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Giant photovoltaic effect

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A giant photovoltaic effect was revealed in silicon-type photoelectronic converters (solar cells) coated with specific antireflecting films developed by our research group. More specifically, it was found that the ratio of photoconversion efficiency for a solar cell with such an antireflective film on its surface to the efficiency for a solar cell without the film equals a second power of relation of photoelectromotive force of a converter with the film to the photoelectromotive force of a converter without the film. The film comprises an antireflecting coating that is high-efficient in the wavelength range of 450 to 1000 nm and that is synthesized on the basis of novel nanomaterials that provide the quasi-zero average complex refractive index of nanocomposite film.

The possibility of obtaining ideal antireflection, i.e., the condition at which reflection of light is completely suppressed, is substantiated by the classic formulas for a single-layer coating on the surface of a semi-infinite optical medium [1]. The formula for amplitude of an s-polarized reflected wave is expressed as follows [1]:

$$R^{\perp}=E_0^{\perp}\frac{r_{12}+r_{23}\exp\left(2\imath\phi\right)}{1+r_{12}r_{23}\exp\left(2\imath\phi\right)}, \qquad (1)$$

where $E_0^{\perp}$ is the amplitude of an incident wave, and r_{12} and r_{23} are Frenel coefficients of refraction on the 1-2 and 2-3 borders, respectively; $\phi = k_0 d_2\left(n_2+\imath\kappa_2\right)\cos\theta_T$, where θ_T is the refraction angle in the layer, d_2 is the thickness of the nanocomposite film, $k_0=2\pi/\lambda$, λ is the wavelength of the incident beam, n_2 is the active part of the refraction index; and κ_2 is the absorption coefficient of the nanocomposite film. If we assume that $n_2\to 0$, $\kappa_2\to 0$, then the condition of ideal optical refraction is expressed as follows:

$$r_{12}=-r_{23}\exp\left(2\imath\phi\right). \qquad (2)$$

By inserting equation (2) into the denominator of formula (1), one can obtain an indeterminate form of the (0/0) type that can easily be eliminated. As a result, we assume that $R^{\perp}=0$, i.e., that refraction of light is absent if $n_2=\kappa_2=0$.

Let us insert condition (2) into the formula for the amplitude of a wave that enters medium 3, i.e.,

$$T^{\perp}=E_0^{\perp}\frac{d_{12}d_{23}\exp\left(\imath\phi\right)}{1+r_{12}r_{23}\exp\left(2\imath\phi\right)}, \qquad (3)$$

where d_{12} and d_{23} are Frenel coefficients of optical light transmission on the borders 1-2 and 2-3, respectively. At $n_2=\kappa_2=0$, we have $d_{12}d_{23}=1+r_{12}r_{23}$, and the following equality can be obtained from (3):

$$T^{\perp}=E_0^{\perp}, \qquad (4)$$

In other words, the amplitude of the wave that passed into the underlayer is equal to the amplitude of the incident wave. It can be easily shown that conditions $R^{\perp}=0$, $T^{\perp}=E_0^{\perp}$ of ideal antireflection occur at different hade and for different underlayers. In addition, if the indices of refraction and absorption turn into zero in a wide range wavelength, the ideal optical antireflection acquires wide-band characteristics. If condition (4) is satisfied, the light-transmission capacity of a nanocomposite film is equal to $T=n_3|T^{\perp}/E_0^{\perp}|^2$, and if $n_3>1$, the light-transmission capacity of a nanocomposite film becomes greater than 1. Such strengthening of intensity of light results from the fact that at $n_2=\kappa_2=0$ all light emitters of the nanocomposite film are coherent.

The condition $R^{\perp}=0$, $T^{\perp}=E_0^{\perp}$ of ideal antireflection was obtained [2] also in a monolayer of spherical nanoparticles at the interface between two media.

