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Numerical study of laser ablation regimes of thin gold films in an aqueous environment

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This work investigates the mechanisms of laser ablation of a thin gold layer deposited on glass in an aqueous environment as a function of laser pulse energy in the range of 0.5–2.0 J/cm^2. The study is performed using the molecular dynamics method, which enables the analysis of the kinetics of nonequilibrium processes at the atomic level. The absorbed laser pulse energy values are determined for a 20 nm thick gold film irradiated by a 1 ps pulse, corresponding to the realization of ablation regimes such as spallation, phase explosion, or their combination. The results of this work are relevant for the development of methods and technologies for surface nanostructuring and the synthesis of metallic nanostructures using short-pulse laser radiation.

Keywords: Thin films, laser ablation in water, molecular dynamics, numerical simulation.

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1. Introduction

The study of modes and mechanisms of laser ablation of thin films in a liquid is of considerable interest for modern science and technology. Laser ablation of thin films is an effective method for directional surface structuring [1], and when irradiated from the glass substrate of metal films, the Laser-Induced Forward Transfer (LIFT) method is actively developing [2]. The effect of the presence of liquid on the efficiency and generation of nanostructures on the target surface has been experimentally shown [3]. Thus, the generation of periodic nanostructures during laser ablation in a liquid has been shown to be an advantageous method for the functionalization of the surface of the irradiated material: modification of hydrophobicity, changes in morphological and optical properties [4,5]. Also, laser ablation in liquid is a promising method that ensures high purity of the resulting nanoparticles, which is especially important for biomedical applications [6]. The latter have especially found effective application in SERS technologies for biomedicine [7].

The relevance of this work is due to the development of a methodology for obtaining nanostructures with the required properties using laser ablation in a liquid. For example, obtaining small fractions with sizes 1–15 nm and a narrow distribution (2 nm) is an important task of their synthesis from the point of view of biomedical applications. The approach of obtaining colloidal solutions from spatially limited thin nanometer films seems promising for this application. However, the ability to control the results of such experiments is severely limited by the complexity of interrelated laser-induced processes occurring simultaneously under highly nonequilibrium conditions.

A simulation of short-pulse laser radiation with a target in an aqueous medium using the molecular dynamics (MD) method was performed in this paper to study and understand the mechanisms responsible for establishing the laser ablation mode. The MD method has been shown to be an effective tool for studying highly nonequilibrium processes with atomic resolution [8]. Moreover, being implemented in a multiprocessor MD mode, the results of full-scale simulations can be directly compared with experimental measurements at the same spatial and time intervals.

The purpose of this paper is to study the interaction of picosecond laser pulses with gold nanofilms (20 nm) in an aqueous medium, as well as to identify laser ablation modes promising for nanostructuring thin films and synthesis of nanoparticles.

2. Modeling using the molecular dynamics method

The interaction of short-pulse laser radiation with a thin gold film was modeled using the MD method in its multiprocessor implementation. To calculate interatomic interactions in a gold film, the Embedded Atom Method (EAM potential) is used with the parameterization proposed by Zhakhovsky in Ref. [9], who also proposed a successful model of water, represented by a single particle, based on the EAM potential, which accurately reproduces its mechanical properties [10]. Finally, we describe the interaction between gold and water atoms at the interface of two media using the Lenard-Jones potential, as proposed in a recent study of on nanostructuring in a liquid medium [11]. Also, the use of a commensurate time step, an explicit description of the interactions of water particles with metal particles, and performing calculations in a multiprocessor mode allows for high calculation efficiency.

At the lower boundary, the film interacts with a fixed substrate. Non-reflective boundary conditions have been established at the upper boundary, with the possibility of their dynamic movement in the Z direction (along the direction of propagation of the laser pulse), and periodic boundary conditions have been applied in the directions X and Y, assuming that the calculated volume is small by compared with the size of the laser spot used in the experiment ($10-30\,\mu$m).

