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DEVELOPMENT OF A METHOD FOR PRODUCING EFFECTIVE CDS/CDTE/CU/AU SOLAR ELEMENTS ON A FLEXIBLE SUBSTRATE DESIGNED FOR BACKUP SUPPLYING SYSTEMS PREVENTION OF EMERGENCY SITUATIONS

Iryna Borysenko
Assistant Scientific Secretary
Central Research Institute of the Armed Forces of Ukraine
Povitroflotskyi ave. 28 b, Kyiv, Ukraine, 03049

Olexandr Burmenko
PhD
Department of Pyrotechnic and Special Training*
*National University of Civil Defence of Ukraine
Chernyshevska str., 94, Kharkiv, Ukraine, 61023

Natalya Deyneko
Corresponding author
Doctor of Technical Sciences, Associate Professor
Department of Special Chemistry and Chemical Engineering**
E-mail: natalyadeyneko@gmail.com

Oleksandr Zobenko
Department of Automatic Safety Systems and Electrical Installations
Chornobyl Heroes of National University of Civil Protection of Ukraine
Onoprienka str., 8, Cherkasy, Ukraine, 18034

Yurii Yivzhenko
PhD, Head of Sector
Sector of Scientific and Educational and Methodological Support for the Training of Professional Junior Bachelors in the System of Professional Pre-Higher Education of the Division of Scientific and Methodological Support of Vocational Education
State Scientific Institution "Institute of Education Content Modernization"
Metropolitan Vasyl Lipkovsky str., 36, Kyiv, Ukraine, 03035

Gennady Kamyshentsev
Doctor of Technical Sciences
Department of Regulatory and Organizational Work of the Personnel Management Department
Administration of the State Border Guard Service of Ukraine
Volodymyrska str., 30, Kyiv, Ukraine, 01601

Volodymyr Muraviov
PhD, Associate Professor
Department of Artificial Intelligence and Telecommunication Technologies
State University of Infrastructure and Technologies
Kyrylivska str., 9, Kyiv, Ukraine, 04071

Yuliia Mykhailovska
PhD
Department of Prevention Activities and Monitoring*

Valerii Khrystych
PhD, Associate Professor
Department of Automatic Security Systems and Information Technologies*

Svitlana Kryvonis
Department of Physics
National Technical University «Kharkiv Polytechnic Institute»
Kyrpychova str., 2, Kharkiv, Ukraine, 61002

The technology of forming film solar cells based on CdS/CdTe configuration of the "superstrat" type on a flexible substrate has been improved. To increase the efficiency of the developed solar cells on a flexible substrate, a chemical etching procedure in a nitrogen-phosphorus mixture was added to the traditional "chemical treatment". The conducted studies of the output parameters of the developed device structures showed that the highest values are observed in the case of chemical etching, both before the "chloride treatment" and after it. In the course of the study, it was found that a mandatory procedure in the formation of effective device structures is chemical etching in a nitrogen-phosphorus mixture both before the "chloride treatment" and after it. Carrying out the described procedures made it possible to obtain solar cells on a flexible substrate with an efficiency of 13.1 %. The increase in the efficiency of solar cells with two-stage chemical etching can be explained by the formation of excess tellurium on the surface, which leads to a decrease in resistance and, therefore, to a more efficient penetration of chlorine during the subsequent chloride treatment. Analysis of the transverse cleavage of the investigated device structures demonstrates significant grain growth and surface smoothness of the base layer, which ensures good adhesion with back contact. A study of the degradation resistance of the developed device structures during operation has been carried out. It was found that the obtained solar cells based on CdTe on a flexible substrate have a high degradation resistance and after 10 bending cycles there is no decrease in the output parameters. Thus, it has been established that chemical etching in a nitrogen-phosphorus mixture is a mandatory procedure for the formation of efficient solar cells on a flexible substrate

Keywords: film photocell, flexible substrate, micromodule, solar cell, cadmium telluride, current-voltage characteristic

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1. Introduction

Modern security and control systems have turned from rarely used technical solutions into a necessary component of almost every facility and presuppose their uninterrupted operation. Since such systems must at any time ensure control over the situation, the safety of personnel and visitors, the safety of material values and information, it is necessary to ensure their uninterrupted operation. Typically, these systems have redundant power supplies that are activated in the event of a power outage. Interruptions in the supply of electricity can be not only as a result of force majeure arising in the power supply system, but deliberate impact from the outside.

