Lithuanian Journal of Physics, Vol. **51**. No. 4, pp. 283–291 (2011)

NANOSCALE MODIFICATION OF DIELECTRICS UNDER ULTRASHORT LASER PULSE ACTION ON THE NANOPARTICLE-AT-THE-SUBSTRATE SYSTEM

V. L. Komolov

St. Petersburg State University of Information Technologies, Mechanics and Optics, Kronverkskiy pr.49, 197101 St. Petersburg, Russia

E-mail: vlkomolov@gmail.com

Received 18 August 2011; accepted 1 December 2011

The results of theoretical analysis of the response of solid nanoparticles on the dielectric surface to the intense ultrashort laser pulse (USLP) action are presented. The estimation of the ionization degree of nanoparticles with permanently changing charge on the composition, intensity and laser pulse duration has been carried out using a simple analytical model. The dynamics of non-thermal destruction of nanoparticles and associated changes in the substrate surface due to the implantation of ions emitted from nanoparticles has been studied using numerical simulation.

Keywords*:* nanoparticle, photoionization, ion implantation, ultrashort laser pulse

PACS: 81.07.-b, 81.16.-c

1. Introduction

The objective of this theoretical research is to analyse the dynamics and mechanisms of nanoparticle destruction under ultrashort high-power laser pulse irradiation and related modifications of substrate surface.

The concrete goal of the study is to verify the possibility of application of the charge equilibrium disturbance processes arising inside nanoparticles under the action of ultrashort laser pulses for the doping of the near-surface layer of solid materials.

We studied the behaviour of the nanoparticle-at-the-substrate system under the action of short high-power laser pulses, when substrates are transparent for the selected wavelength. The possibility of ion doping of solids by the formation of the nanoscale ion source on its surface by laser pulses was analysed, and the conditions and parameters of the impurity implantation in the nanoparticle-at-the-substrate system due to Coulomb explosion of the nanoparticle were estimated.

A large number of papers that were published in the last 10–15 years (see, for example, [1–3]) reported about observation of a very intense electron emission from nano-sized particles. This emission arises due to the particle photoionization under USLP action practically without any delay relative to the light pulse. Although the mechanism of this emission is unclear in detail, it is evident that fast removal of a significant number of electrons from nanoparticles induces an uncompensated positive charge and strong electrostatic fields inside and near the particle. If the ionization degree is high enough, the Coulomb explosion of the particle – rapid expansion of material containing an uncompensated electric charge – becomes possible as a result of the action of repulsive electrostatic forces.

Earlier [4–6], we proposed a simple method of analysis of the Coulomb explosion of nanoparticles due to their photoionization. It was shown that the electric field of uncompensated charge arising during the photoionization of nanoparticles can cause the movement of arising ions and accelerate them up to rather high energies.

2. General remarks

It is clear that if a nanoparticle is placed on a substrate that is transparent for the light radiation, the

scattered ions partially penetrate under the surface and can modify the material properties of the substrate without its damage on a scale comparable with the initial size of the particle (Fig. 1).

The processes that take place in the nanoparticle-at-the-substrate system under USLP action can be separated into two stages: the formation of the ion source **during** the pulse action (Fig. 1(a)), and ion implantation into the substrate **after** the pulse action (Fig. 1(b)).

So, it becomes possible to create a nanoscale ion source on a solid surface under the laser irradiation of the nanoparticle-at-the substrate system and to control the characteristics of ion flows by variation of the parameters of nanoparticles and laser pulses. Finally, it can be claimed that USLP action on the nanoparticle-at-the-substrate system can lead to the creation inside the near-surface layer of the substrate of the nanoscale regions with modified characteristics due to the implantation inside the substrate of some amount of impurity ions from the nanoparticle.