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Table 1

Results of measurement of photoelectromotive force of a solar cell according to the scheme of Fig.1a

Film type	d_2, μm	U_1^c, mV	U_2^c, mV	$\overline{U^c}$, mV	U_1^n, mV	U_2^n mV	$\overline{U^n}$, mV
PMMA+Ag (10 wt.%)	50	62	56	59	102	100	101
PMMA	50	22	18	20	43	62	52.5
PMMA+Ag (3 wt.%)	70	140	126	203	410	346	378
Without film	0	5	6	5.5	30	33	31.5
PMMA+Ag (1 wt.%)	60	22	26	24	97	74	85.5

Designations: d_2 – thickness of nanocomposite film; photoelectromotive force for radiation with collimated light: U_1^c – first measurement, U_2^c – second measurement, $\overline{U^c}$ – average value. For optical beam that passed through the adapter: U_1^n – first measurement, U_2^n – second measurement, $\overline{U^n}$ – average value

Table 2

Results of measurement of photoelectromotive force of a solar cell according to the scheme of Fig.1b

Film type	d_2, μm	U_1^c, mV	U_2^c, mV	$\overline{U^c}$, mV	U_1^n, mV	U_2^n, mV	$\overline{U^n}$, mV
PMMA+Ag (10 wt.%)	50	60	58	59	29	30	29.5
PMMA	50	30	28	29	10	14	12
PMMA+Ag (3 wt.%)	70	198	191	194.5	78	82	80
Without film	0	24	20	22	5	8	6.5
PMMA+Ag (1 wt.%)	60	41	37	39	12	12	12

With some deviations of n_2 and κ_2 from zero, the system of light emitters contained in the nanocomposite film is partially coherent, and this leads to some deviations in amplitudes of reflection and absorption from the values that correspond to ideal antireflection. Regarding quasi-zero values of n_2 and κ_2, formulas for respective amplitudes of reflection and absorption are derived by integrating amplitudes (1), (3) over the values of n_2 and κ_2 their near-zero values. It should be noted that the effect of ideal optical antireflection is applicable even for p-polarized waves as well as for the natural light, e.g., for solar radiation.

We have developed a technique for synthesis of novel transparent quasi-zero average complex refractive index optical materials and methods for application of nanocomposite metal-polymer films, e.g., of (PMMA+Ag) films, onto various substrates, such as glass and silicon. The obtained films are characterized by homogeneity and transparency and may be obtained with a thickness in the range of 10 to 100 μm. Optical measurements show that indices of refraction and absorption of these films are close to zero. When such films are applied onto the surface of chemical glass, an absolutely transparent specimen is obtained for light having wavelengths in the range of 450 to 1000 nm, but application of such film onto the surface of a silicon-based solar cell forms a blackbody, i.e., the entire external radiation enters the silicone-based solar cell without reflection. Given below are results of photovoltaic measurements, showing that coating of the silicon-based solar cells with our synthesized films provides a multifold increase in the electromotive force developed by the cell.

Tables 1 and 2 show protocols of measurement of electromotive forces obtained when one unit of a six-unit silicon-based solar cell was locally illuminated with a light source comprised of a light guide and a halogen lamp. Illumination conditions through an adapter correspond to a light source emitting light from the light guide to a tube; the collimated illumination corresponds to a light source of the waveguide through a tube and is limited by a slit that prevents background illumination of the remaining units of the cell. Resistance of the external load was $R_N = 1\,\mathrm{M\Omega}$, and because of high internal resistance of the solar cell, current in each measurement did not exceed 10^{-6} A.

Let us present a ratio η/η_0 of efficiency η for a solar cell with the film to the efficiency η_0 for a solar cell without the film by the following equation:

$$\frac{\eta}{\eta_0} = \frac{UI}{U_0 I_0}, \tag{5}$$

where U and I are values of photoelectromotive force and current, respectively, when only one unit of the solar cell is coated with antireflecting film synthesized according to the use of our technique. U_0 and I_0 are respective values of photoelectromotive force and current for the

Table 3

Experimental values of photoelectromotive forces, photocurrents, and powers (products of photocurrent by photoelectromotive force) of a solar cell at different outer load resistances

