1. Introduction

It is known that effectiveness of the CdTe-based solar cells (SC) reduces during operation. The authors of paper [1] suggested two mechanisms in the degradation of such solar cells. The first is predetermined by the generation of defects in the area of semiconductor contact, caused by excessive charge carriers and defects of semiconductor layers. The second relates to an increase in the potential barrier at the rear ohmic contact. According to studies [2, 3], for the case of forming a tunnel rear contact, the degradation of SC is predetermined by the diffusion and interphase interactions between a nano-sized copper layer and a base layer [4]. Thus, degradation of SC renders relevance to the search for structural-technological solutions aimed at improving the degradational stability of the specified instrumental structures.

2. Literature review and problem statement

Despite the global development of solar power engineering, the effect of SC degradation under the action of light is typical for any photoconverter. The processes that define the mechanisms of SC degradation and, accordingly, the efficiency recovery techniques, have not been investigated enough. Among existing studies, the greatest attention was paid
to the second generation SC [5, 6]. For example, paper [7] demonstrated a technique for recovering the second-generation SC using the light whose intensity is less than the intensity of the initial light source. The authors of works [8–10] investigated the specificity of CdTe-based SC degradation. Currently, there are several hypotheses that offer different mechanisms of CdTe-based SC degradation. One of the first attempts to explain the mechanisms of degradation implied the consideration of processes of defects generation under the action of light. However, this theory could not explain the existence of samples resistant to degradation. The most popular now is the theories of electromigration, mainly copper, from metal contacts to the interface CdTe–CdS. The processes to form shunting defects have also been considered. Paper [11] shows that it is possible to form a network of shunting defects in the form of dendrites, and study [12] emphasizes a precursor mechanism. However, in most of these works, the authors note that the probability of the implementation of a given degradational mechanism becomes higher in proportion to a decrease in the thickness of a solar battery layers. However, the existence of exceptionally stable samples was confirmed that are not subject to aging, in addition, certain samples even showed an increase in efficiency over time. Papers [13, 14] considered one of the conditions for obtaining stable solar cells based on CdS/CdTe. It was stated that the necessary condition for creating such SC is to thermally treat CdTe in the atmosphere containing Cl₂. Typically, this treatment is conducted by depositing a thin film of CdCl₂ atop CdTe by heating in open air at a fixed temperature. However, this stage is impractical under large-scale production. The authors of work [15] replaced this treatment by using a gas (HCF₂Cl), which is stable, inert, and non-toxic at room temperature, and eliminates the stage of CdCl₂ evaporation, as well as the procedure for subsequent chemical etching.

Given the degradation processes of CdTe-based SC during operation, it is necessary to undertake a research aimed at the development of a recovery technique for such instrumental structures.

3. The aim and objectives of the study

The aim of this work is to develop a technique for restoring the efficiency of the film ITO/CdS/CdTe/Cu/Au SC after degradation.

To accomplish the aim, the following tasks have been set:
– to explore changes in the output parameters and light diode characteristics after the accelerated degradation of ITO/CdS/CdTe/Cu/Au SC;
– to explore changes in the output parameters and diode characteristics of ITO/CdS/CdTe/Cu/Au SC with different types of n-p heterojunctions after exposure to direct polarity voltage;
– to define the conditions for the recovery of efficiency of the film ITO/CdS/CdTe/Cu/Au SC after degradation.

4. Samples and methods to study the output parameters of ITO/CdS/CdTe/Cu/Au SC

The examined instrumental structures of ITO/CdS/CdTe/Cu/Au were obtained by the method of thermal vacuum evaporation. The equipment and conditions for obtaining the examined samples are described in detail in [3]. We applied the ITO films (a mixed indium-tin oxide) using the method of non-reactive magnetron spraying at direct current at the laboratory setup VUP 5 applying the original material-saving magnetron. The length of a charge gap that represents the distance between the magnetron and the substrate was 70 mm. The power used by the magnetron was 0.2 W/cm². Temperature of the substrate (T) was 300 °C. Initial pressure in the vacuum chamber was 3×10⁻⁷ mm Hg, working pressure of the argon-air mixture during spraying was (2.1–2.6)×10⁻⁷ mm Hg. In order to press the ITO mixtures that contain indium oxide (95 % by weight) and tin oxide (5 % by weight), we fabricated a specialized pressing machine (Fig. 1).