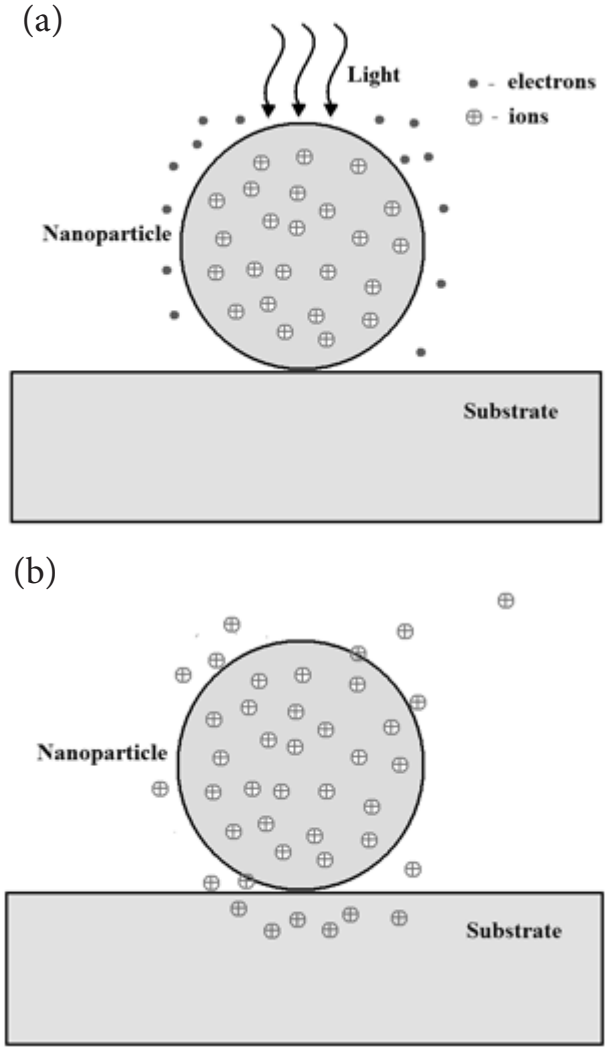

Fig. 1. (a) Formation of the ion source (**during** the pulse action). (b) Ion penetration into substrate (**after** the pulse action).

Advantages of the proposed method:

- Implantation of ions into the substrate occurs on a scale comparable with the initial size of nanoparticles, which permits to adjust the implantation area by selection of the nanoparticle size (R). It is a serious difference from other laser methods of surface modification where the typical size of the modified area is defined by wavelength $\lambda \gg R$.
- The permanent presence of an electrostatic field that accelerates ions during the whole period of implantation allows them to penetrate into the substrate much deeper than in beam-based implantation methods, even when ion energy is relatively small ($\leq$ keV).

Weak points of the method:

- Selection of an impurity–substrate pair is limited by the following requirements: (i) radiation should not cause ionization and / or heating of the substrate (it means the restriction on the light wavelength λ selection), and (ii) radiation should not cause substrate damage (it means the restriction of the upper value of light intensity q).
- There is no stage of ion energy selection that leads to non-uniformities of doping depth.

To verify the possibility of realization of the above-discussed implantation technique, one must:

- estimate the possibility of ionization under short pulse action and analyse the ionization degree of the nanoparticle as the function of the parameters of the particle and light pulse;
- retrace the dynamics of the outflow of the produced ions outside from the nanoparticle, including their implantation into the substrate.

To pursue these goals, the study includes two steps that are discussed below.

3. Evaluation of ionization degree

We assume that the ionization of a metal nanoparticle irradiated by extremely high power ultrashort laser pulses occurs due to the field emission of electrons from the particle in the field of light wave.

For further analysis it is essential that at high light intensities, q~10^{11}–10^{14} W/cm^2, the tunneling current can be calculated in the stationary approximation.

Let us estimate the characteristic time of ionization τ, which shows when the tunneled electron can gain in the external field the energy sufficient for irreversible removal from the solid surface.

This time, in fact, is close to the electron time of flight through the barrier (Fig. 2) with the width $l = \varphi / (eE,)$ where φ is the work function, μ is the Fermi energy, E is the field strength in the light wave.

As the average electron velocity is $\langle v \rangle \approx \sqrt{\varphi / m}$, we can get the following estimation for τ:

$$\tau = \frac{l}{\langle v \rangle} = \frac{\varphi}{eE\sqrt{\varphi / m}} = \frac{\sqrt{\varphi \cdot m}}{eE}. \quad (1)$$

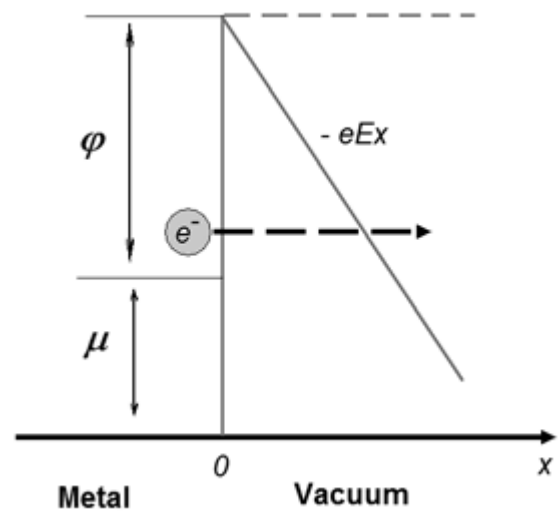

Fig. 2. Potential barrier at the metal / vacuum boundary.

In Table 1, you can see the calculated values of the characteristic ionization time τ [s] for several metals at different light intensities. The data in this table shows that for the IR and visible light in the whole range of parameters it can be assumed that the electron gains the required energy during half of the period of optical oscillations. It means that the tunneling current density is determined by the instantaneous value of the light wave intensity, and we can actually carry out our further estimations using the stationary approximation.

