PECULIARITIES OF PHOTO-ELECTRIC PROCESSES IN THIN-FILM CdS/CdTe/ITO HETEROSYSTEMS

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By analyzing the spectral dependence of the coefficient of quantum efficiency, the peculiarities of photo-electric processes in thin-film CdS/CdTe/ITO heterosystems with bilateral photosensitivity have been studied for the first time. Physical mechanisms that describe the observable experimental regularities have been proposed.

Film solar cells (SCs) manufactured on the basis of the CdTe/CdS heterosystem are perspective for largescale terrestrial applications [1]. One of the directions of enhancing their efficiency is the creation of tandemlike SCs, where two base layers with different widths of the energy gap are used, which ensures the photoelectric conversion of the solar energy in a wide spectral range [2]. The construction of the SC frontal with respect to the incident light flux, whose base layer possesses a larger energy gap, has to transfer the long-wave part of sunlight to the back SC with minimal losses.

The absence of transparent electrodes attachable to cadmium telluride films prevented from the creation of tandem-like photo-electric converters with frontal SCs on the basis of the CdTe/CdS heterosystem. Recently, we have tested a new construction of the CdTe/CdSbased film SC with a transparent back film electrode made up of indium and tin oxides (ITOs) [3].

In the present work, the peculiarities of photo-electric processes in the CdS/CdTe/ITO film heterosystems have been studied for the first time. With this purpose in view, complex researches of the spectral dependences of their coefficients of quantum efficiency $Q(\lambda)$ have been carried out. Those dependences allow us to analyze the physical mechanisms of formation of a photocurrent in the instrumental structure, when photons with different wavelengths are absorbed.

The CdS/CdTe/ITO film heterosystems were prepared on the glass substrates covered with a layer of SnO_x:F, using the method described in work [3]. In order to form an interlayer of p^+ -CdTe, which reduces the resistance of the back contact, the surface of cadmium telluride underwent etching in a bromine– methanol solution. After etching, each specimen was divided into two parts. On the first part, an ITO film was deposited by non-reactive magnetron sputtering [3], while a conventional Cu/Au back electrode was formed by thermal evaporation on the second one.

According to work [4], the coefficient of quantum efficiency $Q(\lambda)$ is the ratio of the number of nonequilibrium current carriers, which take part in the creation of a photocurrent, to the number of photons with wavelength λ , which strike the heterosystem surface:

$$Q(\lambda) = \{ (hc/\lambda) J_{\rm sh}(\lambda) \} / \{ q J_c(\lambda) \}, \tag{1}$$

where hc/λ is the energy of a photon, $J_{\rm sh-c}(\lambda)$ is the density of a short-circuit current, q is the electron charge, and $J_c(\lambda)$ is the illumination intensity at the heterosystem surface.

The measurements of $J_{\rm sh-c}(\lambda)$ were carried out at the Laboratory of Thin Film Physics of the Swiss Federal Institute of Technology (Zürich). We used an optoelectronic system consisted of a halogen tube with power and cooling units, a pulse light modulator, a monochromator, and a detector block for measuring the amplitude and polarity of photocurrent pulses generated by a heterosystem when being illuminated by a pulse signal. The photocurrent polarity in the CdS/CdTe/Cu/Au heterosystem was adopted as positive, the opposite one as negative. The optoelectronic system provided an opportunity to apply a constant voltage V across a researched heterosystem in the course of measurements. The 230-Hz modulation of a light flux was used to avoid the influence of external light sources and the constant voltage applied to the structure on the measured values of $J_{\rm sh-c}(\lambda)$. It allowed the constant component of the photocurrent to be compensated automatically during measurements. The measuring procedures and the processing of data were carried out with the help of a PC. For a comparative analysis of CdS/CdTe/ITO and CdS/CdTe/Cu/Au heterosystems, the absolute values of $Q(\lambda)$ were normalized by the maximal value of the quantum efficiency coefficient measured for the CdS/CdTe/Cu/Au heterosystem at V = 0.



Fig. 1. Energy charts of the CdS/CdTe/Cu/Au (a) and CdS/CdTe/ITO (b) heterosystems

Comparative studies of the $Q(\lambda)$ dependences, obtained for the fabricated heterosystems, were carried out. The specimens were illuminated from the side of their frontal surfaces (from the side of the CdS layer). The results of researches can be easily explained by using the energy charts of the investigated heterosystems (Fig. 1). According to contemporary ideas, the frontal potential barrier in the CdS/CdTe heterosystems is a n-CdS_xTe_{1-x}-p-CdTe heterojunction, rather than a n-CdS-p-CdTe one. It was shown [5] that, during manufacturing the film heterosystem, an interlayer consisting of $CdS_{x}Te_{1-x}$ solid solutions (with x <0.07) was formed at the CdS/CdTe phase interface. According to the data of work [1], this layer had the n-type of conductivity; with the thickness of the interlayer being able to reach 1 μ m [5]. The formation of the n-CdS_xTe_{1-x} interlayer raised the efficiency of photo-electric processes, because it induced a shift of the built-in electric field from the defect CdS/CdTe interface into the depth of the base layer of cadmium telluride [6]. A substantial concentration of the surface recombination centers at the CdS/CdTe interface was caused by the different lattice constants of cadmium sulfide and cadmium telluride; the difference being equal to 9.7% [3]. According to the energy charts of the investigated CdS/CdTe/Cu/Au and CdS/CdTe/ITO heterosystems, tunnel junctions were formed on the back side of such instrument structures. The height of the potential barrier, when the Cu/p⁺-CdTe contact was being formed, amounted to 0.3 eV [5] (Fig. 1,a). When considering the formation of the n^+ -ITO- p^+ -CdTe contact, the difference between the work functions for current carriers in the adjacent layers makes it possible to predict theoretically a significantly larger value for the potential barrier height (Fig. 1,b).

