Проведено дослідження прозорих тильних контактів Cu/ITO для сонячних елементів на основі CdTe, призначених для використання в тандемних і двосторонньо чутливих приладових структурах. Створення омічного контакту до базових шарів p-CdTe в умовах промислового виробництва не є економічним, оскільки тільки платина має необхідну для формування омічного переходу роботу виходу електронів. Тому традиційно формують тунельні контакти, використовуючи при цьому тонкі плівки, що містять мідь або халькогенід міді. Однак дифузія міді в базовий шар призводить до деградації вихідних параметрів плівкових сонячних елементів на основі CdS/CdTe. Тому умови створення прозорих тильних контактів при використанні прошарку міді потребують дослідження. Встановлено, що попереднє нанесення нанорозмірного шару міді на поверхню CdTe для формування тильного електрода дозволяє сформувати якісний тунельний контакт. Показано, що отримані приладові структури мають високу деградаційну стійкість. Після 8 років експлуатації величина ККД досліджуваних ФЕП практично збігається з початковим. Дослідження світлових вольт-амперних характеристик сонячних елементів SnO2:F/CdS/CdTe/Cu/ITO при освітленні з обох сторін дозволило встановити суттєві відмінності у вихідних параметрах і світлових діодних характеристиках при освітленні з боку скляної підкладки і з боку прозорого тильного електрода. Встановлені відмінності обумовлені впливом тильного діода на ефективність фотоелектричних процесів в базовому шарі. В досліджуваній структурі реалізується режим зверненого діода, коли тильний контакт являє собою діод, включений послідовно по відношенню до основного діоду, що призводить до низьких значень ефективності при освітленні зі сторони тильного електроду. Отримані результати демонструють необхідність у зменшенні товщини базового шару для створення ефективних двосторонньо чутливих елементів

Ключові слова: телурид кадмію, прозорий тильний контакт, тандемна структура, двосторонньо чутливий фотоперетворювач

RESULTS OF STUDYING THE Cu/ITO TRANSPARENT BACK CONTACTS FOR SOLAR CELLS SnO$_2$:F/CdS/CdTe/Cu/ITO

N. Deyneko
PhD*
E-mail: natalyadeyneko@gmail.com
O. Semkiv
Doctor of Technical Sciences,
Vice-rector, Head of Department**
E-mail: semkiv@nuczu.edu.ua
O. Soshinsky
PhD*
E-mail: soshinsky@ukr.net
V. Streletc
Doctor of Technical Sciences, Senior Researcher*
E-mail: vstrelec1956@ukr.net
R. Shevchenko
PhD, Senior Researcher*
E-mail: shevchenko605@i.ua
*Scientific department of problems of civil protection
and technogenic and ecological safety of
the scientific and research center***
Department of service organization*
***National University of Civil Defence of Ukraine
Chernyshevska str., 94, Kharkiv, Ukraine, 61023

1. Introduction

One of the most promising directions to improve efficiency of the photoelectric conversion of solar energy and the ability to work consistently over a long period of time is the development of tandem and two-side sensitive photoelectric converters (hereinafter referred to as PEC). Development of multi-layered tandem structures implies the use of several base layers with a varying width of the bandgap. This makes it possible to efficiently convert solar radiation over a wide spectral range. Thus, photons that have large energy are absorbed at the first base layer, the rest of the radiation coming to the lower-placed PEC with a base layer, which has a smaller width of the bandgap. The main requirements when creating the tandem structures is a small thickness and a transparent rear contact between PEC and a wide-zone base layer [1]. That is necessary for the passage of a long-wave part of the spectrum through the base layer with minimal losses. For the two-side sensitive photoelectric converters the main requirement is the effective conversion of solar radiation when illuminated on both sides. Given the high radiation resistance of cadmium telluride, the two-side sensitive solar cells based on it have the prospect of being applied to supply energy to spacecraft. The rear part of the solar battery of a space ship turns out to be illuminated by the solar radiation reflected from the hull. Therefore, it is necessary to undertake a research into conditions for creating transparent rear electrodes for photoelectric converters based on CdTe, intended for application both in tandem and two-side sensitive structures.