Thus, we can use for estimation of current density a Fowler–Nordheim expression for the triangular barrier in an electric field with constant strength E [7]:

$$j = \frac{e^3}{2\pi h} \cdot \frac{\mu^{1/2}}{(\varphi + \mu) \cdot \varphi^{1/2}} \cdot E^2 \exp\left[-\frac{4k_0}{3eE} \cdot \varphi^{3/2} \right], \quad (2)$$

where μ is the Fermi energy, φ is the work function, $k_0 = 8\pi^2 m/h^2$.

If φ and μ are denominated in eV, and E is dominated in V/cm, this equation can be rewritten as

$$j = 8.87 \cdot 10^{-6} \cdot \frac{\mu^{1/2}}{(\varphi + \mu) \cdot \varphi^{1/2}} \cdot E^2 \exp\left[-6.85 \cdot 10^7 \cdot \frac{\varphi^{3/2}}{E} \right] \left[\text{A/cm}^2 \right] \cdot \quad (2a)$$

This expression will be used below for evaluation of the ionization degree of nanoparticles caused by the field emission of electrons.

When estimating the ionization degree, we must take into account that due to electron emission process we must expect **strong changes in the total charge of the particle** that leads in turn

Table 1. Characteristic ionization times τ [s] for several metals.

Intensity q [W/cm^2] (Field strength E [V/cm]) / **Metal (φ, eV)**	**$5 \cdot 10^{11}$** ($1.9 \cdot 10^7$)	**10^{12}** ($2.7 \cdot 10^7$)	**$5 \cdot 10^{12}$** ($6.1 \cdot 10^7$)	**10^{13}** ($8.7 \cdot 10^7$)
Cesium (1.8)	$1.7 \cdot 10^{-15}$	$1.2 \cdot 10^{-15}$	$5.2 \cdot 10^{-16}$	$3.7 \cdot 10^{-16}$
Barium (2.5)	$2.0 \cdot 10^{-15}$	$1.4 \cdot 10^{-15}$	$6.2 \cdot 10^{-16}$	$4.3 \cdot 10^{-16}$
Argentum (4.3)	$2.6 \cdot 10^{-15}$	$1.8 \cdot 10^{-15}$	$8.0 \cdot 10^{-16}$	$5.7 \cdot 10^{-16}$
Aurum (4.6)	$2.7 \cdot 10^{-15}$	$1.9 \cdot 10^{-15}$	$8.4 \cdot 10^{-16}$	$5.9 \cdot 10^{-16}$

to a permanent increase of the work function value φ during emission, as electrons carry away a negative charge ΔQ from the particle.

The additional potential ΔU at the surface of a spherical drop can be written as $\Delta U = \Delta Q/C$, where C is the capacity of the particle. As the capacity of a spherical particle is proportional to its radius R, $C = 4\pi\varepsilon\varepsilon_0 R$ ($\varepsilon \approx 1$, $\varepsilon_0 = 8.854 \cdot 10^{-12}$ F/m), we can expect the increasing in potential barrier height at the particle boundary due to outflow of the charge ΔQ.

The work function growth is given by the following expression:

$$\Delta\varphi = \Delta Q/(4\pi\varepsilon\varepsilon_0 R). \quad (3)$$

As it was mentioned above, in the interesting interval of light intensities we can use the stationary approximation for calculating emission. It means that we can get a rough estimation of the field emission rate under the permanent growth of the drop charge by using a simple recursive scheme:

1. For the **fixed** value of the work function (at the 1st step using the standard value for the electrically neutral drop ($\varphi_k = \varphi_0$)) we calculate the emission current density $j_k = j(\varphi_k)$ using Eq. (2) and the total current $I(E,\varphi,t) = 2\pi\int jrdr = 4\pi R^2 j$ from the whole drop surface for a half-period of light wave (Δt). We suppose that the charge of the drop will change only slightly for this interval (in other cases we can always choose a smaller time interval for which this assumption will be surely correct);
2. Using the calculated value of the total current, we have to estimate the variation of the drop charge, ΔQ_{k+1}, for the given time interval, $\Delta Q_{k+1} = 4 \cdot \pi \cdot R^2 \cdot j_k \cdot \Delta t$, and to calculate a new value of the work function, $\varphi_{k+1} = \varphi_k + \Delta Q_{k+1}/(4\pi\varepsilon\varepsilon_0 R)$, for the *charged* drop;
3. At the next time step, we must repeat the calculations of the emission current using **the new value** of the work function, and so on…

The application of the above-described procedure makes it possible to estimate the ionization degree of the nanoparticle under the light action (with the pulse duration τ_{eff}). It is evident that the ionization degree for a nanoparticle with radius R is defined by the total losses of negative charge Q_{emission} during the pulse action and can be estimated as $Q_{\text{emission}} \sim 4 \cdot \pi R^2 \cdot \sum_{\Delta t}^{\tau_{\text{eff}}} j(\varphi)\Delta t$. In the stationary case, the emission occurs independently for every half-period of light wave, and the total electron losses are simply summarised for the whole pulse duration. We must only keep in mind that the density of emission current varies in time, tracing the work function variations due to the permanent growth of the positive charge of the drop.