The size of the computing area is $40 \times 40 \times 1000$ nm (gold film thickness is 20 nm, 1960000 atoms; water layer is 100 nm, 6895040 atoms), which is sufficient for modeling laser-induced processes and the formation of laser ablation products with sizes up to 20 nm. The initial sample was thermalized for 15 ps until the Maxwellian particle velocity distribution in the studied area of the model and acoustic stress relaxation resulting from the assembly of the computational cell were achieved. The criterion for the accuracy of the implementation of the numerical algorithm of the physical model was the conservation of the total energy of the system after the laser pulse.

The simulations were performed in the range of embedded energies $0.5-2.0\,\mathrm{J/cm^2}$. The heating rate of the target, due to the action of short-pulse laser radiation, is determined by the rate of energy transfer from the electronic subsystem to the phonon vibrations of the atomic lattice. Its value and time contour were determined in preliminary calculations using a dual-temperature model (DTM) at the level of 5 ps for the case of a pulse with a duration of 1 ps with a falling energy density of $1\,\mathrm{J/cm^2}$ and directly taken into account in this study. At the same time, the values of the thermodynamic functions included in the two-temperature part of the combined model (such as the heat capacity of free carriers and the value of the electron-phonon bond strength) were taken into account taking into account the electronic temperature and the density of the distribution of carrier states based on DFT calculations demonstrated in Ref. [12]. From preliminary DTM studies, it was found that the heating of a thin (20 nm) gold film, due to laser irradiation, occurs uniformly without the development of temperature gradients, due to rapid electronic thermal conductivity. Thus, the absorption of laser radiation was approximated using a Berenson thermostat, where the thermal energy $E_{\Delta t}$ is released in a thin film due to the absorption of laser radiation. Each step Δt is set by a Gaussian in time, and the velocities of all particles $V_{x,y,z}$ will be calibrated each MD step according to the following rule:

$$V^{\mathrm{new}}_{x,y,z} = V^{\mathrm{old}}_{x,y,z} \cdot \xi, \qquad (1)$$

where $\xi = \sqrt{1 + \frac{E_{\Delta t}}{\Sigma_i Q_i}}$, Q_i is the kinetic energy of the ith atom, $E_{\Delta t}$ is the energy release per unit volume of the irradiated sample for 1 MD step:

$$E_{\Delta t} = F_{\mathrm{inc}}(1 - R_{\mathrm{int}})\,\frac{1}{\tau_{\mathrm{las}}}\sqrt{\frac{\omega}{\pi}}\,\exp\Big(-\omega\,\frac{(t-t_0)^2}{\tau^2_{\mathrm{las}}}\Big)\Delta t, \quad (2),$$

where $t_0 = 2.5\tau_{\mathrm{las}}$, τ_{las} is the laser pulse duration, F_{inc} incident energy density (fluence), ω is the normalization coefficient equal to $4\log 2$ and integral value R_{int} of reflection over the entire pulse for the case of a laser wavelength of 800 nm. The Rint value was obtained using DTM, where the reflecting function was represented by a model that takes into account its dependence on the electron temperature [13], as well as the presence of possible interband $d-s$ transitions recorded in experimental studies [14,15].

Thus, the proposed computational approach is aimed at identifying and studying the general modes involved in the laser ablation process at the early stages of the evolution of an irradiated thin-film target in the presence of a layer of water.

3. Results and discussions

The calculations performed were aimed at determining the values of the incident energy fluxes at which such laser ablation mechanisms as spallation and phase explosion are realized. It is shown that at a laser pulse duration of 1 ps and an incident energy density of $0.5-2.0\,\mathrm{J/cm^2}$, the gold nanofilm can transition into various phase states — from the molten state to the supercritical liquid and gas phase, depending on It depends on the amount of energy invested, which significantly affects the size and morphology of the resulting nanostructures.

Figure 1 shows three different characteristic variants of the early evolution of an irradiated gold nanofilm. Figure 1, *a* shows a case of ablation, in which the entire film is detached from the substrate (spallation), which shows how cavitation of the gold target occurs at 25 ps, accompanied by the formation of voids, the volume of which initially increases to 50 ps, but they collapse as when 100 ps is reached. Figure 1, *c* shows that the so-called ablation mode is realized by 5 ps, based on the mechanism of a phase explosion, in which the irradiated target undergoes a spontaneous phase transition to metal vapor due to reaching supercritical temperatures. In the intermediate energy range of the laser pulse (see Figure 1, *b*), a mode is realized in which the voids formed by 25 ps continue to grow and merge, which leads to mechanical stratification of the film with the formation of larger nanoclusters by 100 ps.

