REGULAR ARTICLE



Improvement of the Physical and Technical Characteristics of the Thin-Film Solar Cells under their Modification by the Plasmonic Nanoparticles

A.V. Korotun^{1,2,*} , S.I. Shylo¹, V.I. Reva¹, I.M. Titov¹

¹ Zaporizhzhia Polytechnic National University, 69063 Zaporizhzhia, Ukraine
 ² G.V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine, 03142 Kyiv, Ukraine

(Received 03 January 2025; revised manuscript received 15 February 2025; published online 27 February 2025)

This work deals with the study of such an important task of plasmonic photovoltaics as the improvement of thin-film solar cells by introducing metal nanoparticles into their absorbing layer. The frequency dependences of photocurrent amplification, radiation efficiency and electric field amplification in the neighborhood of the nanoparticles, as well as an expression for volt-ampere characteristic of Schottky barrier formed at the boundary of metallic nanoparticle and the semiconductor absorbing layer are obtained. The mathematical model, proposed in this work, takes into account all mechanisms of electron relaxation in metallic nanoparticle. The calculations have been performed for the case of Ag and Pt nanoparticles embedded into TiO2 and Si layer. The fact of the significant amplification, of photocurrent with decreasing the thickness of the absorbing layer and increasing the radius of embedded plasmonic nanoparticles has been established. In this case, the spectral range of thin-film solar cells is determined by the properties of the semiconductor, primarily by the width of the forbidden zone of the absorbing layer. The calculations showed the weak size dependence of the frequency of the surface plasmonic resonance and the strong dependence of the position of the maxima of the spectral characteristics on the material properties of the nanoparticles and the absorbing layer. It has been demonstrated the advantage of silver nanoparticles over platinum nanoparticles, as they provide greater radiation efficiency at the same frequencies. The results of the calculations of the frequency dependences of the amplification of electric fields in the neighborhood of plasmonic nanoparticles indicate its growth with decreasing radius of platinum nanoparticles, while the highest maximum value of the amplification will be in the neighborhood of silver nanoparticles of intermediate sizes, which is explained by the weakening of the process of electron relaxation in silver nanoparticles of such sizes. The sharp (3-4 orders of magnitude) increase in the current in the modified solar cells compared to conventional ones at voltages exceeding the Schottky barrier is shown, which is explained by the excitation of plasmonic resonances on the surface of metallic nanoparticles.

Keywords: Thin-film solar cell, Spherical metallic nanoparticle, Photocurrent, Plasmonic resonance, Volt-ampere characteristics.

DOI: 10.21272/jnep.17(1).01013 PACS numbers: 79.60.Bm, 84.60.Jt

1. INTRODUCTION

One of the most interesting properties, demonstrated by metallic nanoparticles, is their strong resonance response to electromagnetic fields. In general case, when photons interact with metallic nanoparticle whose size is comparable to or smaller than the wavelength of light, they can induce collective coherent oscillations of conduction electrons. For the nanoparticles, these oscillations occur at the specific frequency known as the localized surface plasmonic resonance frequency (SPR) [1, 2]. The result of this interaction has two aspects. On the one hand there is efficient photon scattering, which makes plasmonic nanoparticles important for applications involving photon rescattering in waveguides, for capturing light inside the thin-film solar cells, and in optical computing, requiring efficient light deflection in small volumes [3-7]. On the other hand, plasmonic resonances are also associated with enhanced absorption of photons by the nanoparticles. The subsequent conversion of this absorbed energy for the generation charge carriers and/or phonons is used in applications such as photocatalysis, photothermal imaging and cancer therapy, plasmonic heating and heated magnetic recording [5, 8-11]. In addition, the excitation of plasmonic resonances on the surface of nanoparticles, embedded into the semiconductor layer, leads to the amplification of photoemission current and, as a consequence, to the improvement of the technical characteristics of photodetectors [12]. In this context, one of the most important challenges in the field of plasmonic nanostructures is to understand how to tune and/or control the plasmonic interaction process so that the nanostructures can be optimized to enhance either radiative or absorptive (non-radiative) effects.

The properties of resonant plasmonic interaction such as the position of the plasmon frequency and the resonance intensity, determined by the resonance bandwidth, depend on the shape, size, and material of the nanoparticle and the environment [5, 13-15]. Thus,

2077-6772/2025/17(1)01013(8)

01013-1

https://jnep.sumdu.edu.ua

^{*} Correspondence e-mail: andko@zp.edu.ua

it is natural to expect that the optimization of radiation and non-radiation effects will also depend on these factors. Indeed, as was first demonstrated in [13], it is possible to tune the bandwidth of plasmons by changing the shape of the nanoparticle so that the predominant process inside the nanoparticle is the process of radiation damping. Since it is not always easy to change the shape of the nanoparticle, other ways of tuning the plasmonic properties are being sought.

