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Antireflection Nanocomposite Thick Film Coatings with Quasi-Zero Refractive Index for Solar Cells

O. N. Gadomsky*, I. A. Shchukarev, and E. A. Pereskokov
Ulyanovsk State University, Ulyanovsk, 432017 Russia
**e-mail: famous_lynx@mail.ru*

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Abstract—Application of nanostructured composite coatings with a quasi-zero refractive index synthesized using the proposed patented technology provides a 25–30% increase in the efficiency of solar cells as compared to that of analogous solar cells with traditional (e.g., silicon nitride) single-layer interference antireflection coating.

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There are various well-known types of interference antireflection coatings for silicon solar cells [1], which employ the principle of interferometric blooming to reach minimum reflection and maximum transmission at a preset wavelength under stringent conditions for the thickness and refractive index of the coating [2, 3].

Previously, we reported [4, 5] on development of the patented synthesis technology [6, 7] of composite materials containing silver nanoparticles. The results of measurements of the reflection and transmission spectra of these composite films on glass and ceramics showed that the synthesized coatings actually possess a quasi-zero refractive index in a broad interval of wavelengths (from 450 to 1200 nm) and small ($\sim 10^{-3}$) absorption. The optical properties of layers of these composites are close to theoretical predictions [8] according to which the exact zero of the refractive index implies that the amplitude of reflected light wave vanishes and the amplitude of transmitted light wave is equal to that of the incident wave. The effect of ideal optical blooming is independent of the angle of incidence, wavelength, layer thickness, and optical properties of the surrounding media. The interference of light in thick composite layers was experimentally observed, and the arrangement of interference minima was used to calculate the quasi-zero refractive index [9]. Experiments confirmed the amplification and focusing of light in a composite layer [10] and the possibility of broadband optical blooming of silicon in a wavelength interval of 450–1000 nm, where a 30-μm-thick single-layer coating ensured a homogeneous decrease in silicon reflectance from 35 to 5% [11]. A theory of the optical properties of composite layers has been developed that adequately describes the experimental spectra [12] and allows new effects to be predicted.

The present work was aimed at demonstrating using the aforementioned phenomena that antireflection coatings of nanocomposite materials with quasi-zero refractive index are free of disadvantages inherent in conventional interferometric antireflection coatings presently used in solar cell technology.

It is important to note that, in comparison to other metamaterials (see, e.g., [13]), a specific feature of the proposed composites is that quasi-zero refractive index is achieved in a broad wavelength interval (at least from 450 to 1200 nm), which is related to the fact that the resonance frequency of silver nanoparticles occurs in the UV range at about 300 nm.

The quality of an antireflection coating is determined by measuring its optical transmittance on a glass substrate. As can be seen from Fig. 1, a polymer film on glass (curve *3*) naturally decreases the transmission of glass. Composite layers increase the transmission of glass in some cases by about 5% (curves *6* and *7*) and up to 8% in other cases (curves *4* and *5*). Silver nanoparticles with radii of about 2.5 nm were uniformly dispersed in all composite layers. The proposed technology of composite synthesis [6, 7] stipulates the formation of stabilizing shells on the surface of silver nanoparticles. The refractive index of these shells coincides with the refractive index of a dielectric matrix. In the samples presented in Fig. 1, this matrix represents polymethylmethacrylate (PMMA) with a refractive index of 1.492.

The energy efficiency of a solar cell according to commonly accepted definition is calculated as