Provided that the CdS/CdTe/Cu/Au heterosystem was illuminated from the frontal side (from the side of the CdS layer) and no electric bias was applied, the corresponding $Q(\lambda)$ dependence, in comparison with that of the CdS/CdTe/ITO heterosystem, had higher values in the whole spectral range of photosensitivity (Fig. 2, a). The largest difference between the corresponding $Q(\lambda)$ -values of the investigated heterosystems amounted to 0.4 at the wavelength $\lambda = 550$ nm (Fig. 2,b). According to the energy structure of cadmium sulfide, the edge of the absorption band of this substance is situated at 520-540 nm, so that, when the studied heterosystems were illuminated from the CdS side, 550-nm photons had the highest energy among those photons that were not absorbed substantially in the layer of cadmium sulfide and reached the base layer of cadmium telluride. In this case, in accordance with the energy of photons, the range of their absorption was located near the CdS/CdTe interface, i.e. in the n-CdS_xTe_{1-x} interlayer (Fig. 1). Thus, the revealed difference between the corresponding $Q(\lambda)$ values of the investigated heterosystems testifies to that recombination losses in the n-CdS_xTe_{1-x} interlayer of the CdS/CdTe/Cu/Au heterosystem were lower than those in the CdS/CdTe/Cu/Au heterosystem itself. The authors of work [1] believe that copper atoms, diffusing over the grain boundaries, passivate the grainboundary surface of the n-CdS_xTe_{1-x} interlayer in the course of the formation of back Au/Cu contacts. This reduces the rate of recombination in this layer and results in an increase of $Q(\lambda)$ for the CdS/CdTe/Cu/Au heterosystem.

If a bias which is reverse with respect to the frontal n-CdS_xTe_{1-x}-p-CdTe heterojunction is applied to the CdS/CdTe/ITO heterosystem, we observe an insignificant growth of $Q(\lambda)$ in the long-wave range

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Fig. 2. (a) Coefficients of quantum efficiency $Q(\lambda)$ of the CdS/CdTe/Cu/Au heterosystem at V = 0 (1) and of the CdS/CdTe/ITO heterosystem at V = 0 (2) and V = -1 V (3) illuminated from their frontal sides; the differences between them are shown in b [curve 1 - curve 2] and c [curve 3 - curve 2]

(Fig. 2, *a*). The maximal difference between the $Q(\lambda)$ values for *V* within the interval from 0 to -1 V did not exceed 0.05 (Fig. 2, *c*). An increase of the reverse bias was accompanied by an increase of the thickness of the space-charge region (SCR) in the *n*-CdS_xTe_{1-x}-*p*-CdTe heterojunction. As a result, the energy losses of non-equilibrium current carriers generated under the action of photons from the long-wave range of the spectrum diminished [4].



Fig. 3. Coefficient of quantum efficiency $Q(\lambda)$ of the CdS/CdTe/ITO heterosystem illuminated from its frontal side at various direct biases: V = 0 (1), V = 0.4 V (2), 0.6 (3), and 0.7 (4) (a) and V = 0.8 V (5), 0.9 (6), and 1.2 V (7) (b)

If the CdS/CdTe/ITO heterosystem was illuminated from the frontal side and the applied electric bias was positive, the growth of electric voltage resulted in a reduction of the $Q(\lambda)$ values in the whole spectral range of photosensitivity (Fig. 3, a). In this case, the amplitude of reduction increases as the photon wavelength grew from 650 to 820 nm. An increase of the direct bias resulted in a reduction of the electric field in the SCR of a frontal heterojunction. This stimulated the rise of the recombination losses of non-equilibrium current carriers in the SCR. The growth of the direct bias also resulted in a narrowing of the SCR, which caused an increase of the recombination losses of generated current carriers in the bulk when the radiation wavelength increased. When carrying out the measurements of the CdS/CdTe/ITO heterosystem 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. 3. The change of the photocurrent polarity was caused by the existence of two heterojunctions in the CdS/CdTe/ITO heterosystem, which were in the opposite connection,

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Fig. 4. (a) Coefficient of quantum efficiency $Q(\lambda)$ of the CdS/CdTe/ITO heterosystem illuminated from its back side at various reverse biases V = 0 (1), V = -1 V (2), and -1.5 V (3); the difference between curve 2 and curve 1 is shown in b

namely, the n-CdS_xTe_{1-x}-p-CdTe and p^+ -CdTe- n^+ -ITO ones (Fig. 1,b). The electroresistance of the n-CdS_xTe_{1-x}-p-CdTe heterojunction decreased as the direct bias grew, so that the greater part of the voltage began to drop across the p^+ -CdTe- n^+ -ITO one, for which such a polarity of the voltage 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 equilibrium current carriers by this potential barrier. In so doing, most effectively were distributed those current carriers which were generated near the SCR of the p^+ -CdTe- n^+ -ITO heterojunction when the heterosystem was illuminated from its back side with photons from the long-wave range of the spectrum.

