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Front contact to the GaSb-photovoltaic converter: Properties and thermal stability

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Issues related to the thermal stability of front contacts, based on Cr–Au and Cr–Au–Ag–Au, to GaSb-based photovoltaic cells have been considered at the operational (the cell temperature is 50°C) and standard conditions as well as at the forced thermal degradation (at 125 and 200°C). It is shown that the photovoltaic converter with the silver-containing contact is preferable in terms of the stability of contact resistivity, external quantum yield, FF, V_{oc}, and therefore, the cell efficiency and service life. The durability of the cells is determined at operational and elevated temperatures.

Keywords: contact, degradation, photovoltaic converter, GaSb.

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1. Introduction

The most important parameter of solar panels is the service life and stability of electrical characteristics, which depend on the choice of materials, instrument structure and design of photovoltaic converters (PVC), the quality of manufacture and strict compliance with the features of technological processes, the degree of coordination of individual components of the module, as well as on the actual climatic conditions in which they are operated.

Common sequences of technical qualification tests have been developed for photovoltaic converters and modules based on them, which are conducted in accordance with the requirements of standards (for example, GOSTP 56980-2016 for ground-based silicon batteries [1] or GOST P 56983-2016 for concentrator modules [2]). The qualification test is usually used to assess the quality of solar cells and modules before starting their production [3], as well as during the production for non-destructive testing and rejection of finished products and verification of conformance with the accepted technological cycle of their production. According to [1], testing for resistance to prolonged exposure to an aggressive environment is conducted at a temperature of 85°C and relative humidity 85% (test duration 1000 h). Additionally, thermal cycling with the temperature range of $-40-+85^\circ$C (up to 110°C in concentrator modules), resistance to local overheating is tested. In addition, the capability of the module to withstand ultraviolet radiation, mechanical (i.e. wind, snow, ice) loads, hail is determined and other tests are performed.

When developing new types of photovoltaic converters, the testing tasks are different and are reduced to assessing design flaws and opportunities for improving the quality, reliability and service life of solar cells, to identifying the best materials, etc. The choice of a contact system is the most important component of designing/testing of the PVC production technology, since the quality of contact significantly affects not only its parameters, but also for reliability and operating life. Regular tests in this case will not be effective enough, they will be unreasonably long and time-consuming. The standard outgoing inspection procedure can be simplified and reduced, for example, to testing for resistance to prolonged exposure to temperature.

The study of the stability of gold- and silver contact compositions to p-GaSb is covered in [4]. It was noted that under conditions of extreme (200°C) heating of the PVC, degradation was manifested by the fusion of a thin $p-n$-junction by metallization, as well as by the deterioration of the surface condition and partial shedding of the contact layers. This paper provides the results of studies of thermally initiated degradation of the front contacts of the PVC heated to ~ 80 and 120°C. Testing at $T \sim 80^\circ$C is close to the recommendations of the standard [1] and the operating conditions of the PVC, the heating of which, as a rule, does not exceed 50–70°C and depends on the method it is operated — in solar panels [5–9], thermophotovoltaic generators [10–12], in laser radiation conversion. The temperature of 120°C is selected as another forced degradation condition. The operability of the converters at $T \sim 50^\circ$C due to the duration of the experiment was estimated theoretically using experimental data for $T \sim 200, 120$ and 80°C (see section 2.6 below).

The purpose of this study was to compare stability and service life of two contact systems: the traditional GaSb-based composition Cr–Au for PVC and its modification based on silver Cr–Au–Ag–Au.

Special attention should be paid to the value of the contact resistance when choosing gold- or silver-containing contact compositions and methods of their formation. The literature contains quite little information about the temperature-time stability of metallization to GaSb. The paper [13] studied gold-based contacts (without a chromium sublayer) initially annealed for 60 s at a temperature of 200°C in an atmosphere of hydrogen and nitrogen (forming gas). When annealing was repeated during 60 s at $T = 250^\circ$C, the values of the specific contact resistance deteriorated from $\rho_c \sim 5 \cdot 10^{-8}$ Ohm · cm^2 to $\rho_c \sim 10^{-6}$ om · cm^2. At lower temperatures (100°C), the contacts remained stable in magnitude $\rho_c > 10$ h.