It should be noted that magnetron spraying is one of the most promising methods for obtaining all transparent electrodes [16, 17]. This is predetermined by a high degree of precision when transferring the composition of a mixture onto the substrate, by reproducibility and control over the process of magnetron spraying [18, 19].

A matrix of the obtained solar cells is shown in Fig. 2. The initial values for efficiency coefficient of obtained SC were 9.4–10.4 %. Next, all SCs were placed in a non-transparent plastic sealed box with air medium typical of non-industrial premises. After 48 months, the box, which was kept over this time at a temperature of 15–25 °C, was unsealed to carry out a comprehensive research into the parameters of SC that were stored inside it. Among SCs on the matrix, which were exposed to the accelerated...
degradation, part of SC was shunted. Among those suitable for recovery, we selected 7 SC samples to investigate the influence of a direct polarity voltage. Smooth (S) p–n junctions: two samples (No. 2, No. 6); unidentified (U) p–n junctions: three sample (No. 8, No. 12, No. 16); sharp (Sh) p–n junctions: two samples (No. 19, No. 20).

Selected samples were exposed to the action of a bias voltage of direct polarity $V_{oc}^{max}$=675±5 mV at maximum duration $\tau_s=2$ hours under a shaded mode at room temperature, and then we acquired the current-voltage characteristic of light. We studied the light current-voltage characteristic for experimental samples under the following conditions: illumination – 1.000 W/m², solar spectrum – AM1.5, ambient temperature – 25 °C. The equipment and methods to study the output parameters and the light diode characteristics for experimental samples are described in detail in paper [20].

The specified magnitude $V_{oc}^{max}$ is chosen based on condition $V_{oc}^{max}<V_d=V_{min}$, where $V_{min}$ is the voltage that corresponds to the point of maximum power at the light current-voltage characteristic, and $V_{oc}$ is the smallest voltage of idling over the entire totality of values $V_{oc}$ for the examined SC.

Development of the recovery method implies determining the dependence of SC efficiency on the effect of a bias voltage of direct polarity on it. It is known that efficiency of any SC is calculated from formula [21]:

$$\eta=(P_{oc}/P_s)*100\%=\left[P_{oc}/(P_s*St)\right]100\%, \quad (1)$$

where $P_s$ is the specific absorption rate at the SC photo-receiving surface; $St$ is the area of SC photo-receiving surface.

Because

$$P_{oc}=J_{oc}V_{oc}FF, \quad (2)$$

where $J_{oc}$ is short circuit current density, $V_{oc}$ is the voltage of idling, FF is the fill factor of current-voltage characteristic, then, along with ratio (1), we use the following expression

$$\eta=\left[J_{oc}V_{oc}FF/(P_s*St)\right]100\%. \quad (3)$$

As seen from (3), effectiveness of solar cell increases with an increase in each of the three key output parameters for SC – $I_{sc}$, $V_{oc}$ and $FF$.

In turn, the expression for determining $V_{oc}$ takes the following form:

$$V_{oc}=\frac{kT}{q}\ln\left[\frac{J_{sc}}{J_0}+1\right], \quad (4)$$

where $J_{sc}$ is the short circuit current density, $J_0$ is the diode current density of saturation, $q$ is the charge of the electron; $k$ is the Boltzmann constant, $T$ is the temperature of a solar cell.

As shown in (4), the idling voltage depends on $I_{sc}$ and $J_0$. Therefore, the high values for $V_{oc}$ require the low values for $J_0$.