This is especially true for objects located far from the central power lines of central electrical networks, where the restoration of a damaged source of electricity can take longer than the operation of backup power sources. For such cases, the way out of this situation is to use alternative renewable energy sources. Among the existing options, the most suitable from the point of view of ease of delivery, speed of installation and deployment, are lightweight film solar cells.

It is these elements that include CdTe-based film device structures, since they have insignificant weight relative to traditional silicon ones and, at the same time, have a high level of efficiency. However, these characteristics are typical for frame film solar cells.

The next important step and, therefore, the actual direction for expanding the range of their use is the transition from frame types to flexible ones without significant loss in the values of the output parameters.

2. Literature review and problem statement

Thin-film solar cells (SC) based on CdTe were first presented in the early seventies of the last century [1]. The authors of [2] proposed this type of solar cells as an alternative to traditional silicon ones as part of a hybrid installation, but the disadvantage of such solar cells is their low efficiency. This type of solar cells is most easily adapted to large-scale production [3]. Such attention to cadmium telluride-based film solar cells is due to the fact that CdTe is very strong and chemically stable. Cadmium telluride can be applied to a substrate using a wide variety of methods available, making it ideal for large area production. It has an optimal band gap of about 1.5 eV, which can provide an efficiency of about 30 % at an open circuit voltage of more than 1 V and a short-circuit current density of more than 30 mA/cm^2 [4]. Research by scientists who are engaged in film solar cells based on CdTe are focused on finding approaches aimed at increasing the efficiency of such device structures, as well as increasing their degradation resistance [5], this is especially typical for solar cells on a flexible substrate. Since solar cells on a flexible substrate change their configuration in the film during operation, excessive stresses arise. This leads to a deterioration in the output parameters, hence to a drop in the efficiency. Thus, in [6], based on the analysis of degradation processes occurring in SC based on cadmium telluride, a method for their recovery was proposed, but the issue of increasing the efficiency was not resolved. For a long time, one of the problems standing in the way of reaching the theoretical maximum was the creation of a back contact, since only platinum is suitable for creating an ohmic one. The solution to this problem was the creation of a tunnel contact using a Cu/Au compound. Thanks to the work of various research groups [7], it was possible to increase the efficiency of solar cells based on CdTe/CdS by more than 16.5 % for devices on a glass substrate coated with a transparent conductive oxide (TCO) coating [8]. Significant efficiency gains have been achieved by re-upgrading the CdTe solar cell arrangement, removing CdS, and taking into account new features such as bandgap gradation, chloride treatment and a more transparent n-layer. With these changes, First Solar introduced a device with an efficiency of 21.5 % [9] and later improved to 22.1 % [10], a striking fact is that these results were obtained on materials adapted to industrial production. The next step towards improving solar cells based on cadmium telluride was even more weight reduction and the transition from wireframe models to flexible ones. To create flexible solar cells, both metals and polymers are used as a substrate. Among metals, the most popular are molybdenum, titanium and stainless steel, and among polymers – polyamide, polyethylene terephthalate and polyethylene naphthalate.