So, the total ionization degree of a nanoparticle to the pulse end can be estimated as

$$\chi = \frac{Q_{\text{emission}}}{e \cdot N \cdot V_{\text{drop}}} = \frac{3}{4}\frac{Q_{\text{emission}}}{e \cdot N \cdot \pi \cdot R^3}, \quad (4)$$

where N is the electron density in metal.

Figures 3–5 illustrate some results obtained using the above-described procedure for the Cs nanoparticle ($\varphi = 1.8$ eV, $\mu = 1.5$ eV) with radius R.

It should be emphasized that the estimations were carried out on the basis of the simplest model for the *massive metal* and *triangular barrier*. For the quantitative calculations, the model should be modified taking into account two factors:

- The shape of the real potential barrier is determined by the superposition of two potentials: the potential of the external field, and the internal Coulomb potential of the nanoparticle itself, which varies in time with the growth of uncompensated charge inside the particle;
- As we deal not with a massive metal, but with a small particle the size of which is comparable both with the penetration depth of radiation into the metal and the electron free path length, the correct model should take into account the spatial redistribution of the electron density inside the particle due to the partial penetration of the external field into it. This redistribution should also affect the tunneling probability, at least for the particles that are smaller than the depth of the skin-layer.

Methods of calculating the tunneling probability for the barrier with arbitrary shape are well known (see, for example, [8–10]). Unfortunately, their practical application is possible only by using the numerical calculations. This may strongly obscure the model, which we tried to avoid at this stage of the study. That is why we have used in this paper the simplest model, which gives rather good estimations of the order of magnitude for the parameters of interest.