$$\eta = \frac{FFV_{oc}I_{sc}}{EA_c},$$

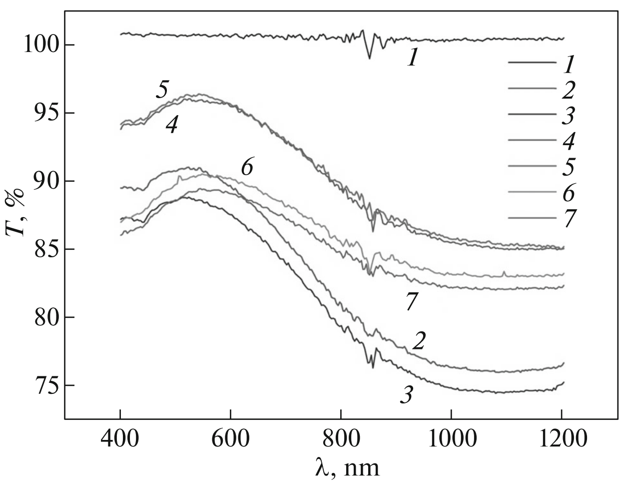

Fig. 1. Experimentally measured spectra of optical transmittance T of polymer and composite films on glass substrate, (*1*) instrument transmission without a sample, (*2*) clean glass substrate, (*3*) sample with a 17-μm-thick polymer film, and (*4–6*) samples with 17-μm-thick composite films pneumatically applied in different modes (silver content, 5 wt %).

where FF is the fill factor determining the ratio of the maximum power to $V_{oc}C_{sc}$ product, V_{oc} is the open-circuit voltage, I_{sc} is the short-circuit current, E is the irradiance (W/m^2), and A_c is the surface area (m^2).

The efficiency of an antireflection coating for solar cells is conventionally determined using the short-circuit photocurrent [1]. The number of photons $N(\lambda)$ in the corresponding formula can be calculated using the solar radiation spectrum [1] and dividing $E(\lambda)$ by photon energy $\hbar\omega(\lambda)$ at the corresponding wavelength. Numerical estimate of the efficiency of a traditional interferometric single-layer antireflection coating based on a diamond-like carbon film was obtained in [4] for a film with a refractive index of about 2, absorbance of about 0.1, and thickness of about 80 nm. The radiation intensity for AM 1.5 and AMD conditions was calculated using data on the solar spectrum [1]. The quantum yield was assumed to be $Q = 1$, which implies that every photon generates an electron–hole pair in silicon. The zenith angle in these calculations was set to be zero. The optical transmittance of diamond-like carbon films strongly depends on the wavelength in the interval from $\lambda_{min} = 0.4$ μm to $\lambda_{max} = 1.11$ μm and reaches maximum $T = 0.9$ at 675 nm. The short-circuit current of silicon solar cell without antireflection coating was $I_{sc} = 33.261$ mA/cm^2 at AM 1.5 and $I_{sc} = 42.484$ mA/cm^2 at AMO. The coating thickness was set to be 96 nm.

Let us write an expression for the short-circuit current of silicon solar cell as dependent on the current time t during a day, e.g., from midday to sunset. Taking into account the formula of short-circuit photocurrent [1] and the expression for the spectral density of solar radiation and using the notion of air mass, we eventually obtain the following formula:

$$I_{sc} = e \times 0.7^{(AM(\theta)^{0.678})} \int_{\lambda_{min}}^{\lambda_{max}} \frac{dN(\lambda)}{d\lambda} T(t,\lambda) Q(t,\lambda) d\lambda.$$

Here, $N_0(\lambda)$ is the number of photons in AMO radiation at wavelength λ incident per unit time on unit area of solar cell, $T(t, \lambda)$ is the optical transmittance as dependent of the current time and wavelength, $Q(t, \lambda)$ is the quantum yield of solar cell as function of t and λ, $AM(\theta)$ is a dimensionless quantity dependent on zenith angle θ according to an empirical formula [1], and the zenith angle varies with time as

$$\cos\theta(t) = \sin\delta\sin\varphi + \cos\delta\cos\varphi\cos(\omega(t)),$$

where δ is the declination, φ is the geographic latitude, and $\omega(t)$ is the hour angle calculated as $\omega(t) = 15°(t - 12)$. Assuming that $\delta = 7.53°$ and $\varphi = 56°$, we can determine the ratio $I_{sc}(t)/I_{sc}(t_0)$, where t_0 is the initial moment of time.