The authors of [11] used molybdenum as a substrate, but the efficiency of the obtained samples did not exceed 5 %, which is due to imperfect current collection in the region of the rear contact. In [12], molybdenum and stainless steel were used as flexible substrates. The low efficiency of the obtained samples, as shown by the X-ray diffractometry method, is due not only to the complexity of the formation of the rear contact, but also to the presence of defects in the form of dislocations in the base layer. Polymer substrates for flexible solar cells are used in "superstrat" type device structures. In [13], the results of studies of solar cells on a flexible molybdenum substrate as part of a micromodule are presented. The efficiency of such a micromodule was 5.3 %, which is very different from the theoretical maximum. In [14], the authors described the process of obtaining solar cells with record efficiency. The authors noted that, since transparent polymers have low thermal stability, the options for their use are limited by temperature conditions. At the same time, polymer substrates capable of withstanding high temperatures are usually opaque and inapplicable for superstrat solar cells [15]. In [16], to create base layers of cadmium telluride on a flexible polyimide substrate, use low-temperature methods for obtaining base layers. The samples obtained showed an efficiency of less than 10 %. The authors of [17] demonstrated the creation of tandem structures, but despite the prospects in this direction, the efficiency of the developed device structures did not exceed 14 %. Another important procedure that causes discussion is the chemical treatment and annealing of the device structure after the deposition of the base layer [18]. In [19], the authors demonstrated that chloride treatment followed by annealing is a mandatory procedure for the formation of efficient solar cells, since during the chemical treatment grain growth and boundary passivation occur [20].

Consequently, SCs based on CdTe are promising and in demand device structures, but to create efficient SCs, i. e., with a high level of efficiency, on a flexible substrate, it is necessary to optimize the physical and technological foundations of their formation.

3. The aim and objectives of research

The aim of research is to develop a method for producing solar cells based on cadmium telluride on a flexible substrate with a high efficiency. This will make it possible to expand the scope of application of film solar cells.

To achieve this aim, it is necessary to solve the following objectives:

– to study the output parameters of solar cells on a flexible substrate with an optimized layer formation technology;

– to investigate the degradation of produced solar cells on a flexible substrate after multiple bending cycles.

4. Materials and methods of research

4. 1. Obtaining ITO/CdS/CdTe/Cu/Au solar cells "superstrat" configuration on a flexible substrate

Solar cells based on CdS/CdTe of the "superstrat" configuration were fabricated on borosilicate glass 200 μm thick. Indium and tin oxide was formed by DC magnetron sputtering. ITO films were formed at a deposition temperature of 300 °C. The initial partial pressure was 10^{-4} Pa. The specific power of the magnetron was 1.5 W/cm^2, which corresponds to the range of values usually used to obtain transparent and electrically conductive ITO films [21]. Sputtering of ITO was carried out in an argon-oxygen mixture at a pressure of $8 \cdot 10^{-1}$ Pa. Under such conditions, layers were formed with a surface resistance of 10 Ohm/□ and an average transmittance in the visible spectral range of about 90 %. The device heterosystem CdS/CdTe was obtained in a single technological cycle by thermal vacuum deposition from graphite evaporators at an initial vacuum of 10^{-4} Pa. For the deposition of base layers, we used an industrial device UVN67 (Ukraine) (Fig. 1) with modified internal equipment. The volume of the working area of the installation is 0.12 m^3 and includes two resistive evaporators with a capacity of up to 2 kW. This allows several film layers to be deposited in a single cycle on a substrate up to 10×10 cm in size by using nodes for moving the substrates during the deposition process. The temperature control of the substrate was carried out with a thermocouple mounted on the front surface of the substrate.

Fig. 1. General view of the experimental device UVN67: 1, 2 – screens; 3 – evaporator of cadmium telluride powder; 4 – evaporator of powdered cadmium sulfide; 5 – carousel; 6 – substrate heater; 7 – substrate holder [22]

Subsequent sample formation procedures were different from each other.

The first and second groups of samples were subjected to the so-called "chloride treatment". "Chloride treatment" is a mandatory technological operation in the manufacture of high-performance film solar cells based on CdS/CdTe [23]. The processes occurring as a result of the interphase interaction of CdTe-$CdCl_2$ contribute to an increase in the grain size of telluride and cadmium sulfide, and also, as a result of such treatment, an increase in the lifetime of non-equilibrium charge carriers is observed.