The analysis of the evolution of temperature and pressure distributions in the system makes it possible to quantify

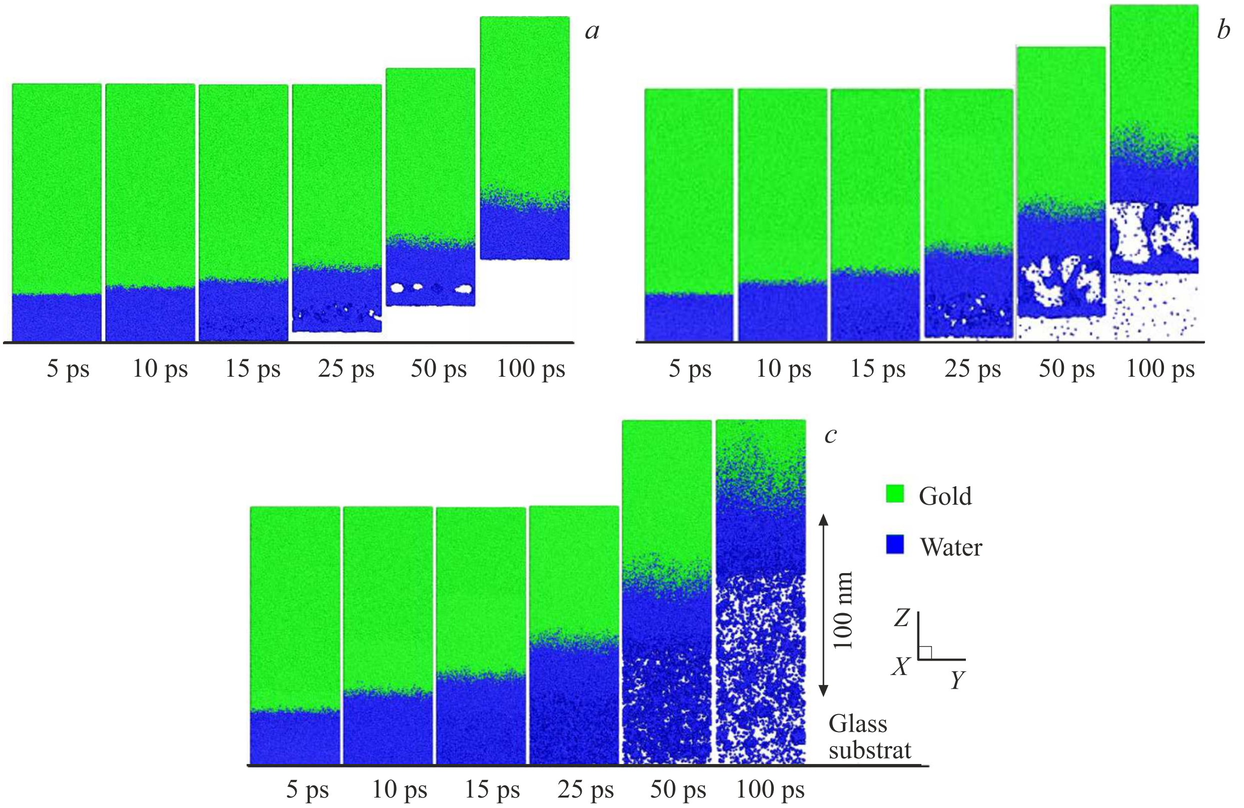

Figure 1. Atomic images of the evolution of the simulated samples in the range of 0–100 ps depending on the incident F_{inc} or absorbed F_{abs} energy fluxes: *a* — $F_{\text{inc}} = 0.5\,\text{J/cm}^2$, $F_{\text{abs}} = 26.1\,\text{mJ/cm}^2$; *b* — $F_{\text{inc}} = 1.0\,\text{J/cm}^2$, $F_{\text{abs}} = 52.1\,\text{mJ/cm}^2$; *c* — $F_{\text{inc}} = 2.0\,\text{J/cm}^2$, $F_{\text{abs}} = 104.3\,\text{mJ/cm}^2$. A slice is shown in the plane *ZY* with a thickness of 1 nm, the color of the atoms corresponds to gold (green) and water (blue). The horizontal black line represents a fixed glass substrate.