The optical transmittance (transmission capacity) of the composite layer with a quasi-zero refractive index is calculated using the formula for T_{123}^p [12], where index p corresponds to allowance for the two p-polarized waves (inside and outside the layer) [4]. According to [10–15], the refractive index of a composite layer is a random quantity with a distribution function having the maximum at some n_2 inside the indicated interval. The ratio $S_3/S_1 > 1$ corresponds to the so-called "tulip" effect [15]. The value of $|t_{123}^p|_1$ term in [12] is determined as

$$|t_{123}^p|_1 = 1 - \frac{i(t_{12}^p)_1(t_{23}^p)_1}{k_0 d_2 \cos\theta_T} F((r_{12}^p)_1(r_{23}^p)_1), \quad (1)$$

$$F(x_0) = \frac{1}{\sqrt{x_0}}\left(\arctan\left(\frac{\Phi_2}{\sqrt{x_0}}\right) - \arctan\left(\frac{1}{\sqrt{x_0}}\right)\right), \quad (2)$$

$$x_0 = (r_{12}^p)_1(r_{23}^p)_1,$$

$$\Phi_2 = \exp(ik_0 d_2 \Delta n_2 \cos\theta_{T1}), \quad k_0 = 2\pi/\lambda, \quad (3)$$

where d_2 is the composite layer thickness; θ_{T1} is the angle of refraction at the 1–2 interface of the composite layer; and $(r_{12}^p)_i$, $(r_{23}^p)_i$, $(t_{12}^p)_i$, $(t_{23}^p)_i$ are the non-Fresnel reflection and refraction coefficients at the layer boundaries [12]. Analogous expression can be written for $|t_{123}^p|_2$ term. The corresponding values for s-polarized can be determined in the same manner.

The reflectance of the composite layer with a quasi-zero refractive index for p-polarized waves is determined by the formula for R_{123}^p [12], in which the term

$$(r_{123}^p)_1 = r_{12}^{(1)}\Delta n_2 + i\frac{1-(r_{12}^p)^2}{2r_{12}^{(1)}k_0 d_2\cos\theta_{T1}} \ln\left|\frac{1 + r_{12}^{(1)}r_{23}^{(1)}\Phi_2^2}{1 + r_{12}^{(1)}r_{23}^{(1)}}\right| \quad (4)$$

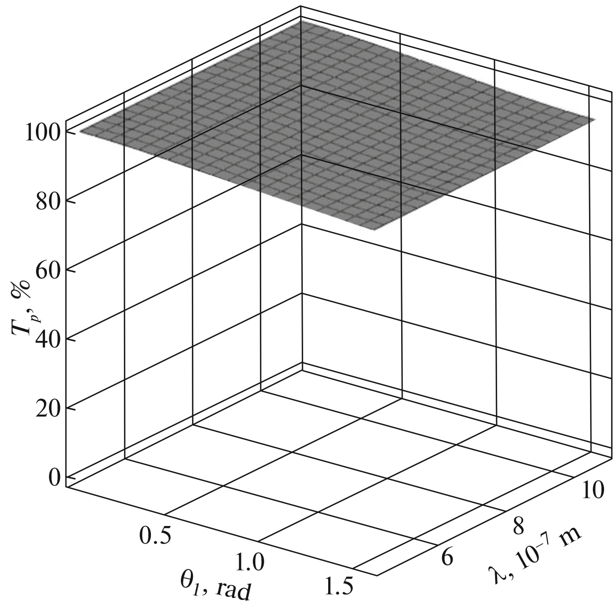

Fig. 2. Transmittance of a composite layer with quasi-zero refractive index on the angle of incidence θ_1 (varied from 1° to 89°) and wavelength (varied from 450 to 1000 nm); $n_3 = 3.4$ (silicon); composite layer thickness, $d_2 = 30$ μm; $\Delta n_2 = 0.36$; $\gamma_2 = 0.78$; $n_2 = 0.29$; $S_0/S_1 = 1.1236$; $\cos\theta_{T3} = \sqrt{1-(\sin\theta_1/n_3)^2}$.