In paper [14] gold-based contacts Au (100 Å)–Zn (100 Å)–Au (800 Å) were deposited and the values of specific contact resistances were measured depending on annealing temperature in the atmosphere 92% N_2 + 8% H_2. The minimum values of $\rho_c \sim 1 \cdot 10^{-5}$ ohms · cm^2 were reached at $T = 300^\circ$C and annealing time 15 min. The study of Auger profiles and Rutherford backscattering spectra confirmed the diffusion of gold in GaSb, as well as the reverse diffusion of Ga and the diffusion of Zn. These factors will influence the predisposition of such a gold-based contact to degradation.

The paper [15] studied the temperature-time stability of Au-, Ag- and Al-contacts to *p*-GaSb (with $p = 10^{18}$ cm^{-3} and $p = 10^{19}$ cm^{-3}). It was found that silver-based contacts remained stable in terms of contact resistivity at a temperature exposure of 350°C in an atmosphere of hydrogen and nitrogen (forming gas) for 100 h. Therefore, it can be expected that these contact systems will also remain stable in case of a prolonged operation of the devices (several thousand hours or more) at lower operating temperatures. Aluminum-based contacts are the least stable and were characterized by a sharp increase of ρ_c already at temperatures of ∼ 100°C. Gold-based contacts showed an increase of the contact resistivity after 30-hour warm-up at $T = 250^\circ$C. Therefore, silver-containing contacts are more stable compared to gold-containing ones because intermetallic compounds of Ag with Ga and Sb are formed at higher temperatures than similar compounds with Au. The conclusion of the authors of the paper [15] about the stability of silver-containing contacts is generally confirmed by the results of the current work (see section 2.2 below).

2. Experimental results

2.1. Manufacturing of photovoltaic converters

Photovoltaic converters based on gallium antimonide were manufactured using the method of two-stage diffusion of zinc from the gas phase into the substrate *n*-GaSb [16,17]. Strip contacts based on Cr compositions (10–40 nm)–Au (1.0–1.5 microns) and Cr(10–40 nm)–Au(100 nm)–Ag(0.9–1.4 microns)–Au(50 nm) were formed to the frontal surface of *p*-GaSb ($p \sim 10^{20}$ cm^{-3}) by resistive thermal evaporation in vacuum at the pressure of residual gases in the chamber $\sim 10^{-6}$ mm Hg. Before evaporation the area under the contact grid was treated by ion plasma. The manufacture of contacts based on Cr–Au consisted in evaporation „of a thin“ ($d \sim 0.3$ microns) contact followed by galvanic deposition of a conductive layer of gold to a total thickness of 1.0–1.5 microns. A two-layer lithography using LOR resists (lift-off resist) was used to form a multilayer contact Cr–Au–Ag–Au with $d \sim 1.0$–1.5 microns applied during a single spraying process. The paper [18] covers the manufacturing of these contacts for a GaSb-based PVC.

The back-surface metallization based on AuGe–Ni–Au was formed before evaporation and annealing of the frontal contact grid. The firing of the rear and front contacts was performed in a hydrogen atmosphere at a temperature of 200–230 and 170°C, respectively. The annealing duration was ∼ (15–60) s.

PVC thermal degradation tests were conducted in the air using a thermostat.

2.2. Temperature-time stability of the contact resistance

The degradation of the properties of contacts under the impact of temperature can be caused by a significant increase of resistivity ρ_c. Our data on the contact resistivity of gold and silver-containing contacts of different types to *p*-GaSb ($p \sim 10^{20}$ cm^{-3}) during short-term annealing in a hydrogen atmosphere are provided in [18]. Changes of ρ_c during prolonged heating of the preliminarily annealing ($T = 225^\circ$C) contacts Cr–Au and Cr–Au–Ag–Au are shown in Fig. 1. Many-hours-heating in air was conducted at a temperature of ∼ 80°C ($t \leq 6000$ h), close to the standard test temperature of photovoltaic converters. The experiments were continued in accelerated mode at $T \sim 120^\circ$C ($t > 6000$ h, Fig. 1, *a*). Similar dependencies of the change of contact resistivity at an extremely high temperature for a photocell ∼ 200°C are shown in Fig. 1, *b*. The contact resistance was measured using the LTML method (linear transmission line model). The data obtained indicate a gradual increase of ρ_c and a better temperature-time stability of the studied silver-containing contacts compared to the gold-containing equivalent. The dependencies $\rho_c(T)$ for contacts with different chrome thicknesses (open and shaded round symbols in Fig. 1, *a* and *b*) are represented by a common curve *1*. Minor differences in the values of ρ_c are within the error margin of the method.