R_N, Ω	U, mV	I, mA	U_0, mV	I_0, mA	P, mW	P_0, mW	P/P_0
27	416	15.52	230	8.58	6.45632	1.9734	3.271673
77	490	6.41	362	4.76	3.1409	1.72312	1.822798
114	520	4.57	408	3.58	2.3764	1.46064	1.626958
164	525	3.22	425	2.6	1.6905	1.105	1.529864
218	528	2.43	436	2.01	1.28304	0.87636	1.464056
266	534	2.01	443	1.66	1.07334	0.73538	1.459572
316	535	1.70	453	1.43	0.9095	0.64779	1.404004
364	536	1.48	452	1.25	0.79328	0.5650	1.404035
418	533	1.28	452	1.08	0.68224	0.48816	1.397575
467	533	1.15	453	0.97	0.61295	0.43941	1.394939

solar cell without antireflecting film. If photoelectromotive forces are designated as $U = IR_N$, $U_0 = I_0R_N$, respectively, where R_N is load resistance, then the following can be derived from the ratio (5):

$$\frac{\eta}{\eta_0} = \frac{U^2}{U_0^2}. \quad (6)$$

As can be seen from the measurement protocols, depending on the film compositions, the measured photoelectromotive forces can vary in a wide range. Also, the provision of antireflecting film makes it possible to provide a multifold increase in photoelectromotive force and to reach values of efficiency ratios (6) as high as $(\eta/\eta_0) \gg 1$. We call this phenomenon a "giant photovoltaic effect".

Table 3 shows a measurement protocol of the volt-ampere characteristics of a solar cell, a part of which is coated with (PMMA+Ag) film synthesized according to use of our technique. The content of silver in this film is 3 wt.%. Dark resistance of the solar cell was approximately 380 Ω, and resistance of ammeter R_A was 14 Ω. Measurements were carried out in accordance with the principle diagram shown in Fig.1b.

Fig.2 illustrates experimental values of power on various portions of the solar cell surface for solar cells with antireflecting coating and without antireflecting coating. It can be seen from the measurement protocol that provision of antireflecting film on the surface of the solar cell significantly changes photoelectromotive force and photocurrent. This occurs with observation of the law of the giant photovoltaic effect (6) according to which at different external loads, a ratio of the power of an area of a solar cell with antireflecting film to the power of an area without antireflecting film equals a second power

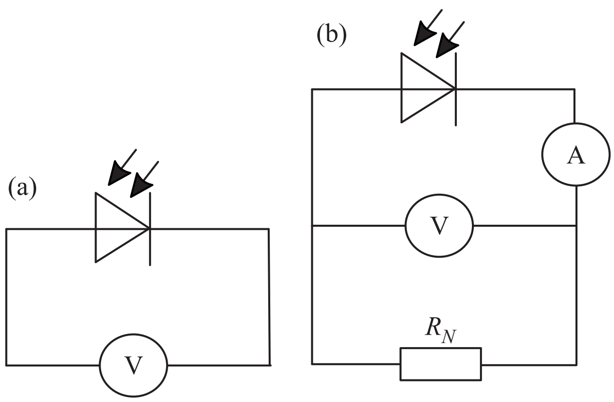

Fig.1. Principle diagrams for measuring photoelectromotive force of solar cell [(a) – without load; (b) – under load)]

of ratio of photoelectromotive force of the area with the film to the photoelectromotive force of the area without the film. The measurements were carried out at local illumination of the cell surface with use of a light guide with a halogen lamp.

If the effect of the wavelength of optical transmission through the silicon surface without antireflecting film is neglected, photocurrent obtained from an area of a solar cell coated with nanocomposite film can be approximately represented by the following equation:

$$I \approx \frac{T}{T_0} I_0. \quad (7)$$

Optical measurements of nanocomposite films produced by our technique show that the indices of refraction and absorption are close to zero and weakly depend on the wavelength of radiation in the wavelength range of 450 to 1000 nm. In this case, refractive index n_2 is con-