After chloride treatment, the second group of samples was immersed in a container with a mixture of nitric and phosphoric acids in the following volumetric ratio HNO_3:H_3PO_4:H_2O=1/3:71:29. Then it was washed and dried in a gas atmosphere of N2.

The third group of samples was subjected to chemical etching in a nitrogen-phosphorus mixture both before and after the "chloride treatment". The formation of rear contacts, which is a Cu/Au film heterostructure of nanosized thickness, was carried out for all three groups of samples using a UVN71-P3 device (Ukraine) (Fig. 2).

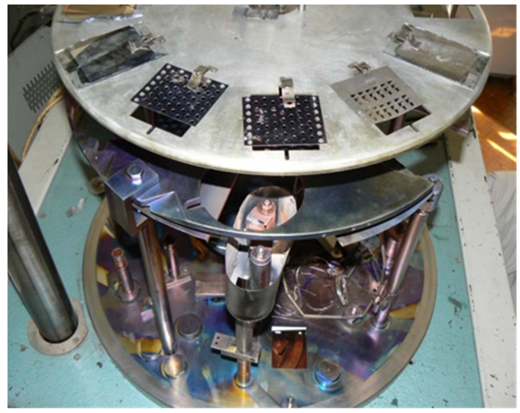

Fig. 2. General view of the UVN71-P3 device [22]

The final procedure was annealing, which stimulates the passage of a chemical reaction leading to the formation of the Cu2-xTe phase, which is a degenerate p+semiconductor of the electrical conductivity type. It is this layer that forms the tunnel junction with the rear current-collecting electrode.

4. 2. Study of ITO/CdS/CdTe/Cu/Au solar cells "superstrat" configuration on a flexible substrate

The study of the obtained samples was carried out by the measurement method with subsequent analytical processing of their current-voltage characteristics (CVC). To measure by the compensation method in a stationary irradiation mode, close to the standard AM 1.5, the light CVC of the SE samples, we used a USO-2 universal LED illuminator, which was installed in a laboratory setup. Along with USO-2, this setup includes: a stabilized direct current source TES 88, a stabilized direct current source HUAYI Electronics HY3020MR and two MASTECH MS8040 multimeters. In addition, the installation circuit is supplemented with a resistive voltage divider to provide a step-by-step change in the voltage in the measuring circuit through 0.01 V. With a step-by-step change in the voltage at the input of the divider through 0.1 V, as well as a store of reference resistances R-33.

Further analytical processing of the light CVC of the investigated SCs was carried out using a personal computer with special software.

The transverse cleavage of the samples under study was identified using a Leo Supra 35 high-resolution scanning microscope (Germany).

To test the flexibility and degradation resistance of solar cells after multiple bending cycles, an arc tube with a radius of curvature of 8 cm was used.

5. Results of the study of ITO/CdS/CdTe/Cu/Au solar cells "superstrat" configuration on a flexible substrate

5. 1. Results of studies of the output parameters of ITO/CdS/CdTe/Cu/Au solar cells with an optimized layer formation technology

The output parameters of the three groups of ITO/CdS/CdTe/Cu/Au solar cell samples under study were obtained by analytical processing of the lightCVC. The research results are presented in Table 1.

The light CVC of the three groups of ITO/CdS/CdTe/Cu/Au solar cells on a flexible substrate are shown in Fig. 3.

Table 1

Output parameters of ITO/CdS/CdTe/Cu/Au solar cells of three groups of samples

Sample group	V_{im}, mV	J_{sc}, mA/cm^2	FF r. u.	Efficiency, %
No etching in a nitrogen-phosphorus mixture	469.9	24.60	0.42	4.8
Etched in a nitrogen-phosphorus mixture after "chloride treatment"	765.6	25.90	0.57	11.3
Etched in a nitrogen-phosphorus mixture before and after "chloride treatment"	781.7	28.95	0.58	13.1

The transverse cleavage of the three groups of ITO/CdS/CdTe/Cu/Au solar cells under study on a flexible substrate is shown in Fig. 4.