2.3. Change of the contact surface under the impact of temperature

Thermal impact can not only affect the parameters of photovoltaic converters, but it also can change the appearance of contacts, causing, for example, surface oxidation, cracking, shedding and peeling of metal films. The appearance of LTLM structures at the end of their heating in air at 200°C (2300 h) is shown in Fig. 2. The samples were photographed with multiple magnification through the lens of an optical microscope. The images show rectangular contact pads located at a distance of 20, 40, 80 and 100 microns from each other. The change of the color of the Cr–Au–Ag–Au contact after prolonged heating (Fig. 2, *c*) indicates that the thickness of the top layer of gold in 50 nm is insufficient

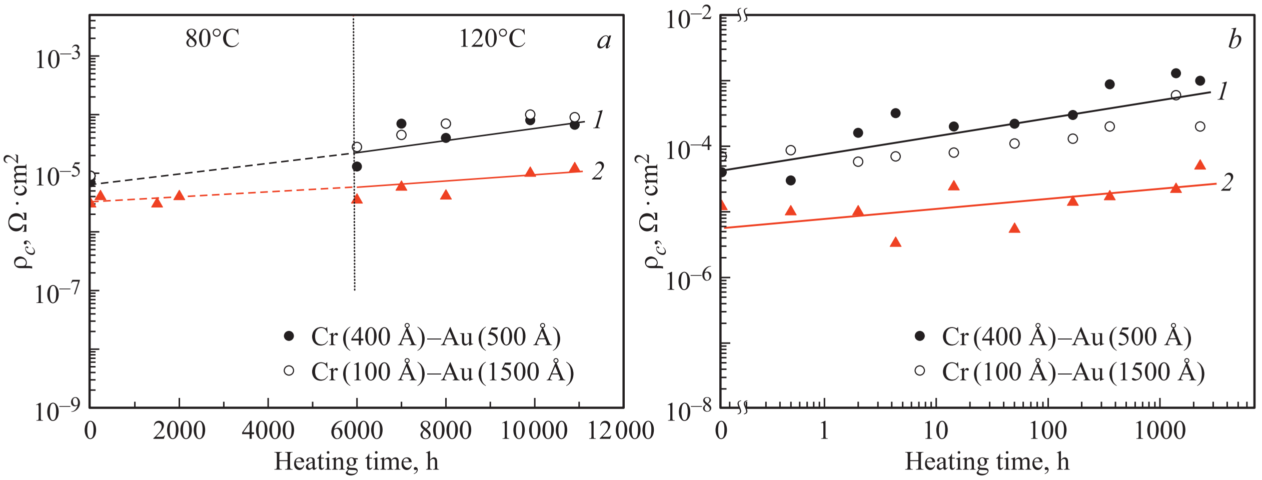

Figure 1. Change of contact resistance after heating up of the structures: *a* — at $T \sim 80$ and 120°C; *b* — at $T \sim 200$°C. *1* — Cr–Au, *2* — Cr–Au–Ag–Au.

to protect the surface from oxygen contained in the air and sulfur. It seems that it should be increased or a barrier layer of chromium, nickel or platinum should be introduced between the upper protective layer of gold and the silver layer to prevent such an adverse effect. An increase of the thickness of the adhesive layer of chromium from 100 to 400 nm improves the morphology of the contact surface (Fig. 2, *a* and *b*) for Cr–Au composition.

2.4. Thermal degradation of contacts at $T \sim 80$°C

Visual inspection of the manufactured PVC, performed using optical microscopes, showed that in case of prolonged heating at 80°C, the Cr–Au contact had a homogeneous structure, while Cr–Au–Ag–Au showed a gradual change of color metallization both in narrow strips and in wide current-collecting buses along the PVC periphery. There was no marked deterioration of the antireflection coatings. At the same time, the Cr–Au open-circuit voltage V_{oc} and the fill factor FF (Fig. 3) dropped already at the initial stage of the experiments, and the photovoltaic converters with a silver-based contact grid had significantly more stable electrical characteristics. V_{oc} does not significantly change in this case (Fig. 3, *b*). The spread of FF values of PVC with Cr–Au–Ag–Au in Fig. 3, *a* may be related to the deterioration of the contact surface.