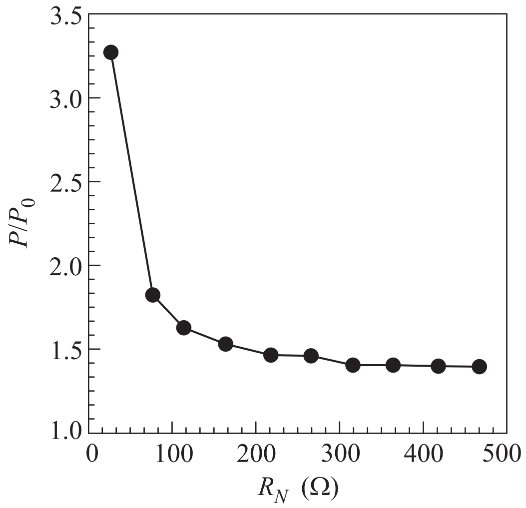

Fig.2. Power relation (product of photocurrent by photoelectromotive force) of solar cell partly coated with nanocomposite film (PMMA+Ag)

siderably higher than absorption coefficient κ_2. In our experiments, we achieved values of n_2 close to 0.015 and values of absorption coefficient κ_2 of the order of 10^{-4}. Under conditions of ideal antireflection, optical transmission T is greater than 1. The following can be written, taking into account ratio (7):

$$\frac{\eta}{\eta_0} = \frac{TU}{T_0 U_0}. \tag{8}$$

The following can be written from comparison of ratios (8) and (6): $U/U_0 = T/T_0$. As shown in Table 3, the following can be achieved under predetermined conditions: $U = 1.8U_0$. The increase in optical transmission of light into silicon with antireflecting coating can be explained by provision of the ideal conditions of antireflection (4). Compared to silicon without antireflection film, silicon coated with such film has increased light transmission by a factor of 1.8. If optical transmission T_0 into silicon without antireflecting film is assumed equal to 0.65, then optical transmission T for silicon coated with antireflection film is equal to 1.18.

Deviation from ideal light transmission, according to which optical transmission into silicon should be equal to 3.4, results from low-ohmic shunting of the solar cell. In the above-described experiments, shunting is caused by illuminating only a part of the solar cell surface, and this corresponds to localized illumination. Probably, in experiments 1 and 2 (see Tables 1 and 2), shunting is much greater than in experiment 3 (Table 3). Therefore, in our experiments, the approximated equation (7) could apply only to cases presented in Table 3.

Thus, we experimentally revealed a gigantic photovoltaic effect (6) that occurred at localized illumination of the surfaces of silicon-type solar cells coated with PMMA+Ag nanocomposite films synthesized in accordance with the technique developed by our research group. It has been shown that coating of solar cell surfaces with such high-efficient antireflecting films leads to considerable increase in photoelectromotive force developed by a solar cell. As seen from the measurement protocols presented in Tables 1, 2, and 3, depending on the situation, the ratios of efficiencies of solar cells with antireflecting coatings and without coatings vary from 1 to 525. Based on the photovoltaic experiments conducted by our research group, it became possible to evaluate optical transmission into silicon with high-efficient antireflecting coating made from optical quasi-zero average complex refractive index materials.

The value of $T/T_0 = 1.8$ was obtained from photovoltaic measurements of the electromotive force and power of a silicon-based solar cell at local illumination of the cell surface. It can be seen that the found value of T/T_0 also remains for integral illumination, and this is a matter of great interest for solar engineering in connection with increase in solar cell efficiency. The increase of efficiency of a solar cell under conditions of integral illumination of the cell surface can be evaluated in terms of the increase in short-circuit current I_{sc}, which is represented by the following formula [3]:

$$I_{sc} = e \int_{\lambda_{\min}}^{\lambda_{\max}} F(\lambda)\, T(\lambda)\, Q(\lambda)\, d\lambda, \tag{9}$$

where e is the electron charge, $\lambda_{\min}$ and $\lambda_{\max}$ are the lower and upper limits of the wavelength range, $F(\lambda)$ is spectral intensity (number of photons absorbed during 1 sec. by 1 m^2 area per unit of the spectral interval) of solar radiation, $T(\lambda)$ is optical transmission through the surface of silicon that is coated with a high-efficient quasi-zero average complex refractive index material, and $Q(\lambda)$ is the quantum yield of solar radiation.