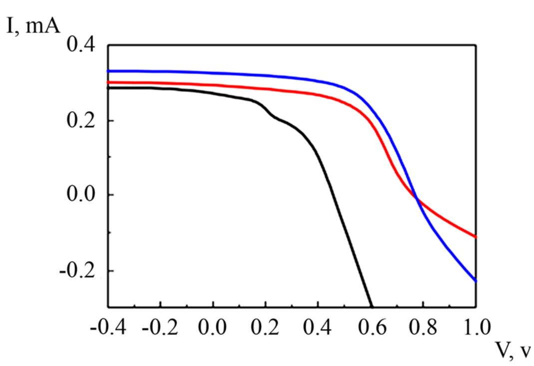

Fig. 3. Light current-voltage characteristics of the investigated three groups of ITO/CdS/CdTe/Cu/Au solar cells on a flexible substrate: black line — without etching in a nitrogen-phosphorus mixture; red line — with etching in a nitrogen-phosphorus mixture after "chloride treatment"; blue line — with etching in a nitrogen-phosphorus mixture before and after "chloride treatment"

As seen from Fig. 4, the chemical etching process and "chloride treatment" have a significant effect on the surface smoothness of the base layer and on the grain size of the device structure.

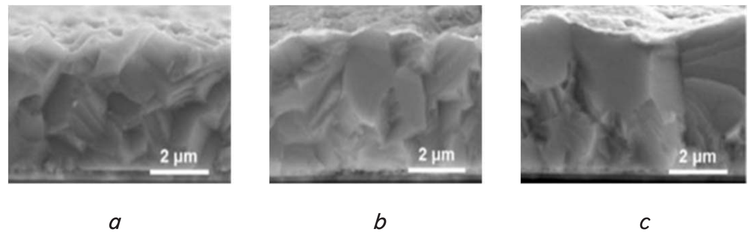

Fig. 4. Cross cleavage of ITO/CdS/CdTe/Cu/Au solar cells on a flexible substrate: *a* — without etching in a nitrogen-phosphorus mixture; *b* — with etching in a nitrogen-phosphorus mixture after "chloride treatment"; *c* — with etching in a nitrogen-phosphorus mixture before and after "chloride treatment"

5. 2. Results of a study of the degradation obtained by solar cells on a flexible substrate after multiple bending cycles

To assess the degradation resistance of the three groups of solar cells under study, tensile deformation was used. The tensile deformation was calculated according to the formula [24]

$$D = t_{sub}/(R\times 2),$$

where t_{sub} – the thickness of the substrate, R – the radius of curvature.

The light current-voltage characteristics of ITO/CdS/CdTe/Cu/Au solar cells on a flexible substrate after multiple bending cycles are shown in Fig. 5.

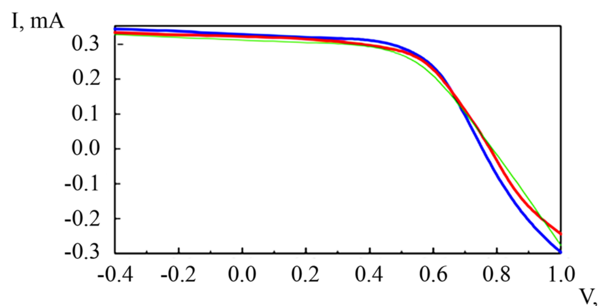

Fig. 5. Light CVC of ITO/CdS/CdTe/Cu/Au solar cells on a flexible substrate after multiple bending cycles: black line — before bending; red line — 3 cycles of bending; blue line — 5 cycles of bending; green line — 10 cycles of flexion

As shown in Fig. 5, the light CVC of the samples before and after tensile deformation practically do not differ. The investigated solar cells ITO/CdS/CdTe/Cu/Au on a flexible substrate demonstrate constant values of the output parameters even after 10 bending cycles.