Metallic nanoparticles are embedded into the absorbing layer of the thin-film solar cells in order to use the effect of localized surface plasmonic resonance (SPR), which is considered to be the promising approach to improve their efficiency. Such solar cells are seen as an important alternative to the conventional solar cells on poly (mono) crystal silicon wafers because of their low cost [16, 17], due to less material consumption and lower production cost. However, thin-film solar cells are severely limited in the practical application due to their weak absorption of visible light [3, 18]. Adding metallic nanoparticles to the absorbing layer and using SPR phenomenon is an effective means of increasing the light absorption cross-section of such solar cells.

The excitation of surface plasmons is doubly useful for the solar cells. On the one hand, plasmons serve as the powerful scattering center for incident photons, and on the other hand, they create the strong local electric field near the particle, which can support dissociation of excitons in the semiconductor [19]. In the work [20] the introduction of Ag nanoparticles into the absorbing Si layer was considered and it was found that such a structure has greater light absorption than conventional thin-film solar cells. In [21] it was found that the total efficiency of the thin film solar cells improved significantly after introducing 0.1 % Au nanoparticles into them. In the work [22] the possibility of optimizing the characteristics of the thin-film solar cells by introducing arrays of the spherical nanoparticles of the different composition and morphology into them was investigated. This work also provided practical recommendations on the size, structure and composition of the nanoparticles to minimize the reflection coefficient and maximize the radiation efficiency in the visible region of the spectrum.

However, the issues of research of the photocurrent amplification, improvement of the other physical and technical characteristics of the solar cells due to the selection of nanoparticle materials and absorbing layer are presented fragmentarily in the scientific literature, and therefore are actual.

2. PHYSICAL PRINCIPLES OF FUNCTIONING AND MATHEMATICAL MODEL OF PLAS-MONIC SOLAR CELLS

2.1 Principles of Operation of the Thin-Film Solar Cells, Modified by Metallic Nanoparticles

Let us consider the thin-film solar cell, in the absorbing layer of which the spherical metallic nanoparticles of radius R are embedded (Fig. 1).

The great efficiency of the energy transfer in the near-field regime from the plasmons, excited on the nanoparticle surface, to the semiconductor substrate – even if this efficiency is reduced by geometrical factors, i.e., taking into account the magnitude β (ratio of the contact area to the nanoparticle surface area, Fig. 2) – is mainly determined by the contribution from all interzone transitions, which are not forbidden in this case, and not only from direct (vertical) ones, as in the case of the ordinary photoeffect – due to the significant change in quasimomentum of electrons.

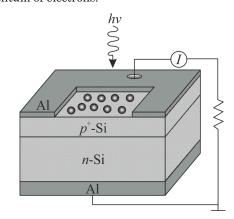


Fig. 1 – The scheme of the thin-film solar cell with embedded spherical metallic nanoparticles [23]

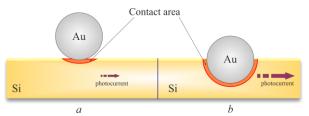


Fig. 2 – The illustration of the dependence of photocurrent in the semiconductor, modified by metallic nanoparticles, on the relative area of contact [24]

Figure 3 shows the schematic-scenario of the energy transfer from photon, incident on diode structure, modified by the nanoparticles, to the semiconductor substrate: the energy from the incident light wave is transferred to the plasmonic dipole oscillation on the surface of the metallic nanoparticle and is immediately fully absorbed by the semiconductor in the near-field regime.

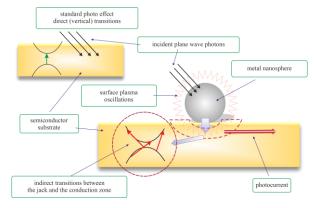


Fig. 3 – The scheme of the photoeffect involving metallic nanoparticles and semiconductor substrate [24]

In the conditions of the steady-state process, i.e. at balance of energy of photons, interacting with metallic nanoparticles, and energy, transferred from plasmonic oscillations to electrons in the semiconductor substrate, one can say that there is the stable transformation of light energy into photocurrent. In this case, the described picture is significantly different from the direct conversion of the energy of photons, absorbed by unmodified solar cells. In the model, which is proposed in the present work, plasmons interact with electrons through near-field photonless electromagnetic dipole-dipole interactions, occurring over the small time interval. Therefore, the increase in the probability of electronic transitions due to the increase in the probability of all kinds of indirect interzone transitions in the semiconductor under the excitation of surface plasmonic oscillations in metallic nanoparticles, located on the semiconductor substrate, is the reason for the experimentally observed significant enhancement of light absorption by the semiconductor and the increase in photocurrent [25–28].