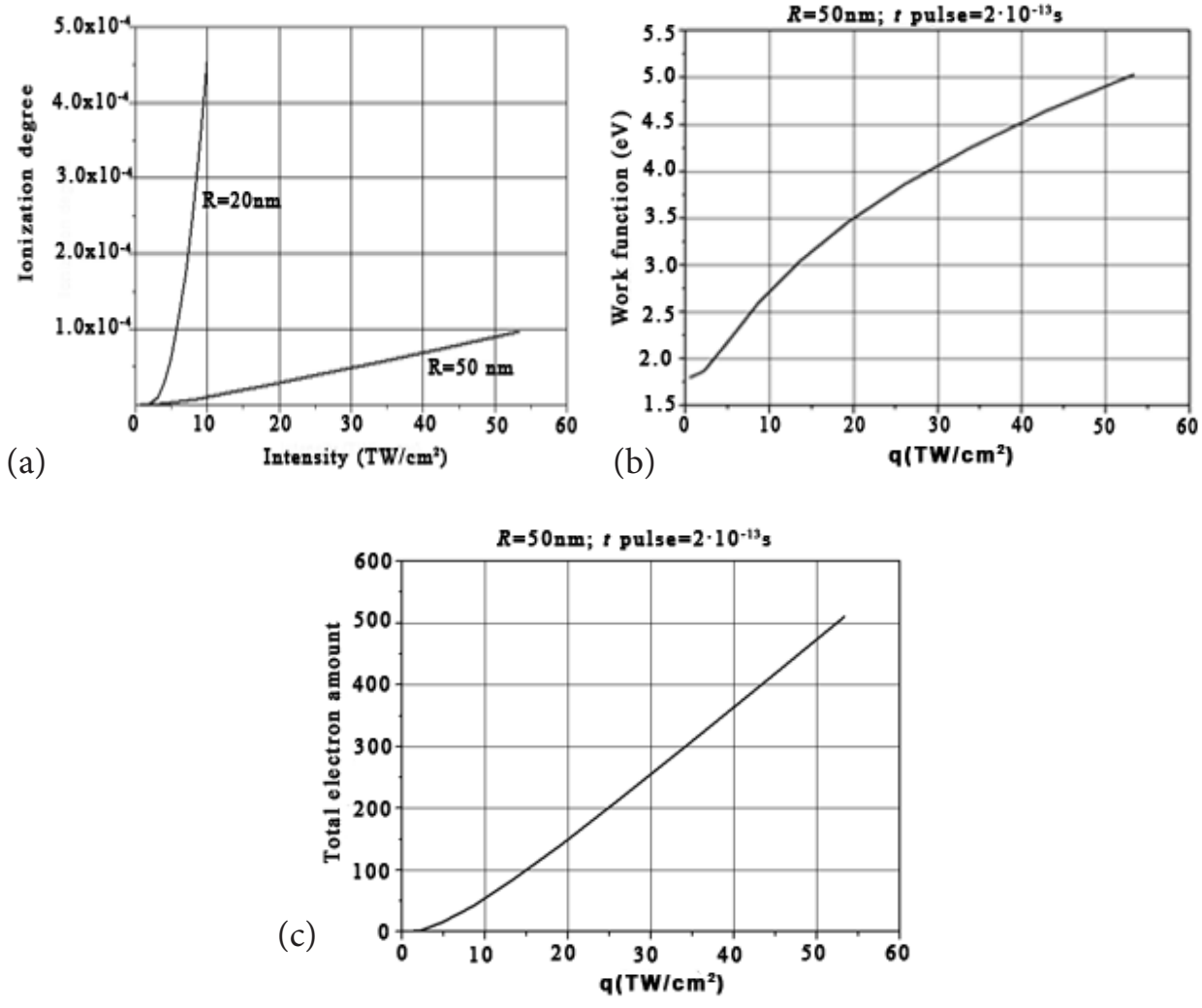

Fig. 3. Dependences of (a) ionization degree, (b) work function, and (c) total number of electrons that left the nanoparticle on light intensity q.

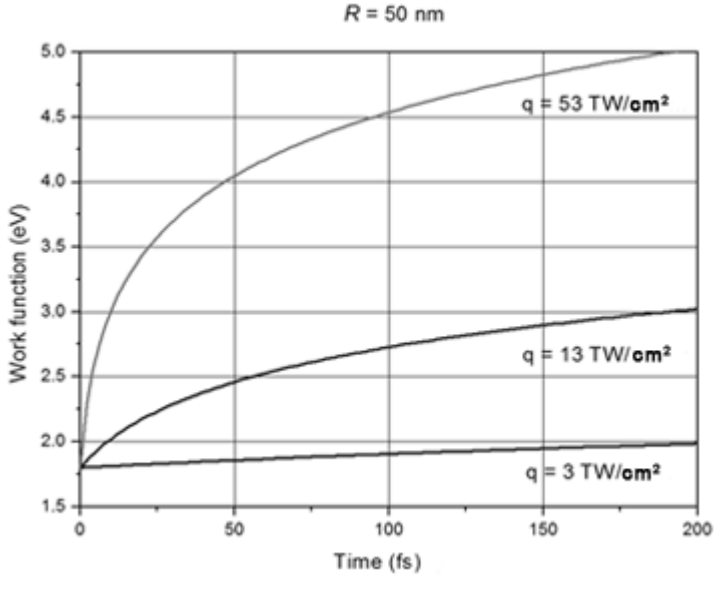

Fig. 4. Time dependences of the work function on different light intensities q.