The current-voltage characteristic fill factor (FF) is determined from ratio:

$$FF=\frac{P_{max}}{J_{sc}V_{oc}^{max}}, \quad (5)$$

In the absence of consistent resistance and the shunting conductivity, the expression for FF can be represented

$$FF=\frac{V_{oc}-\ln(v_{sc}+0.72)}{v_{sc}+1} \quad (6)$$

where

$$v_{sc}=\frac{qV_{oc}}{AkT} \quad (7)$$

In the presence of consequential resistance ($R_s$), the expression for the light current-voltage characteristic fill factor (FF) is transformed in the following way

$$FF=FF_0(1-R_s/R_p), \quad (8)$$

where $R_s$- $V_{oc}/I_{sc}$ is the characteristic resistance. When sequential resistance ($R_s$) and the conductivity of the shunt ($G$) are substantial, the expression for the light current-voltage characteristic fill factor ($FF_{sh}$) takes the form

$$FF_{sh}=FF_0\left[1-(v_{sc}+0.72)FF_0/v_{sc}/(R_pG)\right]. \quad (9)$$

According to expression (9), it is absolutely obvious that a growth in the value for $FF_{sh}$ will be contributed to by a decrease in $R_s$ and $G$.

Thus, in order to construct a method for restoring the SC efficiency, we must establish a change in the output parameters and the light diode characteristics under the influence of a bias voltage of direct polarity.

5. Results of studying a change in the output parameters and the diode characteristics of ITO/CdS/CdTe/Cu/Au SC

5.1. Studying a change in the output parameters and the light diode characteristics after the accelerated degradation of ITO/CdS/CdTe/Cu/Au SC

The parameters for p–n heterojunctions (HJ) in the examined ITO/CdS/CdTe/Cu/Au SC, which were divided into smooth (S), unidentified (U), and sharp (Sh), depending on the magnitude of a potential barrier and the width of the depletion zone, after 48 months of storage, are given in Table 1. The output parameters and the light diode characteristics, as well as the level of degradation in terms of efficiency following the accelerated degradation, are given in Tables 2, 3.
Table 1

Parameters for n-p heterojunctions of film SC after 48 months of storage

| SC | HJ type | $\Phi_{np}$, eV | $W_{np}$ (0), $\mu$m | $W_{max}/W_{min}$, $\mu$m/$\mu$m | $N_{np}$, $10^{14}$ cm$^{-3}$ | $a$, $10^{18}$ cm$^{-4}$ |
|----|---------|-----------------|----------------------|-------------------------------|-----------------------------|------------------------|
| 2  | S       | 2.4             | 3.07                 | 2.85–2.20                     | –                           | 7.5                    |
| 6  | S       | 1.9             | 3.06                 | 3.04–1.99                     | –                           | 2.8                    |
| 8  | U       | 0.6             | 3.07                 | 3.07–1.15                     | 0.5                         | –                      |
| 12 | U       | 0.9             | 3.06                 | 3.06–2.00                     | 0.9                         | –                      |
| 16 | U       | 1.4             | 2.92                 | 2.92–2.24                     | 2.2                         | –                      |
| 19 | Sh      | 1.5             | 3.08                 | 3.08–2.22                     | 1.8                         | –                      |
| 20 | Sh      | 1.5             | 2.93                 | 2.98–2.12                     | 2.0                         | –                      |

Table 2

Density of photocurrent, diode, and output parameters of SC after accelerated degradation

| SC | $j_{ph}$, mA/cm$^2$ | $j_0$, mA/cm$^2$ | $A_r$, rel. units | $R_s$, Ohm cm$^2$ | $R_{sh}$, Ohm cm$^2$ | $f_{sc}$, mA/cm$^2$ | $V_{oc}$, mV | FF, rel. units |
|----|----------------------|------------------|-------------------|------------------|---------------------|-------------------|--------------|----------------|
| 2  | 13.7                 | 1.6 $\times$ 10$^6$ | 1.53              | 20.5             | 236                 | 12.6              | 705          | 0.46           |
| 6  | 17.2                 | 9.0 $\times$ 10$^6$ | 1.50              | 10.7             | 210                 | 16.4              | 725          | 0.54           |
| 8  | 6.3                  | 1.5 $\times$ 10$^6$ | 1.34              | 19.8             | 893                 | 6.1               | 758          | 0.62           |
| 12 | 9.9                  | 1.7 $\times$ 10$^6$ | 1.40              | 13.6             | 485                 | 9.7               | 720          | 0.60           |
| 16 | 17.1                 | 1.1 $\times$ 10$^6$ | 1.49              | 12.0             | 171                 | 16.0              | 710          | 0.51           |
| 19 | 12.3                 | 2.9 $\times$ 10$^6$ | 1.66              | 8.6              | 316                 | 14.9              | 749          | 0.59           |
| 20 | 31.3                 | 5.5 $\times$ 10$^6$ | 1.87              | 15.9             | 50                  | 23.6              | 717          | 0.35           |