6. Discussion of the results of the study of ITO/CdS/CdTe/Cu/Au solar cells on a flexible substrate

The study of the output parameters of three groups of ITO/CdS/CdTe/Cu/Au solar cells on a flexible substrate showed that the lowest values of the output parameters are observed in the group of solar cells, in which the samples were subjected only to "chloride treatment". The efficiency of such samples was only 4.8 %. For the second group of samples, which after the "chloride treatment" were subjected to chemical etching in a nitrogen-phosphorus mixture, a significant increase in efficiency is observed. The increase in efficiency is due to the growth of output parameters such as V_{im} and FF. So, for example, V_{im} increased to 765.6 mV in comparison with the corresponding value for the first group of samples (469.9 mV), and the FF value for the second group of samples is 15 relative units higher. in comparison with the first group. The short-circuit current value did not increase significantly. A significant increase in the output parameters and, consequently, the efficiency of solar cells of the second group is due to chemical etching in a nitrogen-phosphorus mixture. As is known, chemical etching removes natural oxides (TeO_2) and promotes the formation of a Te-rich layer on the surface of a thin CdTe film and, as a consequence, reduces the series resistance of the element.

The third group of samples, which was subjected to chemical etching in a nitrogen-phosphorus mixture both before and after the "chloride treatment", demonstrated record results of the output parameters. The efficiency of the samples of the third group reached 13.1 %. This can be explained by the fact that when the samples were spilled in a nitrogen-phosphorus mixture before the "chloride treatment", excess tellurium was formed on the surface. The formation of excess tellurium leads to a decrease in resistance and, therefore, more efficient penetration of chlorine during the subsequent chloride treatment. The analysis of the transverse cleavage of the investigated device structures (Fig. 4) showed that in the sample from the first group (Fig. 4, *a*) it is possible to observe irregularities on the surface, which are formed after "chloride treatment" due to recrystallization. The presence of such irregularities prevents good adhesion during the formation of the rear contacts, which, as a result of repeated bending of the device structure, leads to a violation of the current collection, and, consequently, to a decrease in the efficiency of the solar cell. In contrast to the previously carried out only "chloride treatment", the introduction of an additional procedure of chemical etching made it possible to introduce significant changes in the morphology of the device structure. After chemical etching (Fig. 4, *b*), the edges of the grains become more rounded, and the gaps between the grains practically disappeared. This leads to a decrease in series resistance and an increase in electrical contact between the back contact and the base layer, which leads to an increase in efficiency (efficiency). Chemical etching preceding the "chloride treatment" and after it leads to an even smoother surface of the base layer and a noticeable increase in the size of the CdTe grain (Fig. 4, *b*). This leads to an even greater increase in the output parameters and, accordingly, an increase in efficiency. Thus, it can be argued that in order to create efficient solar cells based on CdTe on a flexible substrate, chemical etching both before and after the "chloride" treatment is a mandatory procedure in the formation of the device structure.

Subsequent studies will be aimed at analyzing the losses in the output parameters of solar cells on a flexible substrate and ways to achieve their theoretical maximum efficiency (30 %).

7. Conclusions

1. Research of the output parameters of solar cells based on CdTe on a flexible substrate has been carried out. It has been established that chemical etching in a nitrogen-phosphorus mixture both before and after the "chemical treatment" is an obligatory procedure in the formation of effective device structures. Carrying out the described procedures made it possible to obtain solar cells on a flexible substrate with an efficiency of 13.1 %, previously achievable only for frame film elements.

2. A study of the degradation resistance of the developed device structures during operation has been carried out. It has been found that the obtained solar cells based on CdTe on a flexible substrate have a high degradation resistance and after 10 bending cycles there is no decrease in the output parameters.

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