the implementation of the ablation modes mentioned above. A sharp heating of the target in the first 5 ps (Figure 2, *a*) to 5100 K also leads to a sharp increase in pressure to 30 GPa due to mechanical locking by an aqueous layer, which in turn leads to heating of the film at a constant volume. The subsequent relaxation of the stresses generated in the film occurs due to a shock wave, the propagation of which can be observed at time intervals of 10–50 ps as a moving front of increased pressure. The achievement of this shock wave of non-reflective boundary conditions leads to their upward movement. Thus, the relaxation of internal stresses without the development of significant temperatures under these conditions causes the irradiated film to mechanically detach from the substrate, which corresponds to the spallation mode.

Analyzing the dynamics of thermodynamic parameters (temperature and pressure) from Figure 2, *c*, it is possible to observe a spontaneous transition to the state of a supercritical liquid and further to an explosive transition to the gaseous phase. Thus, an increase in temperature above 12,000 K and pressure up to 108 GPa corresponds to the conditions of complete destruction of the initial structure of the gold layer, which is associated with reaching the threshold at which the conditions of the so-called phase explosion are realized.

Finally, in the intermediate mode, where temperatures of ~ 7400 K and pressures of 50 GPa are reached, both modes (spallation and phase explosion) are realized, as can be seen from Figure 1, *b*, as the joint formation of large clusters, stratification of the irradiated target and the formation of a large amount of metal vapor. At the same time, the calculated gold temperatures correspond to their supercritical values according to the published data [16,17].

The analysis of the obtained results suggests a joint role of the ablation modes described above to a greater or lesser extent. With a relatively small energy input of 0.5–1.0 J/cm^2, the spallation mode is mainly implemented, while a significant phase explosion mode is implemented to a certain extent with energy input of 1.5–2.0 J/cm^2.

Due to the significant difference between the characteristic size of the laser spot (tens of microns) on the surface of the irradiated target and the size of the calculation cell presented in the study, the direct use of modeling results in the interpretation of experimental data is limited to the size of structures up to 20 nm. However, the results obtained are an important step towards developing a methodology for obtaining nanostructures with specified characteristics.