Table 3

Level of SC degradation in terms of efficiency after 48 months of storage

| SC | Efficiency coefficient, % | Degradation, % |
|----|----------------------------|----------------|
|    | 2                          | 4.1            | 54–60           |
|    | 6                          | 6.4            | 28–38           |
|    | 8                          | 2.9            | 67–72           |
|    | 12                         | 4.2            | 53–59           |
|    | 16                         | 5.8            | 35–44           |
|    | 19                         | 6.6            | 26–36           |
|    | 20                         | 6.0            | 53–42           |

5.2. Studying a change in the output parameters and the diode characteristics of ITO/CdS/CdTe/Cu/Au SC with different types of n-p heterojunctions after exposure to a voltage of direct polarity

The selected samples were exposed to the action of a bias voltage of direct polarity $V_{d, max} = 0.68$ V at maximum duration $\tau_{ex} = 2$ hours under a dark mode at room temperature; next, we acquired the dark VAP.

Fig. 3–8 show the dark current-voltage characteristic for each type of p-n heterojunction, measured before and after the specified exposure, as well as dependences of direct current $I_d$ that passed through these same SCs at $V_{d, max} = 0.68$ V on the time of the exposure $\tau_{ex}$.

The magnitude of relative change in the output parameters and the diode characteristics for SC with various types of n-p heterojunctions after the shaded SC were exposed to a direct polarity voltage of $V_{d, max} = 0.68$ V at maximum duration $\tau_{ex} = 2$ hours at room temperature is given in Table 4.
5.3. Determining the conditions for restoring the efficiency of film ITO/CdS/CdTe/Cu/Au SC after degradation

Following the exposure over $\tau_{ex} \sim 2$ hours to a voltage of $V_{dmax} = 0.68$ V, the SC operational performance is 62.5%. An increase in efficiency by 47% in the examined SC is predetermined mainly by an increase in $I_{ph}$. For the remaining 43% of SC within such a category an increase in efficiency is due to an increase in $J_{ph}$ and $R_{sh}$, as well as due to a decrease in $R_{0}$, which led to a rise in $FF$. And in one of such SCs, along with the indicated changes, an increase in efficiency is also predetermined by a significant decrease in $J_{0}$.

The results described point to a possibility to improve the effectiveness of film SC operation, after degradation, by their further exposure at a moderate temperature under a bias voltage of direct polarity of the n-p heterojunction $V_{dmax} < V_{dmax} \leq V_{dmax}$ for about 2 hours. Such a recovery of efficiency is possible if the diode structure of SC in the process of degradation did not have the time to form the defects in the form of alternating self-restoring electrical micro-breakdowns.

In addition, based on the analysis of results similar to those specified in Fig. 2–7 and Table 4, one can explain the likely mechanisms of influence of the direct polarity voltage on photocurrent, diode, and the output parameters of such SC.