2.5. Forced degradation at $T \sim 120$°C

The results of experiments on forced degradation of PVC at $T \sim 120$°C are shown in Fig. 4. The specified value T significantly exceeds the average operating temperature range [5–12] for both solar panels and thermophotovoltaic converters. However, the behavior of the PVC under such abnormal conditions can also be interesting from a practical point of view: in thermophotovoltaic generators, the converter should be as close as possible (up to 1–3 cm) to the heated emitter, while its overheating will greatly increase. The emitter–PVC distance is usually obviously greater than the minimum limit in existing thermophotovoltaic systems which is associated with the risk of deterioration of V_{oc} converters under the impact of temperature and reduction of their service life in extremely unfavorable conditions.

Table 1. Photocurrent of converters after heating at a temperature of 120°C

Type contacts	Time impact at $T \sim 120$°C, h	Photocurrent density, mA/cm^2	
		AM0	AM1.5G
Cr–Au–Ag–Au	0	41.1	31.6
	5500	41.1	31.6
Cr–Au	0	41.1	31.6
	5500	40.5	31.2

The absence of a noticeable degradation of the spectral photosensitivity of the PVC under the impact of heating in air is confirmed by the results of Table 1. Data for the illumination of converters by cosmic (AMO) and terrestrial (AM1.5G) solar radiation are provided.

2.6. Estimation of the time of degradation of a photovoltaic converter

A period of time during which the output power drop did not exceed 15% of the initial value was selected as a parameter determining the operability of the PVC and the safety of the contact (see Fig. 5). This period is less prolonged than the physical service life of the photovoltaic converter when the device continues to function, but due to the effect of aging and degradation works inefficiently. In the strictest sense, this time is not the service life of the

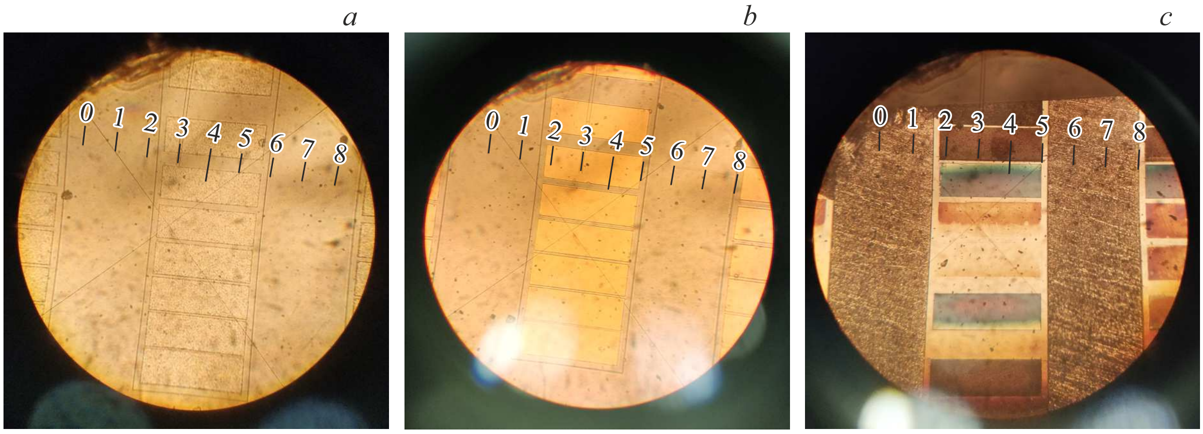

Figure 2. Contact surface morphology in LTLM structures (heating at 200°C, 2280 h): *a* — Cr (100 nm)–Au; *b* — Cr (400 nm)–Au; *c* — Cr–Au–Ag–Au.