2. Literature review and problem statement

It is promising for the creation of tandem structures to use film PEC with base layers of CdTe and CuInSe$_2$ [2]. It is

known that the width of CdTe bandgap is 1.46 eV [3], and the width of CuInSe$_2$ bandgap is 1.10 eV [4]. A combination of the energy structure of such PEC could ensure effective conversion of solar radiation, both under ground-based and over-atmospheric conditions. However, the use of PEC based on CdTe, in tandem structures, is hindered by the complexity of fabricating the rear contacts suitable for industrial production. This relates to that only platinum has the work of electrons required for the formation of ohmic transition. Other metals form a Schottky barrier with cadmium telluride that affects the efficiency of photovoltaic processes in the cell elements based on it [5]. That is why the basic approach for creating low-resistance electrodes are the formation of a tunnel electrodes containing copper. However, the diffusion of copper to a base layer leads to the degradation of initial parameters of the film solar cells based on CdS/CdTe. Authors of paper [6] proposed forming a rear contact without the use of copper. However, efficiency of the examined samples did not exceed 6.2 % while their degradation resistance lasted only for one year, which is not sufficient for operation under ground-based and over-atmospheric conditions. Paper [7] reported research into creation of ohmic rear contacts when using an organic layer of the conducting polymer PEDOT-PSS, which did not contain copper as well. However, effectiveness of the obtained samples did not exceed 2 %. As shown by the authors, low efficiency of the experimental samples was due to the work of an instrumental structure under a mode of the through diode. Authors of study [8] investigated several types of metal oxides as a buffer layer for creating a quality rear contact for solar cells based on CdTe. This approach, however, complicates the adaptation to the industrial production.

Thus, at present, the task on creating the effective and transparent rear contacts to the CdTe-based solar cells without using copper has remained unsolved. Therefore, it is necessary to undertake a research into optimization of the structural- technological solution aimed at creating transparent rear electrodes using copper.

3. The aim and objectives of the study

The aim of this work is to study transparent rear electrodes of Cu/ITO for the photovoltaic converters SnO$_2$:F/CdS/CdTe/Cu/ITO.

To accomplish the aim, the following tasks have been set:

– to analyze the degradation resistance of photoelectric converters based on CdTe with the transparent rear contact Cu/ITO;

– to analyze the initial and light diode characteristics of the CdTe-based photoelectric converters with the transparent Cu/ITO contacts at illumination from the front and rear sides.

4. Materials and methods to study initial parameters of photoelectric converters based on CdTe

4. 1. Materials and equipment used for obtaining the photoelectric converters SnO$_2$:F/CdS/CdTe/Cu/ITO

The examined instrument structures with an area of the photo-receiving surface up to 2 cm^2 were obtained by the method of thermal vacuum evaporation employing the vacuum installation UVN67 with modified internal equip-

ment. The thickness of the base layer of CdTe was 2.5 μm. The outlay of internal equipment of the installation is shown in Fig. 1.

Fig. 1. Internal structure of the installation for spraying CdS and CdTe: 1, 2 — screens, 3 — evaporator for the powdered cadmium telluride; 4 — evaporator for the powdered cadmium sulfide; 5 — carousel, 6 — substrate heater; 7 — holder of the substrate

Applying the ITO films (oxides of indium and tin) was performed using the method of non-reactive magnetron sputtering at direct current in the vacuum installation VUP-5M (Fig. 2). It should be noted that the magnetron sputtering is one of the most promising methods for obtaining all transparent electrodes [9, 10]. This is due to the high degree of accuracy in transferring the composition of the target on the substrate, to the reproducibility and manageability of the magnetron sputtering process [11, 12].
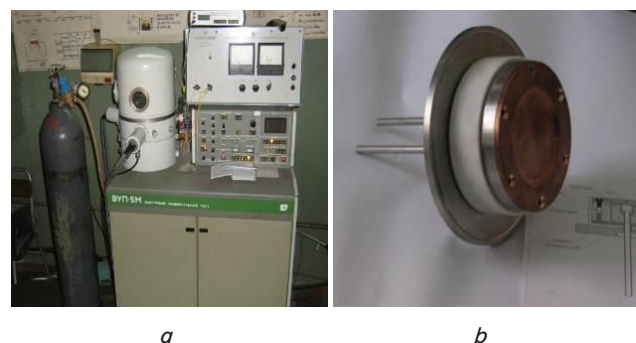

a *b*

Fig. 2. Vacuum installation VUP-5M: *a* — image of the vacuum installation; *b* — image of the material-saving magnetron

Since it is not possible, without a layer of copper, to obtain effective instrument structures, we deposited, before applying ITO on the surface of cadmium telluride, a nanodimensional layer of copper with a thickness of 2 nm. Minimizing the thickness of the layer of copper was aimed at increasing the degradation resistance of the instrument structure.