2.2 Photocurrent amplification

The current amplification in the photocell due to the excitation of the surface plasmonic resonance is determined by the relation [24]

$$\frac{I_m(\omega)}{I(\omega)} = 1 + \frac{q_m}{q} \,, \tag{1}$$

where the probability of energy transfer of single incident photon to the semiconductor due to the excitation of plasmonic resonance on the surface of the metallic nanoparticle

$$q_{m} = \frac{\beta C_{0} e^{2} \omega^{2} \mathcal{A}_{f}^{2}(\omega) R^{3}}{8 \pi^{6} \hbar^{4} \epsilon_{m}} \frac{\left(m_{n}^{*} m_{p}^{*}\right)^{3/2}}{m_{n}^{*} + m_{p}^{*}} (\hbar \omega - \Delta E_{g}), \qquad (2)$$

and the probability of the energy absorption in the semiconductor per one photon

$$q = \frac{2\sqrt{2}}{3\pi^6} \frac{e^2 \left(\hbar\omega - \Delta E_g\right)^{3/2}}{\hbar^3 \omega \epsilon_m m_p^{*2}} \left(\frac{m_n^* m_p^*}{m_n^* + m_p^*}\right)^{5/2}, \tag{3}$$

where m_n^* and m_p^* are effective masses of electrons and holes; ΔE_g is the width of the forbidden zone; $\epsilon_{\rm m}$ – dielectric permittivity of the solar cell substance;

$$C_0 = \frac{4\pi R^3}{3} \frac{n_s}{H},$$
 (4)

where H is the thickness of the thin-film element; n_s is the surface density of metallic nanoparticles, and the amplitude function

$$\mathcal{A}_f(\omega) = \frac{\omega_{sp}^2}{\sqrt{\left(\omega_{sp}^2 - \omega^2\right)^2 + 4\gamma_{\text{eff}}^2 \omega^2}},$$
 (5)

In formula (5) ω_{sp} is the frequency of the surface plasmonic resonance, and $\gamma_{\rm eff}$ is effective electron relaxation rate in the nanoparticle

$$\gamma_{\text{eff}} = \gamma_{\text{bulk}} + \gamma_{\text{s}} + \gamma_{\text{rad}}$$
, (6)

where bulk relaxation rate $\gamma_{bulk} = const\,$ for certain metal, and surface relaxation rate and radiation damping rate

$$\gamma_{\rm s} = \mathcal{N}(\omega, R) \frac{v_{\rm F}}{R},$$
 (7)

$$\gamma_{\rm rad} = \frac{V}{6\pi} \sqrt{\frac{\epsilon^{\infty} + 2\epsilon_{\rm m}}{\epsilon_{\rm m}}} \left(\frac{\omega_{p}}{c}\right)^{3} \mathscr{N}(\omega, R) \frac{v_{\rm F}}{R}, \qquad (8)$$

In formulas (7) and (8): $v_{\rm F}$ is Fermi electron velocity; $V=4\pi R^3/3$ is the volume of the nanoparticle; ω_p is plasma frequency; ϵ^∞ is the contribution of interzone transitions into the dielectric function, and the size-frequency dependence of the coherence loss parameter has the following form [29]

$$\mathscr{N}(\omega, R) = \frac{3}{4} \frac{1}{\epsilon^{\infty} + 2\epsilon_{\mathrm{m}}} \left(\frac{\omega_{p}}{\omega}\right)^{2} \times \left[1 - \frac{2\nu_{s}}{\omega} \sin \frac{\omega}{\nu_{s}} + 2\left(\frac{\nu_{s}}{\omega}\right)^{2} \left(1 - \cos \frac{2\nu_{s}}{\omega}\right)\right], \tag{9}$$

where $v_s = v_{\rm F}/2R$ is the frequency of the individual oscillations of electrons.

Substituting (2), (3) into (1), we obtain

$$\frac{I_{m}(\omega)}{I(\omega)} = 1 + \frac{3\beta C_{0} R^{3}}{16\sqrt{2}\hbar} \frac{\omega^{2} \mathcal{A}_{f}^{2}(\omega)}{\left(\hbar\omega - \Delta E_{g}\right)^{1/2}} \frac{m_{p}^{*}}{m_{n}^{*}} \left(m_{n}^{*} + m_{p}^{*}\right)^{3/2}. \quad (10)$$

2.3 Frequency of the surface plasmonic resonance

Let us find the frequency of the surface plasmonic resonance from the condition

$$\operatorname{Re} \epsilon \left(\omega_{sp} \right) + 2\epsilon_{\mathsf{m}} = 0 \,, \tag{11}$$

where, according to Drude model, the real part of the dielectric function

$$\operatorname{Re}\epsilon\left(\omega_{sp}\right) = \epsilon^{\infty} - \frac{\omega_{p}^{2}}{\omega_{sp}^{2} + \gamma_{\text{eff}}^{2}\left(\omega_{sp}\right)},\tag{12}$$

and the dependence $\gamma_{\rm eff}\left(\omega_{sp}\right)$ can be obtained from the formulae (6) – (9) under the condition $\omega=\omega_{sp}$.