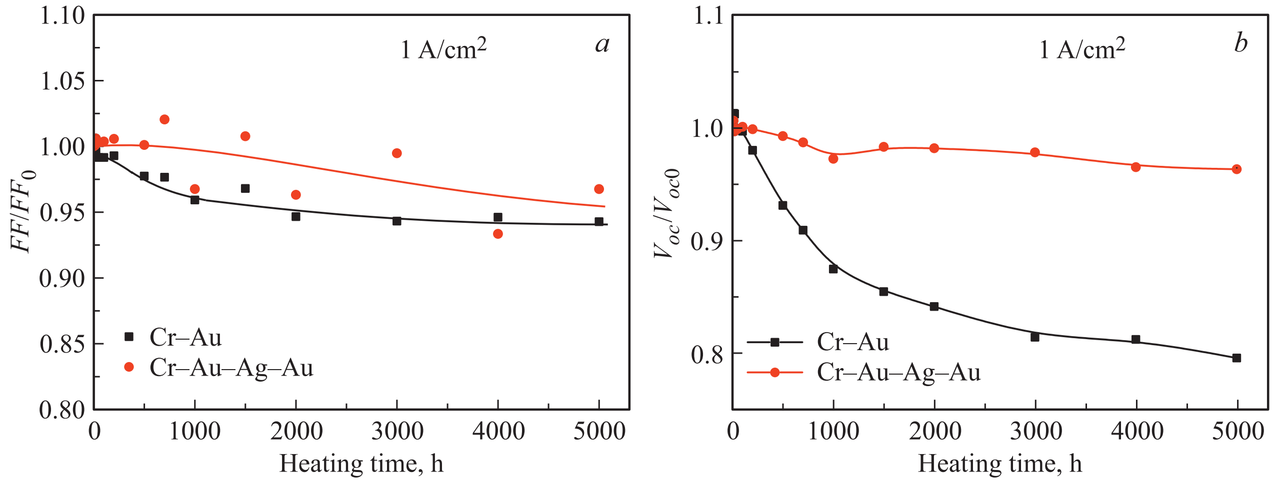

Figure 3. Change of FF and V_{oc} (normalized values) after heating of photovoltaic converters at $T \sim 80°C$.

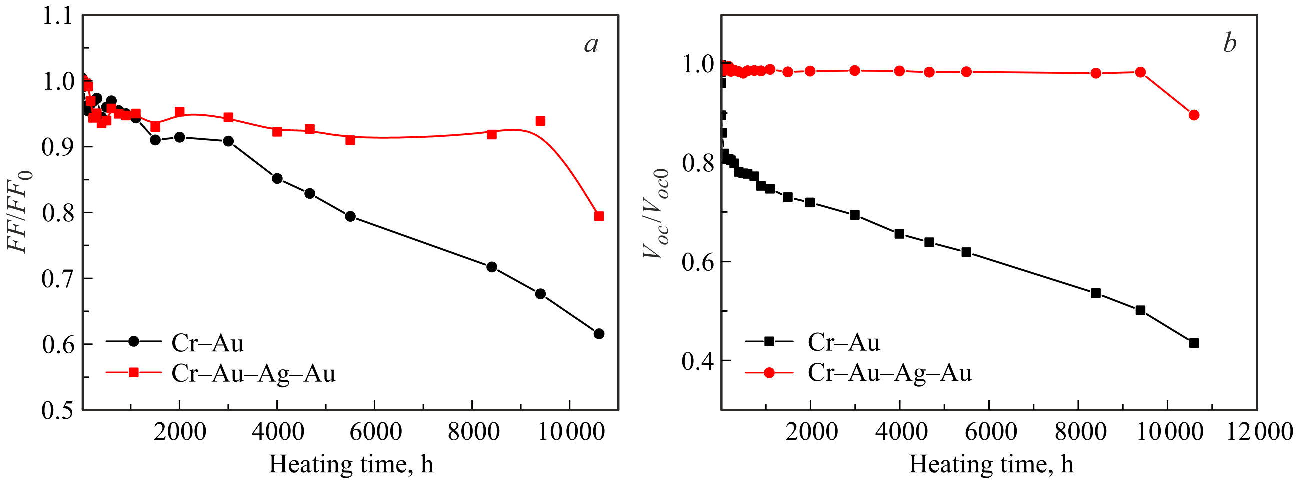

Figure 4. Change of FF and V_{oc} (normalized values) of photovoltaic converters with different contact systems after heating at $T \sim 120°C$, $J_{sc} = 1$ A/cm^2.