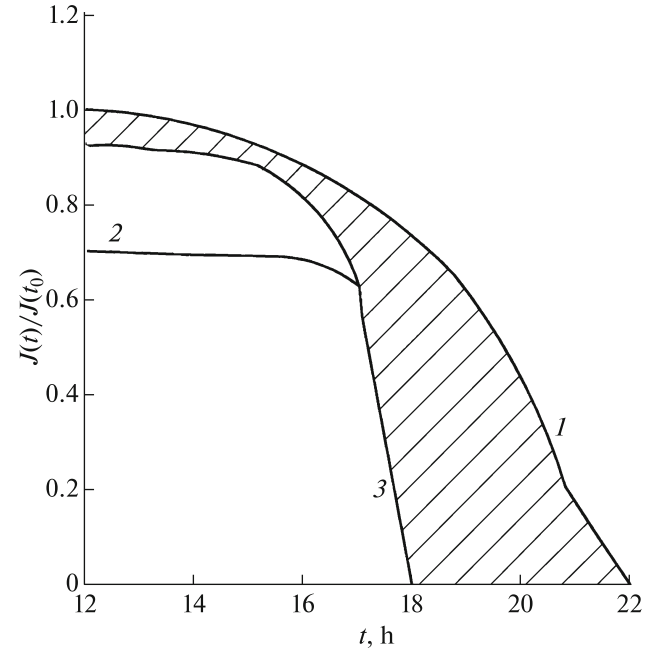

Fig. 3. Temporal variation of the relative photocurrent of silicon solar cells during daylight hours: (*1*) solar sell with high-efficiency composite antireflection coating, (*2*) pure silicon solar cell without coating, and (*3*) silicon solar cell with interferometric antireflection coating of silicon nitride with a refractive index of 2.02.

is defined via non-Fresnel reflection coefficients [12] and the value of $(r_{123}^{3})^2$ is obtained from Eq. (4) by replacing $r_{12}^{(1)}$, $r_{23}^{(1)}$ with $r_{12}^{(2)}$, $r_{23}^{(2)}$.

Optical transmittance T_{123}^{p} can be approximated by the following formula:

$$T_{123}^{p} = 2\frac{n_3 S_0 \cos\theta_{T3}}{S_1}(\Delta n_2)^2,$$

which is obtained by taking into account that $t_{123}^{(1)}$, $t_{123}^{(2)} \sim 1$ and $S_3 = S_0\cos\theta_1$. The ratio S_0/S_1 is determined from the normalization condition $T_{123}^{p} + R_{123}^{p} = 1$. This formula explains the almost wavelength-independent optical transmittance observed in experimental spectra of the composite layer. Figure 2 shows the dependence of transmittance T_{123}^{p} on the angle of incidence and wavelength for real angles of refraction in the composite layer obeying the following relations:

$$\gamma_2 = \sin\theta_{T1}, \quad \cos\varphi_2 = \sqrt{1-n_2^2\gamma_2^2},$$
$$\cos\theta_{T1} = \sqrt{1-\gamma_2^2}.$$

Figure 3 presents plots of the silicon solar cell photocurrent versus time, where the cross-hatched region shows the reserve of photocurrent increase that can be achieved with the aid of the proposed composite antireflection coatings due to the weak dependence of the optical transmittance of this composite on the wavelength and angle of incidence of solar radiation. Calculations were performed for the natural light and optical transmittance defined as the arithmetic mean of that for *s*- and *p*-polarized waves. As can be seen, the reserve of photocurrent increase due to antireflection coatings with quasi-zero refractive index amounts to 25–30% relative to the photocurrent obtained using traditional interferometric antireflection coatings.

Thus, we have demonstrated that, due to a significant increase in the time of effective generation of electric energy, the solar cells with the proposed composite antireflection coating provides for a 25–30% increase in the amount of energy generated during daylight hours as compared to that obtained using a traditional interferometric antireflection coating and for an about 40% increase as compared to the same solar cell without any antireflection coating. This effect is equivalent to the use of sun trackers [1] jointly with black silicon based solar cells. Another very important property of the proposed composite layers with a quasi-zero refractive index is that their optical properties weakly depend on those of the substrate. This means that a 25% increase in the efficiency of commercial solar cells can be achieved by merely applying one layer of our composite on their surface with existing antireflection coatings of various types.

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