According to [13], technology of forming the tunnel electrodes implies conducting, before applying an electrode, the chemical etching, at which a layer of Te forms, and the final stage is the annealing, which leads to the formation of the Cu$_{2-x}$Te, which is a degenerated conductor.

4. 2. Procedure of measurement and analytical processing of light volt-ampere characteristics

We measured light volt-ampere characteristics (VAC) in line with the procedure, which is described in [14]. The simulation of solar radiation, approximated to the standard regime AM 1.5, was enabled by a system of light emitting diodes.

In order to measure, using a compensation method, under a stationary mode of irradiation, approximated to the standard AM 1.5, light VAC of SC samples, we determined the initial parameters and the light diode characteristics of the CdTe-based photoelectric converters based on the experimental light volt-ampere characteristics. Analytical processing of light VAC of the examined PEC was performed using a PC.

The relation between effectiveness of PEC and the light diode characteristics in the implicit form is described by the theoretical light VAC of PEC:

$$J_l = -J_{ph} + J_0\{\exp[e(V_l - J_lR_s)/(AkT)] - 1\} + (V_l - J_lR_s)/R_{sh}, \tag{1}$$

where J_l is the density of the current flowing through the load, e is the electron charge; k is the Boltzmann constant, T is the temperature of the solar element; V_l is the voltage drop on the load.

According to the program of numerical simulation [15], analytical expression (1) for light VAC transforms into an expression that takes the form:

$$I_l = A_0 - A_1 V_l - A_2\exp(A_3V_l + A_4I_l), \tag{2}$$

$$A_0 = (I_{ph} + I_0)R_{st}/(R_s + R_{st}), \tag{3}$$

$$A_1 = 1/(R_s + R_{st}), \tag{4}$$

$$A_2 = I_0R_{st}/(R_s + R_{st}), \tag{5}$$

$$A_3 = e/(AkT), \tag{6}$$

$$A_4 = eR_s/(AkT). \tag{7}$$

Using expression (2) and experimentally derived values of I_l and V_l, by varying the values of the above-specified coefficients A_0, A_1, A_2, A_3, A_4, one achieves the best approximation of the experimental data $I_l = I_l(V_l)$ for the curve that is described by the transformed theoretical expression (2). Typically, at analytical processing, a standard deviation does not exceed 10^{-8}, which corresponds to the relative error in determining the initial parameters and the light diode characteristics at the level not larger than 1 %. Upon finding the specified coefficients, which ensure the best approximation, one determines the initial parameters for PEC: $I_{sc}, V_{oc}, FF, P_{nm}$, efficiency. Light-emitting diode characteristics R_s, R_{sh}, A and I_0 are calculated based on the derived coefficients A_0, A_1, A_2, A_3, A_4 applying ratios (3) to (7) [16–18]. Error in determining the initial parameters and the light diode characteristics is defined not only by the

magnitude of a standard deviation, but by the error in measuring light VAC as well.

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5. Results of studying the light volt-ampere characteristics of the photovoltaic converters SnO$_2$:F/CdS/CdTe/Cu/ITO

By processing the light VAC analytically (Fig. 3), we analyzed the initial and the light diode characteristics of the fabricated PEC.
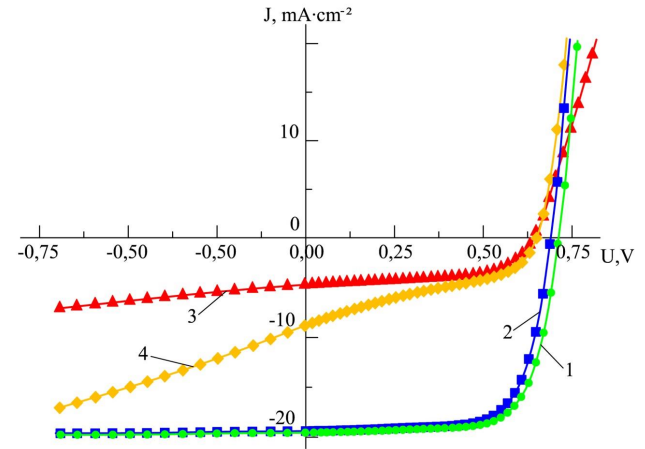

