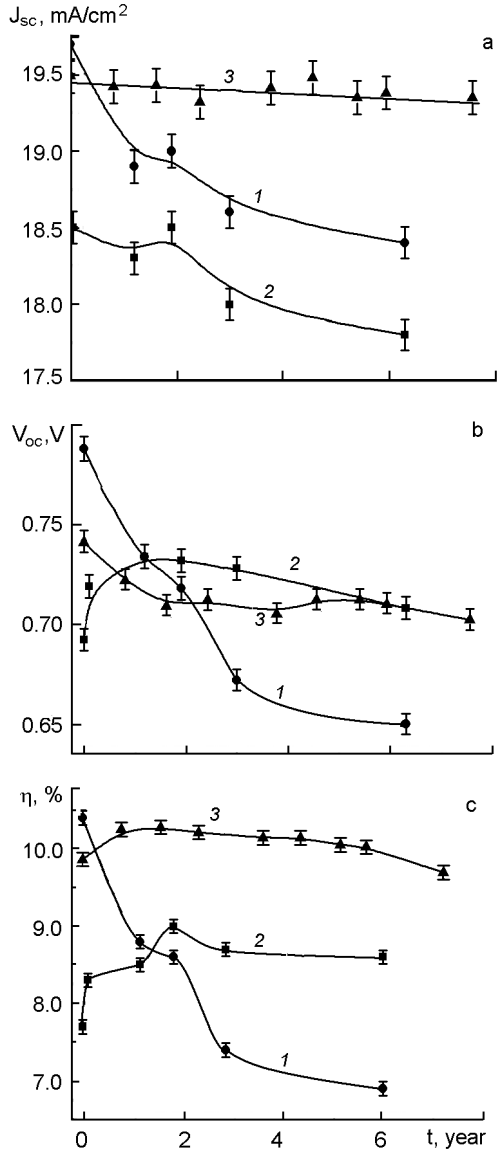

Fig. 3. Change of short-circuit current (a), open circuit voltage (b) and efficiency (c) SC during the service time: curve *1*, Cu/Au contact; curve *2*, ITO contact; curve *3*, Cu/ITO contact.

defect complexes and transformation thereof into electrically active Cl_{Te}–V_{Cd} defect complexes. This results in an additional doping of CdTe base layer.

4. Conclusion

The investigation in spectral dependence of quantum efficiency has established that the lower efficiency of SC on the CdS/CdTe base with ITO back contact as compared to those with Cu/Au back contact is caused by following reasons. First, the negative influence of the surface grain-boundary of the base layer on the diffusion and separation of non-equilibrium carriers which are generated by short-wave photons. This negative influence is compensated by formation of p-p^+ isotype junction between the grain volume and boundary at the grain-boundary diffusion of Cu which is an acceptor. Second, formation of a low-quality n^+-ITO/p^+-CdTe tunnel heterojunction results in a limited collection efficiency of non-equilibrium carriers. This negative influence also is compensated by using of Cu in back contact at formation of degenerate p^+-$Cu_{2-x}Te$ layer with high conductivity.

A new structure of the transparent back electrode based on Cu/ITO composition is proposed. By comparative studies of glass/SnO_x:F/CdS/CdTe/ITO, glass/SnO_x:F/CdS/CdTe/Cu/ITO and glass/SnO_x:F/CdS/CdTe/Cu/Au film SCs, it has been shown that the formation of a Cu nanolayer prior to the deposition of transparent ITO film contact provides the stable bifacial solar cells with efficiency exceeding 10 %, which can be used for tandem SC.

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Розробка тильного контакту для тонкоплівкових сонячних елементів CdS/CdTe

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Вивчено особливості фотоелектричних процесів у тонкоплівкових сонячних елементах CdS/CdTe з різним типом тильного електроду (Cu/Au, ITO). Показано, що відсутність міді у сонячних елементах з тильним електродом ITO приводить до формування тунельного гетеропереходу n^+-ITO/p^+-CdTe низької якості і до негативного впливу границь зерен базового шару на процеси дифузії і розділення нерівноважних носіїв заряду. Запропоновано нову конструкцію прозорого тильного електроду на основі композиції Cu/ITO. Показано, що використання наношару Cu дозволяє одержати деградаційно стійкі двостороннє чутливі сонячні елементи з ККД більше 10 %.