The equation for the determination of ω_{sp} follows from the relations (11) and (12):

$$\omega_{sp}^2 + \gamma_{\text{eff}}^2 \left(\omega_{sp} \right) = \frac{\omega_p^2}{\epsilon^{\infty} + 2\epsilon_{\text{m}}}, \qquad (13)$$

In the near-infrared and visible parts of the spectrum the condition $v_s \ll \omega$ is true, therefore the oscillating addends compared to unity can be neglected in the square brackets of the expression (9). Then the expression (6), taking into account the relations (7) – (9),

has the form

$$\gamma_{\rm eff} \left(\omega_{sp} \right) = \gamma_{\rm bulk} + \frac{\mathscr{X}}{\omega_{sp}^2} ,$$
 (14)

where

$$\mathcal{X} = \frac{3}{4} \frac{\omega_p^2}{\epsilon^\infty + 2\epsilon_{\rm m}} \frac{v_{\rm F}}{R} \left\{ 1 + \frac{2}{9} \sqrt{\frac{\epsilon^\infty + 2\epsilon_{\rm m}}{\epsilon_{\rm m}}} \left(\frac{\omega_p R}{c} \right)^3 \right\}. \tag{15}$$

Substituting (14) into (13), we obtain sixth degree equation for determining the frequency of SPR

$$\omega_{sp}^{6} - \left(\frac{\omega_{p}^{2}}{\epsilon^{\infty} + 2\epsilon_{m}} - \gamma_{\text{bulk}}^{2}\right) \omega_{sp}^{4} +$$

$$+ 2\gamma_{\text{bulk}} \mathscr{N} \omega_{sp}^{2} + \mathscr{N}^{2} = 0,$$
(16)

which gives an opportunity to study its size dependence.

2.4 Field Amolification in the Neighborhood of Nanoparticles and Radiation Efficiency

The frequency dependencies of the radiation efficiency and amplification of electric fields in the neighborhood of the plasmonic nanoparticle, embedded into the absorbing layer, are given by the relations

$$\xi_{\rm rad} = \frac{1}{1 + \frac{C_{\rm abs}}{C_{\rm sca}}} \,. \tag{17}$$

$$\mathcal{G} = \left| 1 + \frac{2\alpha}{r^3} \right|^2, \tag{18}$$

where the absorption cross-section and scattering cross-section

$$C_{\rm abs} = \frac{\omega}{c} \sqrt{\epsilon_{\rm m}} \, {\rm Im} \, \alpha \,, \tag{19}$$

$$C_{\rm sca} = \frac{1}{6\pi} \frac{\omega^4}{c^4} \epsilon_{\rm m}^2 \left| \alpha \right|^2, \tag{20}$$

polarizability of the spherical metallic nanoparticle

$$\alpha(\omega) = R^3 \frac{\epsilon(\omega) - \epsilon_{\rm m}}{\epsilon(\omega) + 2\epsilon_{\rm m}} . \tag{21}$$

and for the dielectric function, we will consider Drude model to be valid, according to which

$$\epsilon(\omega) = \epsilon^{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma_{\text{eff}})}.$$
 (22)

2.5 Volt-Ampere Characteristics of Schottky Barrier

When plasmonic nanoparticles are embedded into the absorbing semiconductor layer, Schottky barrier appears. Such a barrier is described by the volt-ampere characteristic, which, taking into account the excitation of plasmonic resonance on the surface of the nanoparticle, has the form

$$I = I_s \left[e^{\frac{e\left(U - IR_s\left(1 + \frac{q_m}{q}\right)^{-1}\right)}{\eta k_B T}} - 1 \right], \tag{23}$$

where the reverse saturation current

$$I_s = SA^*T^2 e^{-\frac{e\varphi_B}{k_BT}}$$
 (24)

In formulae (23) and (24): T is temperature; $k_{\rm B}$ is Boltzmann constant; A^* is the effective Richardson constant; η is barrier non-ideality factor; $\varphi_{\rm B}$ is the height of Schottky barrier; $R_{\rm s}$ is series resistance.

Further calculations will be performed according to the formulas (10), (16) - (18), (23) taking into account the expressions (4) - (9), (14), (15), (19) - (22) and (24).

3. RESULTS AND THEIR DISCUSSION

The calculations were performed for the cases of nanoparticles Ag and Pt, embedded into the absorbing layers ${\rm TiO_2}$ and Si. The parameters of materials, necessary for the calculations, are given in Tables 1 and 2.