Fig. 3. Light VAC of PEC SnO$_2$:F/CdS/CdTe/Cu/ITO: 1 — initial state, 2 — illuminated from the front side for 8 years, 3 — initial state, 4 — illuminated from the rear side for ~8 years

Upon acquiring the initial light VAC while illuminated from the front and the rear sides, the samples were held at a constant light flux in a special chamber under a mode of idling. The lighting was performed by an incandescent lamp with a power of 500 W, temperature of the sample was 80 °C. Paper [19] showed that such light modes increase the rate of degradation by 100 times. At time intervals that conditionally matched: 0; 0.5; 1.4; 3.6; 4.2; 5.4; 6.02 and 8 years, we repeated the measurement of light VAC. Results of the analytical processing of light VAC while illuminated from the front side are given in Table 1.

Table 1

Initial parameters and the light diode characteristics of PEC ITO/CdS/CdTe/Cu/ITO while illuminated from the front side

t, h	0	0,5	1,4	3,6	4,2	5,4	6,02	8
J_{sc}, mA/cm^2	19.4	19.4	19.4	19.4	19.5	19.4	19.4	19.4
V_{oc}, mW	740	720	710	710	710	710	710	700
FF	0.68	0.73	0.75	0.74	0.73	0.73	0.73	0.71
Efficiency, %	9.8	10.2	10.3	10.1	10.2	10.1	10.0	9.7
J_{ph}, mA/cm^2	19.5	19.0	19.5	19.4	19.5	19.4	19.4	19.4
R_s, Ohm·cm^2	1.6	1.2	0.5	0.3	0.7	0.4	0.3	0.6
R_{st}, Ohm·cm^2	1031	911	882	965	821	922	965	951
A	2.28	1.68	1.65	1.77	1.76	1.91	1.94	2.02
J_0, A/cm^2	$6.2\cdot10^{-8}$	$1\cdot10^{-9}$	$9.7\cdot10^{-10}$	$3.3\cdot10^{-9}$	$2.5\cdot10^{-9}$	$9\cdot10^{-9}$	$1.2\cdot10^{-8}$	$2.5\cdot10^{-8}$

Table 1 shows that at the beginning of PEC operation and up to 1.4 years there is an increase in efficiency from 9.9 % to 10.3 %, driven by a growth of the factor of filling the light VAC from $FF=0.68$ to $FF=0.75$ against an insignificant reduction of idling voltage from $V_{oc}=740$ V to $V_{oc}=710$ V and the short circuit current density from $J_{sc}=19.5$ mA/cm^2 to $J_{sc}=$ $=19.4$ mA/cm^2. Upon a longer operation time of up to 6 years, efficiency slowly reduces to 10 %. Afterwards, efficiency decreases faster and with a time of operation approaching 8 years, a decrease in effectiveness to 9.7 % is observed. Reduction in the efficiency is the result of a decrease in the factor of filling the light VAC from $FF=0.75$ to $FF=0.71$; the voltage of idling also continues to decrease to 700 mV. The short circuit current density does not almost change. It should be noted that after 8 years of operation the magnitude of efficiency of PEC SnO$_2$:F/CdS/CdTe/Cu/ITO practically coincides with the initial value, which indicates high degradation resistance of the obtained heterosystems.

An analysis of the light diode characteristics of PEC SnO$_2$:F/CdS/CdTe/Cu/ITO reveals that initially, with a time of operation up to 1 year, the diode saturation current density decreases from $J_0=1.6\times10^{-8}$ A/cm^2 to $J_0=9.7\times10^{-10}$ A/cm^2. In this case, an ideal diode factor decreases as well. When prolonging the time of operation to 7.5 years, the density of diode saturation current increases by almost two orders of magnitude to $J_0=2.4\times10^{-8}$ A/cm^2, the ideal factor grows as well. This may be due to the fact that the atoms of copper, diffusing into a base layer at the grain boundary, reach the region of $p–n$ transition and bridge it partially. In this case, consistent resistance for almost the entire time of operation reduces from $R_s=2.2$ Ohm·cm^2 to $R_s=0.3$ Ohm·cm^2, and only after 7 years of operation there is the reverse increase in it to $R_s=0.6$ Ohm·cm^2. Shunt resistance at first increases from $R_{st}=850$ Ohm·cm^2 to $R_{st}=960$ Ohm·cm^2; after four years, it decreases to $R_{st}=880$ Ohm·cm^2 with a subsequent return to the level of $R_{st}=960$ Ohm·cm^2.