6. Discussion of results of influence of a bias voltage of direct polarity on Fe ITO/CdS/CdTe/Cu/Au SC

When SC is fed voltage $V_d = V_{dmax}$, the forming electric field within a diode structure of SC must enhance the built-in electric field at the rear p–p+ heterojunction and partially inhibit the built-in electric field at the front n-p heterojunction. In this case, at the rear p–p+ heterojunction and in the areas that surrounding it from both sides such processes will be intensified that are associated with the transport of atoms of copper. In addition, there is a restructuring of complexes of point defects, containing copper, and the phase transformations of Cu$_2$Te into Cu$_{2-x}$Te. The consequence of these processes should include:

- a certain additional growth in the component of successive resistance from the side of a rear contact;
- a certain reduction in spectral sensitivity over a long wavelength region of solar radiation;
- additional metallization of plots in the joints of longitudinal boundaries of the absorber grains arranged close to the p–p+ heterojunction.

However, from the plots of longitudinal joints between the grains of absorber from the side of n–p heterojunction the intra-nodal copper should start moving towards the p–p+ heterojunction. This process can lead to the dissolution of chains from copper atoms, which formed earlier and partially shunt the heterojunction from the side of CdTe. This circumstance could lead to an increase in shunting resistance. Since the arrival of copper to CdS from the joints of longitudinal boundaries of the absorber grains has a point character, it is possible, in this case, a point formation of additional quantities of the Cu$_{2-x}$S$_x$ phase, but this should not significantly affect the magnitude of $J_{ph}$. Under the influence of the field induced by a bias voltage of direct polarity, particles of Cu$_{2-x}$S$_x$ from the layer of CdS depletion will start moving to the absorber. Such a move will help reduce the resistance of the Cds layer and can lead to a reduction in the width of the depletion region from the side of absorber. That would en-
hance the spectral sensitivity of SC over shortwave and medi-
iumwave regions of solar spectrum. In addition, we do not rule
out the dissociation, under the action of the specified field, of
the Cu2-xS sublayer, which had formed earlier in the region of
n-p heterojunction with the further electrodiffusion of anions
of sulfur to the absorber, the transformation of copper cations,
formed in CuCuCl, and electrodeffusion of CuCuCl, following
the anions of sulfur. Partial or complete disappearance of the
specified sublayer should lead to an increase in $J_{ph}$. Electro-
diffusion of anions of sulfur to the absorber can intensify the
sprouting of solid solution of CdTe$_{1+}$S$_{y}$ beneath the absorber.
The electrodeffusion of additional amount of CuCuCl to the ab-
sorber must amplify the described-above and related effects of
enhancing the spectral sensitivity of SC. It is obvious that the
totality of the examined transformations under the influence of
$V'_{d}$ leads to the increased efficiency of SC operation via
an increase in $J_{ph}$ and $R_{sh}$ at a decrease in $J_{0}$ and $R_{p}$, which
is observed experimentally.

It is only natural that in actual SC the ratio of intensities
of the progress of the above-examined processes does not
always match such a perfect combination of characters in
change of $J_{ph}$ $R_{sh}$, $J_{0}$ and $R_{p}$. Probably, for example, in some
cases, the flow of copper atoms along the joints at longitudi-
nal boundaries of the absorber grains to the area of n-p het-
erojunction may outperform the outflow to CdS. In this case
it is absolutely clear to us that the powerful emerging shunt-
ing should lead to the release of a joule heat within the chain
of copper atoms, sufficient to rupture it, which is one of the
reasons for self-restoring micro-breakdowns, followed by its
resurrection then again a self-restoring micro-breakdown.

Another interesting effect, not described in other pa-
pers, is what is observed when reducing $V_{d}$ to $V_{d}<0.2$ V
(Fig. 3, 5, 7) – an unintentional switching of SC from the
low-conducting state to the high-conducting state. A given
effect is well explained by an increase in the reverse action
on CuCu on the region of CdS depletion of the built-in field of
n-p heterojunction, which helps saturate the joints of longi-
tudinal boundaries at absorber grains with copper from the
side of the specified junction.