Table 1 – The parameters of metals (a_0 is the Bohr radius) (see, for example, [29-31] and references therein)

Metals	Value					
	r_s / a_0	m^* / m_e	ϵ^{∞}	$\hbar\omega_p$, eV	$\hbar \gamma_{bulk}, eV$	
Ag	3.02	0.96	3.7	9.17	0.016	
Pt	3.27	0.54	4.42	15.2	0.069	

Table 2 – The parameters of the semiconductors [32,33].

1	Semiconductor			
Value	n-Si	$n\text{-TiO}_2$		
m_n^*/m_e	0.98	0.54		
m_p^*/m_e	0.52	1.79		
ΔE_g , eV	1.14	3.20		
$\epsilon_{ m m}$	12	6		

Table 3 – The parameters of Schottky barriers [33,34]

	Barrier				
Value	Pt / n-Si	$\operatorname{Pt}/\operatorname{\textit{n-}TiO}_2$	${\rm Ag}/n\text{-TiO}_2$		
R_s , Ω	80	1480	720		
η	1.1	1.74	1.35		
ϕ_B,eV	0.81	0.87	0.91		
$A^*, rac{A}{\mathrm{cm}^2 \cdot \mathrm{K}^2}$	28	24	24		

The frequency dependences of photocurrent amplification for the thin-film solar cells, modified with spherical Ag and Pt nanoparticles, for the cases of nanoparticles of the different radius and absorbing layers of the different thickness are given in Fig. 4. The significant increase in photocurrent with increasing radius of embedded plasmonic nanoparticles and with decreasing thickness of the absorbing layer is the general trend for the above curves. The introduction of the large nanoparticles into the small thickness absorbing layer is the complicated technological task from the practical point of view. Therefore, there are constraints from above on the radius of the plasmonic nanoparticles and from below on the thickness of the semiconductor layer. The increase in photocurrent with increasing nanoparticle radius is explained by the enhancement of the scattering on nanoparticles as their volume increases (see, for example, [29]). Moreover, it should be pointed out the qualitative difference between the curves $I_m(\omega)/I(\omega)$ for the solar cells with the different absorbing layers and modified by the nanoparticles of different metals. Thus, in the case of the modification of the solar cells by Pt particles, the indicated curves have maximums, while in the case of embedded Ag particles there is a weak monotonic decrease in photocurrent with increasing frequency. Such behavior of the curves $I_m(\omega)/I(\omega)$ can be explained by the fact that their maximums for the structures Pt/Si and Pt/TiO2 correspond to the frequencies of the surface plasmonic resonance, while $\hbar\omega_{sp}^{\rm Ag}<\Delta E_g^{\rm TiO_2}$, and the domain of definition of the function $f(\hbar\omega) = I_m(\hbar\omega)/I(\hbar\omega)$ is $\hbar\omega > \Delta E_g$.

The size dependencies for the frequencies of the surface plasmonic resonance, obtained from the solution of the equation (16), are presented in Fig. 5. Let us point out that in the case of nanoparticles ${\rm Ag/TiO_2}$ the frequency of SPR is almost independent on the radius, and in the case of nanoparticles ${\rm Pt/Si}$ and ${\rm Pt/TiO_2}$ the frequency of SPR decreases weakly with increasing radius of the particles. This indicates that, in most cases, the dissipation-free approximation can be used to determine the frequency of the surface plasmonic resonance, and for spherical nanoparticles

$$\omega_{sp} = \frac{\omega_p}{\sqrt{\epsilon^{\infty} + 2\epsilon_m}} \,. \tag{25}$$

Regarding the frequency dependences of the radiation efficiency, it should be pointed out that the corresponding curves for all the considered structures are qualitatively similar (Fig. 6), and the values of the radiation efficiency at the same frequencies grow with increasing radius of plasmonic nanoparticles, embedded into the semiconductor layer, which is associated with the growth of the scattering cross-section with increasing radius of nanoparticles. Moreover, the radiation efficiency of the particles Ag in ${\rm TiO_2}$ with $R=50~{\rm nm}$ is greater than Pt in ${\rm TiO_2}$ and Pt in Si in the visible part of the spectrum. These results indicate the feasibility of modifying the thin-film solar cells with sufficiently large silver nanoparticles.