The light diode characteristics of PEC SnO$_2$:F/CdS/CdTe/Cu/ITO at the start of operation improve; and after 7–8 years, they deteriorate and return almost to their values at the initial state. Such a behavior of diode characteristics predetermines the observed high degradation resistance.

Thus, the use of a layer of copper with a thickness of 2 nm makes it possible to create a tunnel rear contact Cu/ITO without compromising the degradation resistance of the instrument structure. As the thin-film PEC traditionally warrant a stability of efficiency for 5 years, there are promising prospects to use the proposed transparent rear electrodes under conditions of industrial production of film PEC based on cadmium telluride.

Results of the analytical processing of experimental VAC while illuminated from the rear side are given in Table 2.

Table 2 shows that the PEC efficiency while illuminated from the rear side is significantly less than when illuminated from the front side. The ratio of efficiency over the entire operation period remains within the range from 5 to 7, reaching a minimum difference when efficiency while illuminated from the front and the rear sides reach maximum values. Moreover, the relative increase in efficiency at the beginning of the operation while illuminated from the rear side is larger (23 % compared with the initial value) than when illuminated from the front side (4 % compared with the initial value). Lower values of efficiency are primarily due to the lower values for the fill factor of the light VAC and the smaller density of short circuit current. While illuminated from the rear side, at the initial state, a fill factor of the light VAC is $FF=0.56$; and after 7.5 years, it reduces to $FF=0.32$. It should be noted that while illuminated from the front side, the fill factor reduces insignificantly. The density of short circuit current at the initial state while illuminated from the rear side is 4 times lower than when illuminated from the front side. In one year of operation the ratio of these currents becomes equal to about 2.6 and is maintained unchanged thereafter. The voltage of idling, both while illuminated from the front side and when illuminated from the rear side, changes insignificantly, and differs from the value while illuminated from the front side by the magnitude of $(0.05–0.1)$ V.

Table 2

Initial parameters and light diode characteristics of PEC ITO/CdS/CdTe/Cu/ITO while illuminated from the rear side

t, h	0	1.4	3.6	5.4	6.0	8
J_{sc}, mA/cm^2	4.7	7.5	6.7	6.7	6.9	7.0
V_{oc}, mV	650	660	660	650	650	630
FF	0.55	0.42	0.39	0.39	0.36	0.32
Efficiency, %	1.7	2.1	1.8	1.7	1.6	1.4
J_{ph}, mA/cm^2	4.7	7.7	6.9	6.8	7.1	7.2
R_s, Ohm·cm^2	3.2	4.3	4.6	1.5	3.8	3.1
R_{sh}, Ohm·cm^2	438	146	155	150	132	112
A	1.9	1.2	1.3	1.3	1.1	1.1
J_0, A/cm^2	$6.9\cdot10^{-9}$	$3.1\cdot10^{-13}$	$3.8\cdot10^{-12}$	$1.2\cdot10^{-11}$	$3.6\cdot10^{-13}$	$3.6\cdot10^{-13}$

6. Discussion of results of studying the light volt-ampere characteristics of photovoltaic converters SnO$_2$:F/CdS/CdTe/Cu/ITO

Our study of the light volt-ampere characteristics of PEC SnO$_2$:F/CdS/CdTe/Cu/ITO demonstrated that reducing the thickness of the layer of copper that is applied to the surface of CdTe to ~2 nm enabled the fabrication of degradation-resistant solar cells with a transparent rear contact.