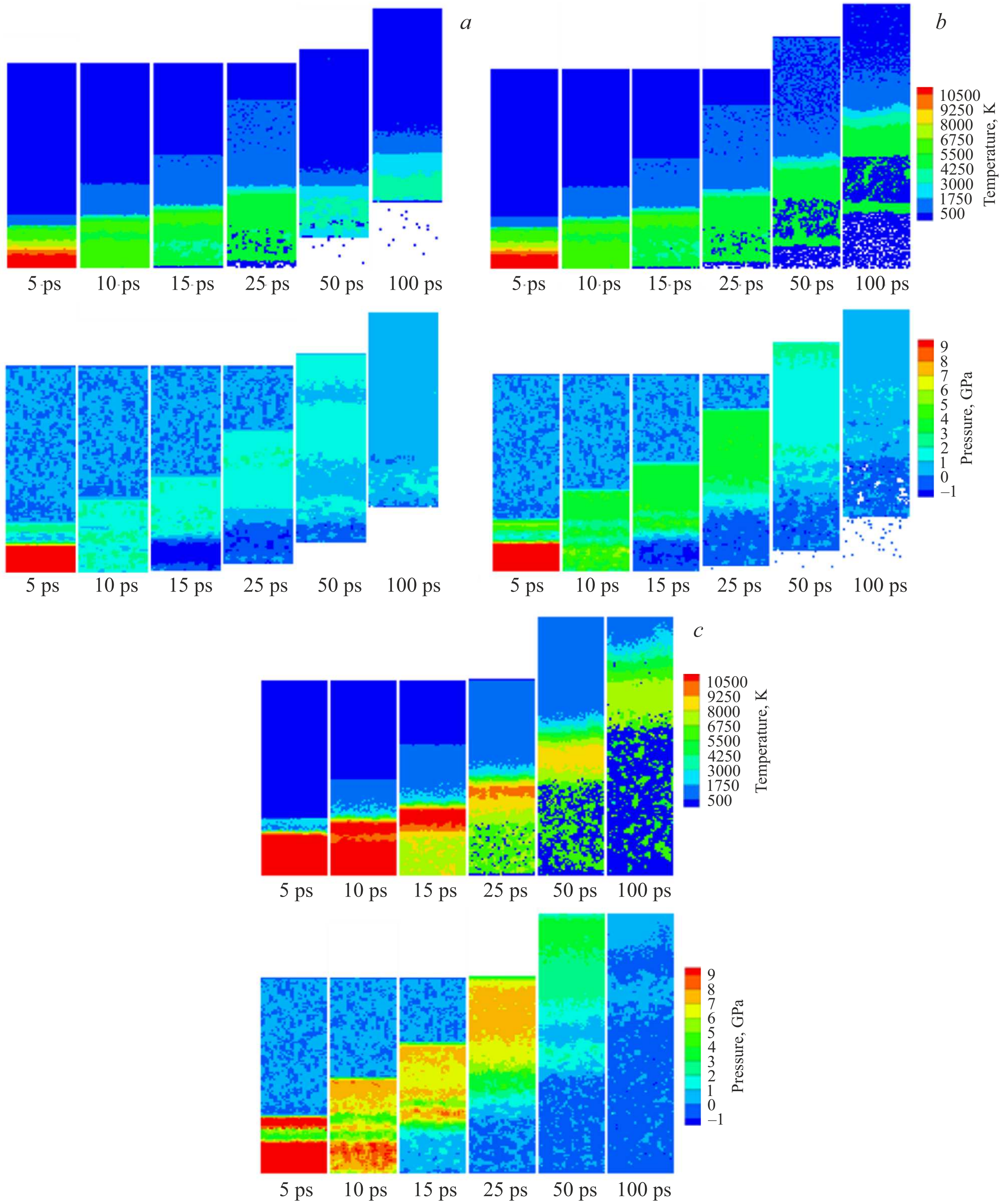

Figure 2. Sequences of temperature and pressure distributions in the calculation cell in the range 0–100 ps depending on the incident F_{inc} or absorbed F_{abs} energy fluxes: *a* — $F_{\text{inc}} = 0.5\,\text{J/cm}^2$, $F_{\text{abs}} = 26.1\,\text{mJ/cm}^2$ ($T_{\max} = 5100\,\text{K}$, $P_{\max} = 30\,\text{GPa}$); *b* — $F_{\text{inc}} = 1.0\,\text{J/cm}^2$, $F_{\text{abs}} = 52.1\,\text{mJ/cm}^2$ ($T_{\max} = 12650\,\text{K}$, $P_{\max} = 70\,\text{GPa}$); *c* — $F_{\text{inc}} = 0.5\,\text{J/cm}^2$, $F_{\text{abs}} = 104.3\,\text{mJ/cm}^2$ ($T_{\max} = 26450\,\text{K}$, $P_{\max} = 108\,\text{GPa}$).

4. Conclusion

The results of simulation of picosecond laser ablation of thin gold films in water indicate the formation of two main ablation modes and an intermediate one between them. The first mode is classical spallation when a thin metal nanofilm is completely detached from the substrate, and this mechanism can be used for surface cleaning by laser ablation. The second mode is associated with the rapid transformation of gold into metallic vapor due to ablation through a phase explosion mechanism. This mode may be of interest for the synthesis of nanoparticles with a diameter in the range of 1–10 nm, as well as the creation of gold-based alloys. The intermediate mode is associated with the mechanical separation of the molten gold film due to the extraction of the material through a combined mechanism of spallation and phase explosion. This mode is interesting for the study of nanostructuring of thin films and the synthesis of nanoparticles with a diameter of > 10 nm.

Conflict of interest

The authors declare that they have no conflict of interest.

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