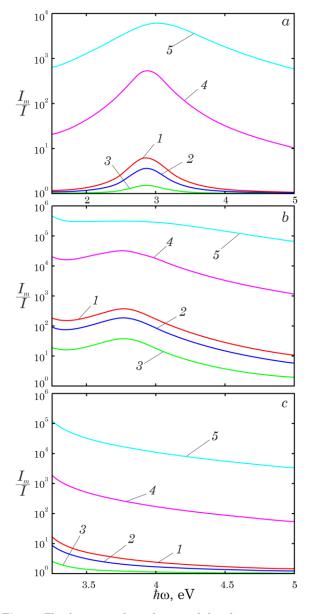


Fig. 4 – The frequency dependencies of the photocurrent amplification in the cells Pt/Si (a), Pt/TiO₂ (b) and Ag/TiO₂ (c) under the different parameters: I-R=10 nm, H=0.5 µm; 2-R=10 nm, H=1.0 µm; 3-R=10 nm, H=5.0 µm; 4-R=25 nm, H=1.0 µm; 5-R=50 nm, H=1.0 µm

The frequency dependencies of the field amplification in the neighborhood of the plasmonic nanoparticles Pt and Ag, embedded in volumes ${\rm TiO_2}$ and Si are shown in Fig. 7. Let us point out that the amplification in the neighborhood of the nanoparticles Pt in ${\rm TiO_2}$ and Si increases under the decrease in their radius, and $\mathscr{G}_{\rm max}$ correspond to the frequencies of the surface plasmonic resonance. At the same time, the amplification in the neighborhood of the nanoparticles Ag, embedded in ${\rm TiO_2}$, is maximal for particles of intermediate sizes ($R=25~{\rm nm}$), since in this case the effective electron relaxation rate in the nanoparticle will be minimal, since for the particles of small radius the surface relaxation dominates, and for particles of larger radius the radiation damping dominates [29].

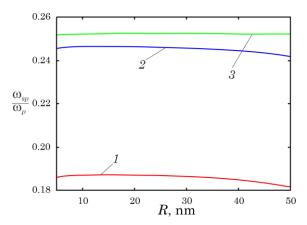


Fig. 5 – The size dependencies for the frequency of the surface plasmonic resonance in the different cells: 1 – Pt/Si; 2 – Pt/TiO₂; 3 – Ag/TiO₂

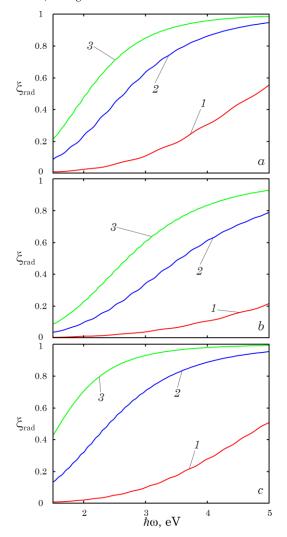


Fig. 6 – The frequency dependencies of the radiation efficiency in the structures Pt/Si (a), Pt/TiO₂ (b) and Ag/TiO₂ (c) under the different radii of the nanoparticles: 1-R=10 nm; 2-R=25 nm; 3-R=50 nm

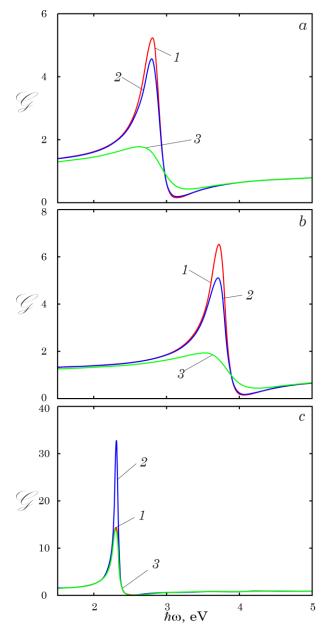


Fig. 7 – The frequency dependencies of the amplification of electric fields in the neighborhood of the plasmonic nanoparticles for the same structures and the same values of the radii of the nanoparticles as in Fig. 6

Volt-ampere characteristics of Schottky barrier Pt/Si, Pt/TiO2 and Ag/TiO2 are given in Fig. 8 (the blue curves – for the regular solar cells, the red curves – for the solar cells, modified by the plasmonic nanoparticles). Let us point out that for all considered barrier structures under $U > \varphi_B$ there is the significant (by 3-4 orders of magnitude) increase in the current, the reason for which are plasmonic effects on the surface of metallic nanoparticles embedded into the semiconductor layer.