The maximal value of $Q(\lambda)$ for the CdS/CdTe/ITO heterosystem under the illumination from its back side and at V = 0 (Fig. 4, a) was several times as small as that obtained when illuminating from its frontal side, with the spectral position of the maximum being shifted



Fig. 5. Coefficient of quantum efficiency $Q(\lambda)$ of the CdS/CdTe/ITO heterosystem illuminated from its back side at various direct biases V = 0 (1), V = 0.3 V (2), and 0.4 (3) (a) and V = 0.5 V (4), 0.6 (5), 0.7 (6), and 0.8 (7) (b)

towards the long-wave range of the spectrum. Such a form of the $Q(\lambda)$ dependence for the CdS/CdTe/ITO heterosystem was caused by the circumstance that if the heterosystem is illuminated from the frontal side, the redistribution of non-equilibrium current carriers is governed by the n-CdS_xTe_{1-x}-p-CdTe heterojunction which is remote from the illuminated surface. The growth of the reverse bias was accompanied by a significant growth of $Q(\lambda)$ (Fig. 4,b), which was caused by an increase of both the built-in electric field and the SCR dimensions of the frontal n-CdS_xTe_{1-x}-p-CdTe heterojunction.

If a direct biase was applied, the growth of the voltage resulted in a decrease of $Q(\lambda)$ (Fig. 5,a). At V > +0.5 V, the change of the photocurrent polarity was observed in the whole spectral range of photosensitivity. The further increase of the direct bias resulted in a substantial growth of $Q(\lambda)$ (Fig. 5,b). The change of the photocurrent polarity in case where the heterosystem was illuminated from the back side was

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connected to the switching-off of the n-CdS_xTe_{1-x}-p-CdTe heterojunction, which was described above, and to the switching-on of the back-side n^+ -ITO- p^+ -CdTe heterojunction if the direct bias increased. The difference lies in a reduction of the direct bias value, at which a change of the photocurrent polarity from V = 0.8 to 0.5 V was observed. It is connected to the fact that the generation region of non-equilibrium current carriers approached the SCR of the n^+ -ITO- p^+ -CdTe heterojunction provided this direction of illumination.

Thus, we have shown that, for the coefficient of quantum efficiency $Q(\lambda)$ of the CdS/CdTe/ITO heterosystem to be enhanced, 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 in the n-CdS_xTe_{1-x} interlayer under the action of photons from the short-wave range of the visible spectrum.

It has been found experimentally for the first time that, at any direction of illumination of the CdS/CdTe/ITO heterosystem, an increase of the voltage, which shifts the frontal heterojunction in a forward direction, brings about the change of the photocurrent polarity in the whole spectral range of the heterosystem photosensitivity. It is caused by a high potential barrier of the n^+ -ITO- p^+ -CdTe tunnel junction. In its turn, applying the voltage of the proper polarity across the CdS/CdTe/ITO heterosystem results in the formation of the SCR near the back contact, which is capable to separate effectively non-equilibrium current carriers generated under the action of light. The author is grateful to Dr. Tiwari A.N. and Dr. Batzner D.L., the collaborators of the Laboratory of Thin Film Physics of the Swiss Federal Institute of Technology (Zürich, Switzerland), for their help in carrying out measurements.

- Bonnet D., Meyers P. // J. Mater. Res. 1999. 13, N 10. -P.2740--2753.
- Fahrenbruch A.L., Bube R.H. Fundamentals of Solar Cells. New York: Academic Press, 1983.
- Tiwari A.N., Khrypunov G., Kurtzesau F. et al. // Prog. in Photovoltaic: Research and Applications.— 2004.— 12.— P.33—38.
- Bube R.H. Properties of Semiconductor Materials. Photovoltaic Materials. — London: Imperial College Press, 1999.— Vol.1.
- Batzner. L., Romeo A., Zogg H. et al. // Thin Solid Films.— 2001.— 387.— P.151—154.
- Agostinelli G., Batzner D.L., Burgelmann M. // Ibid. 2003. 431–432. – P.407–413.

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ОСОБЛИВОСТІ ФОТОЕЛЕКТРИЧНИХ ПРОЦЕСІВ У ПЛІВКОВИХ ГЕТЕРОСИСТЕМАХ CdS/CdTe/ITO

Г.С. Хрипунов

Резюме

Шляхом аналізу спектральних залежностей коефіцієнта квантової ефективності вперше досліджено особливості фотоелектричних процесів у плівкових гетеросистемах CdS/CdTe/ITO із двобічною фоточутливістю. Запропоновано фізичні механізми, що описують спостережувані експериментальні закономірності.