Based on the research conducted, we proposed a tech-
nique to restore the efficiency of SC after degradation. The
 technique implies sequential operations related to measuring
the dark and light current-voltage characteristic and to the
action of a direct polarity voltage. Using the proposed tech-
nique, it becomes possible to reject potentially unreliable
SC included in solar modules, to prolong the duration and
improve the efficiency of operation of potentially reliable
devices. This list of successive operations involving SC is
as follows. Periodically, at intervals of 24 hours, automatic
measurement of light current-voltage characteristic for solar
cells that make a solar module with the subsequent analyti-
cal treatment for determining the output parameters and the
light diode characteristics. When observing a decrease in
the output parameters, it is necessary to perform measure-
ments, during dark hours, of the direct branch of the dark
current-voltage characteristic at voltages $V_{d}$ in the range:

$$0 \leq V_{d} \leq V'_{d},$$

where $V'_{d}$ is the current value for voltage at which its last-
ing impact on SC is observed.

In the absence of anomalies in the dependence of current
strength $I_{d}$ on $V_{d}$ we enter the mode of $V_{d}=V'_{d}$ with the
following exposure of SC to voltage over 2 hours and we
simultaneously register the dependence of $I_{d}$ on the exposure
duration $\tau_{ex}$.

For the case of a monotonic descent in the dependence of
$I_{d}$ on $\tau_{ex}$ (Fig. 3) the specified operation should be continued
for 2 hours, then measure the straight branch of the SC dark
current-voltage characteristic when reducing voltage from
$V_{d}=V'_{d}$ to zero.

If there is a spontaneous switching of SC from the
low-conducting state to the high-conducting state, the
efficiency of instruments in the structure can be partially
restored, which can be automatically controlled based on the
analytical processing of the light current-voltage character-
istic at day light.

If the dependence of $I_{d}$ on $\tau_{ex}$ shows the signs of mi-
cro-breakdowns or there starts a monotonic ascent of $I_{d}$
with an increase in $\tau_{ex}$, the recovery via voltage must be
stopped; a potentially unreliable SC should be replaced
with a new one.

In the absence of anomalies in the dependence of current
strength $I_{d}$ on $V_{d}$ we enter the mode of $V_{d}=V'_{d}$ followed by
exposing SC to voltage over 2 hours and we simultaneously
register the dependence of $I_{d}$ on the exposure duration $\tau_{ex}$.

For the case of a monotonic descent in the dependence of
$I_{d}$ on $\tau_{ex}$ (Fig. 3), the specified operation should be continued
for 2 hours, then we measure the straight branch of the SC
dark current-voltage characteristic when reducing voltage from
$V_{d}=V'_{d}$ to zero.

If there is a spontaneous switching of SC from the low-con-
ducting state to the high-conducting state, the efficiency of in-
struments in the structure can be partially restored, which can be
automatically controlled based on the analytical processing of
light current-voltage characteristic at day light.

If the dependence of $I_{d}$ on $\tau_{ex}$ shows the signs of electri-
cal micro-breakdowns or there starts a monotonic ascent of $I_{d}$
with increasing $\tau_{ex}$, restoring by voltage $V'_{d}$ must be
stopped; a potentially unreliable SC should be replaced
with a new one.

6. Conclusions

1. We have experimentally registered the effect of an electrical
field of direct polarity on the output parameters and the light
diode characteristics of ITO/CdS/CdTe/Cu/Au SC whose efficiency
degraded.

2. We have shown a possibility to improve the efficiency of
film ITO/CdS/CdTe/Cu/Au SC after degradation by
exposing them to a bias voltage of n-p heterojunction if the
diode structure of such SC during degradation did not have
the ability to form defects that over a specified time of exposure
could lead to the alternating self-restoring electrical mi-
cro-breakdowns.

3. We have defined conditions for the restoration of film
ITO/CdS/CdTe/Cu/Au SC, based on exposing SC for at
least 120 minutes to an electric field whose polarity matches
the forward bias of the n-p heterojunction of SC induced
by the external constant voltage of magnitude (0.5–0.9) V.
Under the influence of an electric field, there occurs the
intensification of processes of transporting copper atoms, re-
structuring of complexes of point defects, containing copper,
away as well as the phase conversion of CuCu1 Te. These processes
lead to a decrease in the resistance of the CdS layer and to the
electrodiffusion to the base layer of sulfur anions and the
intra-nodal cations of CuCu.
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