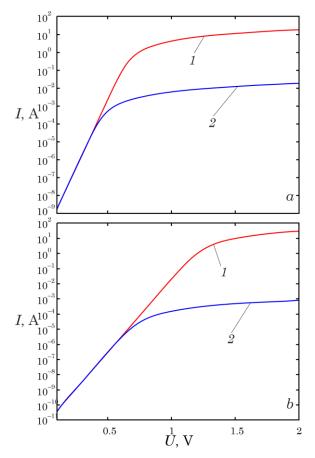


Fig. 8 – Volt-ampere characteristics in the structures Pt/Si (a) and Pt/TiO₂ (b): 1 –solar cells, modified by the plasmonic nanoparticles; 2 – the regular solar cells

4. CONCLUSIONS

The frequency dependences of the photocurrent

REFERENCES

- S.A. Maier, Plasmonics: Fundamentals and Applications (Springer: New York: 2007).
- A.O. Koval, A.V. Korotun, Yu.A. Kunytskyi, V.A. Tatarenko, I.M. Titov, *Electrodynamics of Plasmon Effects in Nanomaterials* (Kyiv: Naukova Dumka: 2021) (in Ukrainian).
- 3. H.A. Atwater, A. Polman, Nat. Mater. 9, 205 (2010).
- D. O'Connor, A.V. Zayats, Nat. Nanotechnol. 5, 482 (2010).
- P.K. Jain, X. Huang, I.H. El-Sayed, M.A. El-Sayed, Acc. Chem. Res. 41, 1578 (2008).
- K. Appavoo, B. Wang, N.F. Brady, M. Seo, J. Nag, R.P. Prasankumar, D.J. Hilton, S.T. Pantelides, R.F. Haglund, Nano Lett. 14, 1127 (2014).
- 7. S. Grillanda F. Morichetti, Nat. Commun. 6, 8182 (2015).
- P.K. Jain, K.S. Lee, I.H. El-Sayed, M.A. El-Sayed, J. Phys. Chem. B 110, 7238 (2006).
- S. Neatu, J.A. Macia-Agullo, P. Concepcion, H. Garcia, J. Am. Chem. Soc. 136, 15969 (2014).
- 10. N. Passarelli, L.A. Perez, E.A. Coronado, ACS Nano 8, 9723
- N.A. Smirnova, R.O. Malysh, A.V. Korotun, V.I. Reva, I.M. Titov, *J. Nano- Electron. Phys.* 13 No 5, 05010 (2021).
- M.Z. Nosirov, S.D. Matbabaeva, N. Mirzaalimov, A. Mirzaalimov, I. Gulomova, J. Nano- Electron. Phys. 16 No 5, 05026 (2024).

amplification in the thin-film solar cell, modified by the spherical metallic nanoparticles, as well as such characteristics of plasmonic nanoparticles as radiation efficiency and amplification of electric fields in the absorbing layer in the neighborhood of the nanoparticle have been obtained. The expression for the volt-ampere characteristic of plasmonic resonance arising at the metal / semiconductor boundary of Schottky barrier is modified taking into account the excitation on the nanoparticle surface.

The significant amplification of the photocurrent in the modified solar cells in comparison with traditional ones has been found, and the photocurrent increases with decreasing thickness of the absorbing layer and increasing radius of nanoparticles, which is associated with the enhancement of the scattering with increasing volume of the particles.

It is shown that the frequency of the surface plasmonic resonance is practically independent of the radius of the nanoparticles, which makes it possible to use the value of this frequency determined in the dissipation-free approximation in most calculations.

The feasibility of modifying thin-film solar cells with silver nanoparticles, demonstrating greater radiation efficiency in the visible frequency range, has been demonstrated.

It is established that the amplification of electric fields in the neighborhood of platinum nanoparticles grows with decreasing of their radius, whereas in the case of silver nanoparticles it will be maximum for intermediate radii, where the effective electron relaxation rate is minimal.

The calculations of volt-ampere characteristics showed that modification of solar cells has the consequence of increasing the photocurrent by three or four orders of magnitude for voltages exceeding Schottky barrier potential.

- C. Sonnichsen, T. Franz, T. Wilk, G. von Plessen, J. Feldmann, O. Wilson, P. Mulvaney, *Phys. Rev. Lett.* 88, 077402 (2002).
- 14. F. Wang, Y.R. Shen, *Phys. Rev. Lett.* **97**, 206806 (2006).
- C. Dahmen, B. Schmidt, G. von Plessen, Nano Lett. 7, 318 (2007)
- J. Müller, B. Rech, J. Springer, M. Vanecek, Sol. Energy 77, 917 (2004).
- J. Meier, S. Dubail, S. Golay, U. Kroll, S. Faÿ, E. Vallat-Sauvain, L. Feitknecht, J. Dubail, A. Shah, Sol. Energy Mater. Sol. C. 74, 457 (2002).
- S.B. Mallick, M. Agrawal, P. Peumans, *Opt. Exp.* 18, 5691 (2010).
- 19. M.W. Dlamini, G.T. Mola, *Physica B* **552**, 78 (2019).
- A.A. Tabrizi, A. Pahlavan, Opt. Commun. 454, 124437 (2020).
- S. Xiao, F. Xu, Y. Bai, J.Y. Xiao, T. Zhang, C. Hu, X.Y. Meng, H.R. Tan, P. Ho, S.H. Yang, Solar RRL 3, 00278 (2019).
- A. Korotun, H. Moroz, I. Titov, V. Reva, S. Shylo, 42nd International Conference on Electronics and Nanotechnoogy (ELNANO-2024), 197 (Ukraine: Kyiv: 2024).
- D.M. Schaadt, B. Feng, E.T. Yu., Appl. Phys. Lett. 86, 063106 (2005)
- W.A. Jacak, Quantum Nano-Plasmonics (Cambridge University Press: 2020).
- 25. S. Eustis, M.A. El-Sayed, *Chem. Soc. Rev.* **35**, 209 (2006).