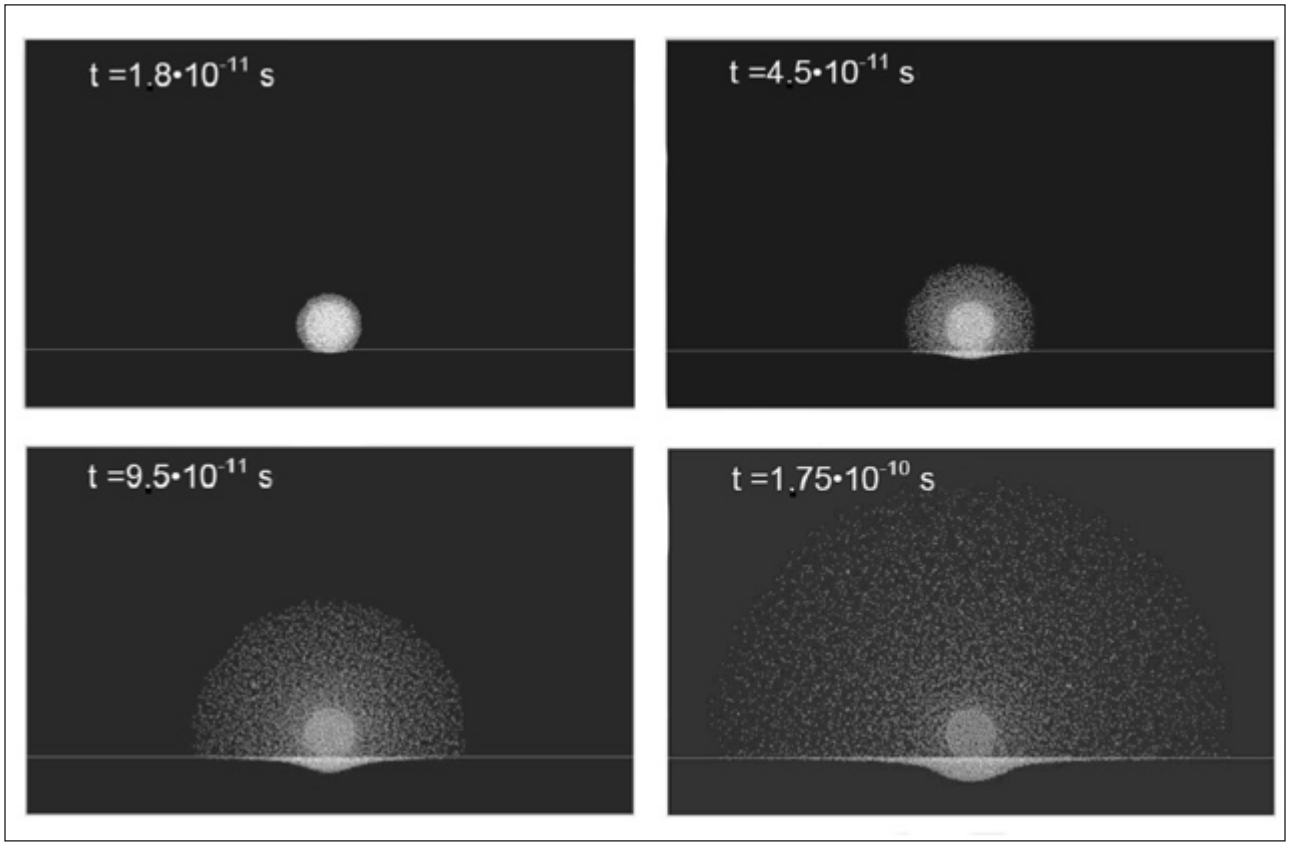

Fig. 5. Dynamics of ion spreading from a spherical particle for the nanoparticle-at-the-substrate system.

It can be seen from Figs. 3–5 that the work function growth strongly affects the achievable value of ionization degree, but it still permits to get the ionization degree of the drop of about 10^{-3}–10^{-4} for the reasonable levels of light intensity.

4. Simulation of ion motion dynamics (continual approximation)

As it can be seen from the above estimations, at light intensity of about several tens of TW/cm^2 the degree of ionization of a nano-sized particle can reach the value of ~10^{-4}–10^{-5}. An uncompensated charge, which arises in this case, is large enough to cause the movement of heavy ions in the electrostatic field induced both inside the particle and outside it. As already noted, some of the emitted ions penetrate under the surface of the substrate, which leads to a modification of substrate parameters near the nanoparticle on a scale comparable with its initial size. Particularly distinctly the mechanism of "nanoimplantation" must appear under the action of an ultrashort laser pulse, when thermal processes cannot occur during the pulse action, so there are no masking effects for the Coulomb explosion of the nanoparticle. Besides, under the USLP action the processes of the formation of the charged area and the outflow of ions from nanoparticles are separated in time (photoionization occurs during the pulse, while the movement of heavy ions starts after its ending). The analysis can be greatly simplified by executing it in two consequent steps: the creation of an ion source (during the pulse) that was discussed above, and ion implantation of the substrate (after the pulse). The dynamics of ion movement in our case is similar to that in the electrolysis of molten salts or in the implantation of the fast ions in a condensed medium. In all these cases, the rate of directional movement of ions in the medium, as the Lindhard–Scharff–Schiøtt model predicts, falls under the linear friction law. However, unlike the case of molten salts, ion mobility is much higher, and their velocity reaches 10^6 cm/s. Therefore, the ions can get out from the nanoparticles during the times $<10^{-12}$ s, that is faster than a neutral core of the particle would damage.

To analyse the dynamics of the ion expansion, we used a simplified model proposed earlier [4–6] for

description of the Coulomb explosion of partially ionized nanoscale particles. It differs from the method of molecular dynamics (MD) widely used for these purposes [1, 2, 11, 12] and allows one to describe analytically the process of destruction (at least, for model situations; for example, for a spherically symmetric geometry). In other cases, this approach permits one to conduct a simple computer simulation of the dynamics of the atoms and ions that make up the nanoparticle, correctly describing the main processes, but consuming the computer resources by several orders less than when using the MD.

Thus, the proposed method makes it possible to trace the outcome of the charge equilibrium violation in real systems containing 10^8–10^9 elements, but not in ensembles consisting of 10^2–10^4 particles, as it can be done by the MD method. In the framework of the simplified model, interaction between ions is calculated exactly, and interaction of ions with electrically neutral particles is calculated only approximately.

The main features of the model are as follows:

- It is assumed that charged particles are initially distributed in space randomly.
- Every step of the calculation of ion motion parameters (position, velocity and acceleration) is performed for each particle due to Coulomb interaction with all other charged particles in the ensemble.
- The collision of charged particles with "neutrals" is taken into account by introducing the mean free path of ions before the collision. Another free parameter used in the model is a part of energy that is lost in the collision. It can vary from 0 (elastic scattering) to 100%.
- It is assumed that the ion motion is stopped if the total Coulomb potential at the point of the ion's disposition is smaller than the activation energy of migration of point defects.