The observed evolution of initial parameters when changing the direction of illumination is predetermined by a change in the light diode characteristics. A reduction in the density of short circuit current is due to a corresponding decrease in the density of the photocurrent. The registered decreases in J_{ph} at a change in the direction of illumination relate to the fact that while illuminated from the front side, active generation of non-equilibrium charge carriers takes place near the $p–n$ transition or inside its area of depletion. As a result, a large part is generated under the action of light from the non-equilibrium charge carriers and enters the region of the built-in electric field of the $p–n$ transition where, upon their splitting, the photocurrent forms. When the instrument structure is illuminated from the rear side, the generation region of nonequilibrium charge carriers is separated from the region of the $p–n$ transition. That is why a considerable part of the generated nonequilibrium charge carriers, as a result of volumetric and surface recombination, does not contribute to the creation of photocurrent.

While illuminated from the rear side, consistent resistance is several times larger than when illuminated from the front side; it does not decrease during the time of operation.

The density of diode current of saturation when illuminated from the rear side reduces by nearly three orders of magnitude; it almost does not change during the time of operation. When changing a direction of illumination from the front side to the rear side, shunt resistance decreases by several times. In addition, the shunt resistance decreases over the time of operation. Thus, at the initial state, the ratio of shunt resistance at frontal illumination to the shunt resistance at rear illumination was 2, and by the end of operation it rapidly grew to 8.

When analyzing the light diode characteristics, it is necessary to consider the possibility to implement in the examined structure a regime of the reversed diode, reported in paper [7], when a rear contact is the diode connected in series relative to the principal diode. The energy structure of diodes is affected by an illumination direction, which causes a change in the consistent resistance and shunt resistance, as well as a change in the density of diode current of saturation. If the main contribution to the magnitude of J_0 is introduced by the energy structure of the principal separation barrier, then a decrease in J_0 at a change in the direction of illumination from the front side to the rear side is predetermined by the exponential decrease in the intensity of its illumination.

This, in turn, lowers the concentration of non-equilibrium charge carriers near the $p-n$ transition. If the main contribution to shunt resistance is introduced by the barrier properties of rear contact, it becomes obvious that a given diode characteristic decreases at a change in the illumination direction from the front side to the rear side. When the rear barrier is illuminated, a concentration of the non-equilibrium charge carriers in the region of a spatial charge increases, which leads to a decrease in shunt resistance resulting from a reduction of the thickness of the depletion layer. The consistent resistance is larger when illuminated from the rear side, because, in this case, there is no a significant quantity of the non-equilibrium charge carriers near the principal $p-n$ transition, while the depletion region grows, which leads to an increase in the consistent resistance.

The evolution of the light diode characteristics over the time of operation is predetermined by the diffusion of copper from a nano-sized layer to the bulk of the base layer, which can occur in line with a grain-boundary and a volumetric mechanism.

Since copper is an acceptor impurity for cadmium telluride, its diffusion to the base layer of cadmium telluride leads to a decrease in the specific resistance of the base layer and, accordingly, to a decrease in the consistent resistance of PEC [20]. The diffusion of an acceptor to a grain-boundary surface leads to the formation of $p-p+$ transition between the boundary and the volume of a grain. Such potential barriers push with their built-in electric field the nonequilibrium electrons to the bulk of a grain, generated under the action of light, which reduces the negative impact of grain-boundary surface as the region with a high concentration of recombination centers. Such an approach makes it possible to expand the range of materials to form a rear contact to the solar cells based on CdTe.

The derived low values for the efficiency of PEC SnO$_2$:F/CdS/CdTe/Cu/ITO when illuminated from the side of a transparent rear contact require a more detailed analysis, as well as conducting further research aimed at optimizing the thickness of the base layer.

6. Conclusions

1. After 8 years of operation, the magnitude of efficiency of PEC SnO$_2$:F/CdS/CdTe/Cu/ITO almost coincides with the initial value, which testifies to a high degradation resistance of the obtained heterosystems. Applying a layer of copper with a thickness of 2 nm makes it possible to create a tunnel rear contact Cu/ITO without compromising the degradation stability of the instrument structure.

2. It is established that a change in the illumination direction of PEC SnO$_2$:F/CdS/CdTe/Cu/ITO leads to a substantial reduction in the effectiveness of the instrument structure. Differences between the initial parameters and the light diode characteristics of PEC SnO$_2$:F/CdS/CdTe/Cu/ITO are predetermined by the influence of the rear diode on efficiency of photovoltaic processes in the base layer.

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