- 26. R. Stuart, D.G. Hall, Appl. Phys. Lett. 73, 3815 (1998).
- J. Meier, S. Dubail, S. Golay, U. Kroll, S. Faÿ, E. Vallat-Sauvain, L. Feitknecht, J. Dubail, A. Shah, Sol. Energy Mater. Sol. C. 74, 457 (2002).
- S. Pillai, K.B. Catchpole, T. Trupke, G. Zhang, J. Zhao, M.A. Green, *Appl. Phys. Lett.* 88, 161102 (2006).
- A.V. Korotun, H.V. Moroz, R.Yu. Korolkov, *Funct. Mater.* 31, 119 (2024).
- 30. A. Korotun, G. Moroz, R. Korolkov, I. Titov, *IEEE XIIIth International Conference on Electronics and Information*
- Technologies (ELIT-2023), 320 (Ukraine: Lviv: 2023).
- H.V. Moroz, V.P. Kurbatsky, A.V. Korotun, N.M. Nagorna J. Nano- Electron. Phys. 16 No 6, 06032 (2024).
- I.I. Nedrygailov, C. Lee, S.Y. Moon, H. Lee, J.Y. Park, *Rev. Sci. Instrum.* 87, 114101 (2016).
- S.W. Lee, H. Lee, Y. Park, H. Kim, G.A. Somorjai, J.Y. Park, Surf. Sci. Rep. 76, 100532 (2021).
- A. Raghav, K. Hongo, R. Maezono, E. Panda, *Comput. Mater. Sci.* 214, 111714 (2022).

Покращення фізико-технічних характеристик тонкоплівкових сонячних елементів при їх модифікації плазмонними наночастинками

А.В. Коротун^{1,2}, С.І. Шило¹, В.І. Рева¹, І.М. Тітов¹

- ¹ Національний університет «Запорізька політехніка», 69063 Запоріжжя, Україна
- ² Інститут металофізики ім. Г. В. Курдюмова НАН України, 03142 Київ, Україна

В роботі досліджується така важлива задача плазмонної фотовольтаїки як удосконалення тонкоплівкових сонячних елементів за рахунок впровадження в їх поглинаючий шар металевих наночастинок. Отримано частотні залежності посилення фотоструму, радіаційної ефективності та підсилення електричних полів в околі наночастинок, а також вираз для вольтамперної характеристики бар'єру Шотткі, що утворюється на межі металевої наночастинки і напівпровідника поглинаючого шару. Запропонована у роботі математична модель враховує всі механізми релаксації електронів у металевій наночастинці. Розрахунки були проведені для випадку наночастинок Ад і Рt, впроваджених у шари TiO₂ i Si. Встановлено факт суттєвого підсилення фотоструму при зменшенні товщини поглинаючого шару та збільшенні радіусу впроваджених плазмонних наночастинок. При цьому спектральний діапазон тонкоплівкових сонячних елементів визначається властивостями напівпровідника, перш за все шириною забороненої зони поглинаючого шару. Розрахунки показали слабку розмірну залежність частоти поверхневого плазмонного резонансу і сильну залежність положення максимумів спектральних характеристик від властивостей матеріалів наночастинок і поглинаючого шару. Продемонстровано перевагу срібних наночастинок перед платиновими, оскільки на однакових частотах вони забезпечують більшу радіаційну ефективність. Результати розрахунків частотних залежностей підсилення електричних полів в околі плазмонних наночастинок свідчать про його зростання зі зменшенням радіусу наночастинок платини, у той час як найбільшим максимальне значення підсилення буде в околиці наночастинок срібла проміжних розмірів, що пояснюється послабленням процесу релаксації електронів у частинках саме таких розмірів. Показано різке (на 3-4 порядки) збільшення струму в модифікованих сонячних елементах у порівнянні з традиційними при напругах, які перевищують бар'єр Шотткі, що пояснюється збудженням плазмонних резонансів на поверхні металевих наночастинок.

Ключові слова: Тонкоплівковий сонячний елемент, Сферична металева наночастинка, Фотострум, Плазмонний резонанс, Вольтамперна характеристика.