To illustrate the calculation results, Fig. 5 and Fig. 6 display the instant spatial distributions of

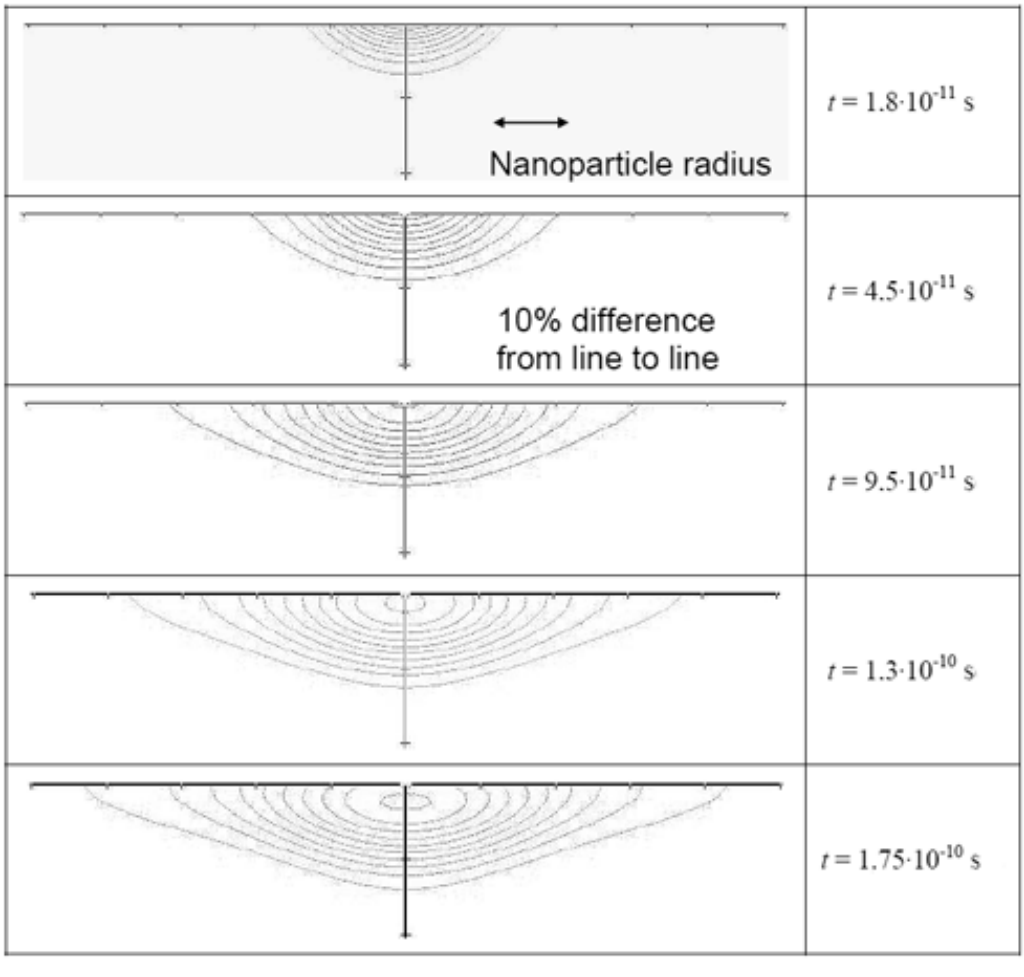

Fig. 6. Concentration profiles $N(r, z)$ of implanted ions for various time moments.

ions both inside and outside the nanoparticle for different times and spatial profiles of the ion concentration which penetrates into the surface layer of the substrate. The typical energy spectra of ions at different calculation steps are shown in Fig. 7.

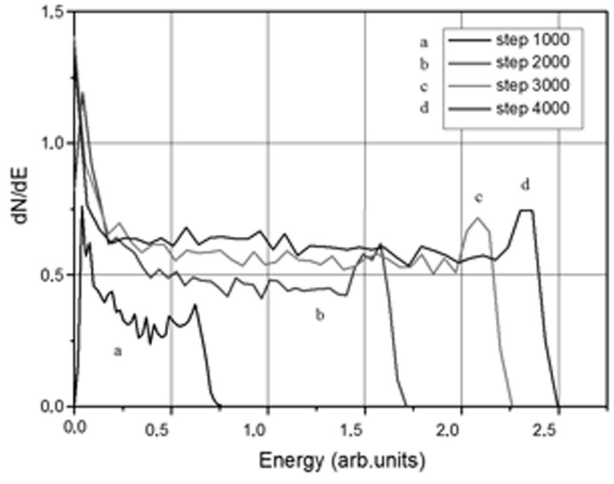

Fig. 7. Energy spectra of ions at different calculation steps.

For estimations we use the following set of parameters: particle radius 75 nm; initial average distance between ions 5 nm (it corresponds to the ionization degree of about 10^{-4} – 10^{-5}); mass of ions $3.2 \cdot 10^{-28}$ g; ion free path length before collision 1 nm; fraction of energy that ion loses in collision 50%; activation energy of point defect migration in solids 1 eV.

The computation shows that even at a rather small initial degree of nanoparticle ionization (i. e. at moderate levels of light intensity) a sufficient amount of ions can penetrate into the near-surface layer of substrate to the depth that is comparable with the nanoparticle size.