Let us determine the increase in short-circuit current of a cell coated with our antireflecting film as compared to short-circuit current $I_{sc}^{(0)}$ when the surface of a silicon-type solar cell does not have such a coating and transmission of solar radiation into the silicon is defined by the value of T_0. Since optical transmission T_0 of light in the wavelength range of 400 to 1100 nm [4] through the surface of pure silicon weakly depends on the wavelength, the value T_0 in the formula for $I_{sc}^{(0)}$ can be placed beyond the integral symbol. The same can be done in formula (9) for current I_{sc} because at $n_2 \to 0$, $\kappa_2 \to 0$ the indices of refraction and absorption for the high-efficient antireflecting coating only slightly depend on λ. Thus, assuming that the provision of antireflecting coating does not affect the quantum yield for the solar cell, the ratio of short-circuit currents can be written as follows: $I_{sc}/I_{sc}^{(0)} = T/T_0$.

The efficiency η_0 of a solar cell without antireflecting coating is a ratio of maximum power (product of maximum-measured current by maximum voltage) to the density of power flow P of solar radiation under standard illumination conditions (standard test conditions $1000\,\mathrm{W/m^2}$) multiplied by the surface area S of the solar cell [5], i.e.,

$$\eta_0 = \frac{I_{\max}^{(0)} U_{\max}^{(0)}}{PS}. \qquad (10)$$

The values of $I_{\max}^{(0)}$ and $U_{\max}^{(0)}$ are determined by gradually changing the external load of the solar cell. The fill factor is represented by the following ratio:

$$F^{(0)} = \frac{I_{\max}^{(0)} U_{\max}^{(0)}}{I_{sc}^{(0)} U_{oc}^{(0)}}, \qquad (11)$$

where $U_{oc}^{(0)}$ is the idle operation of the solar cell without antireflecting coating. For a solar cell having antireflecting coating, respective values of F, η, $I_{\max}$, $U_{\max}$ and U_{oc} are determined in a similar manner [4]:

$$\eta = \frac{I_{\max} U_{\max}}{PS}, \quad F = \frac{I_{\max} U_{\max}}{I_{sc} U_{oc}}. \qquad (12)$$

The closer the coefficient is to 1, the higher the solar cell efficiency [4].

Let us take into account the fact that fill factors of solar cells with antireflecting coating and without such coating are approximately the same, i.e., that $F^{(0)} \approx F$. Then the ratio of efficiencies (12), (10) can be converted into the following form:

$$\eta = \eta_0 \frac{U_{oc}}{U_{oc}^{(0)}} \frac{T}{T_0}. \qquad (13)$$

Formulas (6) and (13) define the giant photovoltaic effect that occurs at local and integral illuminations of the solar cell surface and the effect that is accompanied by significant increase in cell efficiency. By observing this effect at local illumination, it becomes possible to calculate the ratio T/T_0 of optical transmission, which, as follows from Table 3, reaches 1.8. In principle, this ratio may have a higher value and, if the condition of ideal optical antireflection (4) is observed, this ratio may be as high as 5.23 in the limit for silicon-type solar cells.

Fig.3 illustrates experimentally determined dependence of a silicon-type solar cell that is coated with quasi-zero average complex refractive index nanocomposite film from the hade of optical radiation.

As seen from the results of the experiment, short-circuit current only slightly depends on the hade. In