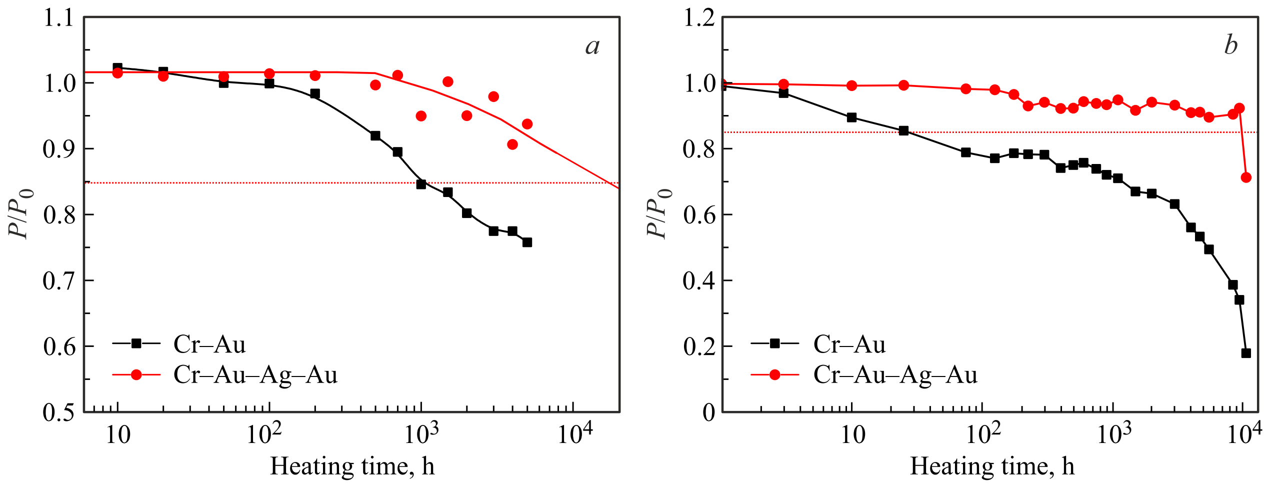

Figure 5. Change of power of photovoltaic converters with different contact systems after heating at temperatures of 80°C (*a*) and 120°C (*b*). The data are given for illumination conditions corresponding to the photocurrent density of 1 A/cm^2.

converter and because it takes into account only the thermal load on the device without its illumination.

The time of the PVC degradation resistance at different temperature (80, 120, 200°C) determined on the basis of the presented data and the results of the study [4] is summarized in Table. 2.

The obtained results of testing of an output power drop at elevated temperatures allow for estimating the time of degradation of converters in operating conditions. The method of determining the reliability of the devices described in papers [18–20] was used. The activation energy of the degradation process Ea and the degradation acceleration coefficient K_a relative to the operating temperature of the PVC ($T_N = 50°\mathrm{C}$) were estimated according to the results of testing at $T_A = 120°\mathrm{C}$ and $T_B = 200°\mathrm{C}$:

$$E_a = k\,\frac{\ln(t_A/t_B)}{(1/T_A) - (1/T_B)}, \tag{1}$$

$$K_a = \frac{\exp(E_a/kT_N)}{\exp(E_a kT_F)}, \tag{2}$$

where k — Boltzmann constant, t_A and t_B — converter degradation time at T_A and T_B, respectively (Table. 2), T_N and T_F — temperature in normal and forced modes.

Table 2. The time of the degradation resistance under conditions of elevated temperature loads (experiment)

	Type contact systems	Temperature heating of the PVC, °C		
		200	120	80
Degradation resistance time, hour	Cr–Au	0.1	30	1050
	Cr–Au–Ag–Au	6	9900	~ 17600*

Note. * Approximation of experimental results Fig. 5.

Table 3. Contact degradation parameters. The values of K_a are given for the forced mode at $T_F = 120°\mathrm{C}$

Contact	E_a, eV	K_a	Degradation time PVC at 50°C, h
Cr–Au	1.13	$1.2 \cdot 10^3$	$4.2 \cdot 10^5$
Cr–Au–Ag–Au	1.58	$2.4 \cdot 10^4$	$3 \cdot 10^8$

The time of forced degradation of τ_F was determined using the data of Fig. 5, *b*:

$$\tau_F = \frac{t_1 - t_2}{\ln(P_2/P_1)}, \tag{3}$$

where t_1 and t_2 — the time values on the linear section of the dependence and the corresponding power values P_1 and P_2.

The degradation time of the τ converters in the rated operating mode was determined by multiplying the time constant τ_F by the acceleration coefficient K_a:

$$\tau = \tau_F \cdot K_a. \tag{4}$$

The results of calculation of the degradation time at a temperature of 50°C are listed in Table. 3.

3. Conclusion

A PVC with a silver-containing front contact Cr–Au–Ag–Au has an advantage over an equivalent with Cr–Au in terms of the time stability of most photovoltaic parameters (photosensitivity, *FF*, V_{oc}, efficiency) and service life both in photovoltaic converter operating conditions and at extremely high temperatures. In aggressive operating conditions (in particular, under conditions of significant thermal heating), the thickness of the protective layer of gold in the composition Cr–Au–Ag–Au should exceed 50 nm. Calculations of the PVC degradation time at a temperature of 50°C showed that the predicted service life of metallization if there are no other destructive impacts is at least 48 years.

Conflict of interest

The authors declare that they have no conflict of interest.

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