The most characteristic feature of ion distribution is that the **maximum of their concentration lies under the surface** at a distance of about the particle size.

The physical nature of this specific profile is evident. Unlike other (beam-based) methods of implantation, where the fixed ion can only lose its initial energy and ion density continuously falls with the depth, in our case the permanent source of induced electrostatic field inside a ionized nanoparticle stimulates the ion acceleration even under the surface. So, ion movement lasts until the Coulomb potential in the point of ion disposition becomes less than the activation energy of ion migration in solids.

We discuss this peculiarity of ion penetration in detail because it gives the opportunity for direct experimental checking of the implantation mechanism by the measurement of impurity density distribution across the near-surface layer after irradiation.

5. Conclusion

We propose a new possible way of laser-induced modification of the dielectric surface layer by using the ionized nanoparticles at its surface. The results of conducted simulation of the damage peculiarities of irradiated nanoparticles show that heavy ions arising in nanoparticles after short-pulsed light action can penetrate rather deep into the near-surface layer of the dielectric substrate and cause serious modification of its structure and properties.

6. Acknowledgements

I would like to thank Dr. S.G. Przhibel'skii for useful discussion and advises during model development and Dr. D.S. Smirnov for creation of a program package for numerical computations.

References

[1] C. Rose-Petruck, K.J. Scafer, K.R. Wilson, and C.P.J. Barty, Ultrafast electron dynamics and inner-shell ionization in laser driven clusters, Phys. Rev. A **55**, 1182–1189 (1997).

[2] I. Last and J. Jortner, Dynamics of the Coulomb explosion of large clusters in a strong laser field, Phys. Rev. A **62**, 013201 (2000).

[3] Y.L. Shao, T. Ditmire, J.W.G. Tisch, E.S. Springate, J.P. Marangos, and M.H.R. Hutchinson, Multi-keV electron generation in the interaction of intense laser pulses with Xe clusters, Phys. Rev. Lett. **77**(16), 3343–3346 (1996).

[4] V.E. Gruzdev, V.L. Komolov, S.G. Przhibel'skii, and D.S. Smirnov, Dynamics of the disruption of a nanoparticle totally ionized by a powerful ultrashort laser pulse, J. Opt. Technol. **73**(6), 378–384 (2006).

[5] V.E. Gruzdev, V.L. Komolov, S.G. Przhibel'skii, and D.S. Smirnov, Breakdown of a nanoparticle partially ionized by a powerful ultrashort laser pulse, J. Opt. Technol. **74**(6), 373–377 (2007).

[6] V. Gruzdev, V. Komolov, H. Li, Q. Yu, S. Przhibel'skii, and D. Smirnov, Photo-ionization and modification of nanoparticles on transparent substrates by ultrashort laser pulses, Proc. SPIE **7996**, 7996–18 (2010).
[7] R.H. Fowler and L.W. Nordheim, Electron emission in intense electric field, Proc. Roy. Soc. **119**(781A), 173–181 (1928).
[8] J.G. Simmons, Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film, J. Appl. Phys. **34**(6), 1793–1803 (1963).
[9] J.G. Simmons, Electric tunnel effect between dissimilar electrodes separated by a thin insulating film, J. Appl. Phys. **34**, 2581–2590 (1963).
[10] J.G. Simmons, Generalized thermal *J*–*V* characteristic for the electric tunnel effect, J. Appl. Phys. **35**, 2655–2658 (1964).
[11] C. Jungreuthmayer, M. Geissler, J. Zanghellini, and T. Brabec, Microscopic analysis of large-cluster explosion in intense laser fields, Phys. Rev. Lett. **92**(13), 133401 (2004).
[12] K. Ishikawa and T. Blenski, Explosion dynamics of rare-gas clusters in an intense laser field, Phys. Rev. A **62**, 063204 (2000).

DIELEKTRIKŲ KEITIMAS NANOMASTU, VEIKIANT „NANODALELĖS PAVIRŠIUJE“ SISTEMĄ ULTRATRUMPAIS LAZERIO IMPULSAIS

V. L. Komolov

Sankt Peterburgo valstybinis informacinių technologijų, mechanikos ir optikos universitetas, Sankt Peterburgas, Rusija

Santrauka

Pateikti kietųjų nanodalelių ant dielektrinio paviršiaus atsako į ultratrumpųjų lazerinių impulsų poveikį teorinės analizės rezultatai. Nanodalelių, visam laikui pakeičiančių krūvį, jonizacijos laipsnis, priklausantis nuo sudėties, intensyvumo ir lazerio impulso trukmės, įvertintas naudojant paprastą analizinį modelį. Nanodalelių neterminio suirimo dinamika ir susiję pokyčiai substrato paviršiuje dėl jonų, išspinduliuotų iš nanodalelių, implantacijos nagrinėti pasitelkiant skaitmeninį modeliavimą.