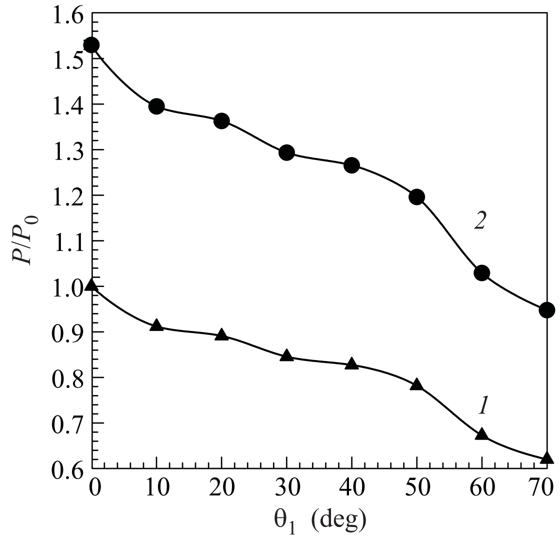

Fig.3. Experimentally obtained dependence of silicon-type solar cell without nanocomposite film (*1*) and solar cell coated with PMMA+Ag nanocomposite film with 3-wt.% content of silver (*2*) ($R_N = 164\,\Omega$)

Fig.3, curve 1 corresponds to the silicon-type solar cell from the surface of which the antireflecting coating was removed. Curve 2 corresponds to the silicon-type solar cell, the surface of which was coated with antireflecting coating made from the materials developed by our research group.

Taking into account weak dependence of short-circuit currents from the hade, let us consider the following algorithm for evaluating efficiency of solar installations. Assume that W is energy consumption (W·hr) assigned by a customer. Then, according to formula (10), the surface area of the solar installation will be determined according to the following formula:

$$S = \frac{W}{\int_0^{\Delta T} \eta_{\exp}^{(0)}(t)\, P(t)\, dt}, \qquad (14)$$

where ΔT is the length of a light day; $P(t)$ is the density of lower flow ($\mathrm{W/m^2}$) of solar radiation as a function of time; and $\eta_{\exp}^{(0)}(t)$ represents experimental values of solar cell efficiency during a light day when the solar cell is not coated with the high-efficient antireflecting coating.

Let us designate the surface area of the solar installation coated with the high-effective antireflecting coating as S' ($\mathrm{m^2}$). Then, the following expression will be obtained at a given value of energy consumption W:

$$\frac{\int_0^{\Delta T} \eta_{\exp}(t)\, P(t)\, dt}{\int_0^{\Delta T} \eta_{\exp}^{(0)}(t)\, P(t)\, dt} = \frac{S}{S'}. \qquad (15)$$

where $\eta_{\exp}(t)$ is the experimentally obtained efficiency value of a solar installation having surface area S coated with a high-efficient antireflecting film. Taking into account the experimental results shown in Fig.3, we obtain the following: $(S/S') \approx 2.2$.

In other words, use of high-efficient optical antireflecting coatings produced from synthesized quasi-zero average complex refractive index material invented by our research group makes it possible to reduce surface area of the solar installation at a given energy consumption. This means that efficiency of the solar installation increases by a factor of (S/S'). Note that in measurements shown in Fig. 3, efficiency of the solar cell that was not coated with antireflecting coating at normal direction of the external radiation was equal to 13%.

Thus, based on experimental data shown in the present article, it is confirmed that use of the nanostructured films developed by our research group leads to considerable increase of efficiency in silicon-type solar cells. Giant photovoltaic effect is caused by a significant enhancement in the optical transmission of light inside the silicon plate, when the relation of optical transmission of the silicon film with and without the film becomes much greater than unity. In this case, the absolute optical transmission becomes, according to that observed experimentally giant photovoltaic effect, greater than unity, which corresponds to the enhancement of optical radiation. This property of optical transmission is consistent with the condition of an ideal optical enlightenment (4), which can be reached at the reference in zero of complex refractive index of the nanocomposite film. Optical materials, synthesized by our research group, have quasi-zero values of indices of refraction and absorption [6]. Thus the amplitudes of optical reflection and transmission for layer is a coherent superposition of amplitudes (1) and (3) with indices of refraction and absorption from area of quasi-zero values. Thus obtained the formula for the reflection and transmission amplitudes allow to compute the corresponding reflectance and transmittance of the layer are in good agreement with the experimental spectra of optical reflection and transmission. The analysis of these spectra on the basis that we developed macroscopic and microscopic approaches will be presented in a separate article. Optical properties of our films are such that they only slightly depend on optical properties of the underlying medium and therefore can be used to improve efficiency for solar cells manufactured from other materials as well.

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