

On the mechanism of polymer sublimation by laser radiation

V.I. Mazhukin, I. Smurov* and C. Surry*

Institute of Mathematical Modeling, Russian Academy of Sciences, Miusskaya Square 4, 125047 Moscow, Russia

** Ecole Nationale d'Ingénieurs de Saint-Etienne, 58 rue Jean Parot, 42023 Saint-Etienne cedex 2, France*

ABSTRACT

The mechanism of laser sublimation of polymers with low absorption coefficient and, as a result, with a volume nature of energy release is simulated. It is shown that the volume character of absorption of laser radiation together with the phase transformation leads to the existence of the overheated metastable state of material. The peculiarities of transient sublimation induced by laser action with the parameters similar for the optical disks formation are analysed.

I. INTRODUCTION

The creation of submicron sized elements is one of the main tasks of the microelectronics and informatics (for example, [1]). Various types of laser technique are widely used for this aim. In particular analogous problem is related to the fabrication of information storage devices involving optical recording (for example, [2,3]). This is why the phenomenon of the solid matter controlled shaping by means of high-power laser radiation is a subject to intensive investigations. The applied problems mentioned above require the investigation of laser action on thin organic films thickness less than 1 μm .

As consequences from experimental observation and from theoretical estimations [2,3], the optimal processing regimes are in the following range of the radiation intensity G and the pulse duration τ : $G=5 \cdot 10^6 - 5 \cdot 10^7 \text{ W/cm}^2$ and $\tau= 10^{-8} - 10^{-7} \text{ s}$.

Studied in greater details by now are the physical phenomena in the laser machining of metals [20-22], while there is a relatively small number of theoretical works devoted to the action on insulating substances. The simulation of laser action on polymer materials of the above mentioned thickness leads to the consideration of the problems concerning the phase transformations accompanied by volume heating. The volume nature of the energy release in insulators is governed by the relation between the thermal penetration depth l_T and the radiation penetration depth l_r . For most of insulators the relation $l_T/l_r \ll 1$ holds.

It is known [4] that the process of substance evaporation, in the beneath-critical range of pressures, is often accompanied by the creation of overheated metastable states. The overheated states may be represented either as overheating of the evaporating surface (in case of surface energy absorption) related to the pressure decrease on irradiated surface as compared to the saturated vapor pressure at given temperature, or as an overheated surface and temperature maximum located under the surface (volume energy release). The shortcomings of the theoretical analysis of the metastable states are primarily connected with the problems of the thermodynamic stability [5] and the decay of the overheated phases.

The present work is aimed to give an analysis of the peculiarities of insulating film destruction (material removal) by means of laser sublimation, provided the film is relatively thin ($l=0.5-2 \mu\text{m}$), has low heat conductivity and low radiation absorption coefficient. As it was already mentioned above, such processes lie in the basis of a number of microelectronic techniques. In the present model it is assumed that the metastable phase is stable enough, so that it does not decay during the laser pulse. The volume evaporation is not taken into account and the process of the surface sublimation is considered to be the main mechanism of the solid-to-vapor phase transition.

2. MATHEMATICAL MODEL

The heat model in case of low absorbing media represents the boundary problem for transient equation of heat transfer with the volume energy source, supplemented by the equation of radiation transfer.

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \lambda \frac{\partial T}{\partial x} - \frac{\partial G}{\partial x} \quad (1)$$

$$\frac{\partial G}{\partial x} + \kappa G = 0 \quad 0 \leq x \leq X_L \quad (2)$$

The initial and boundary conditions:

$$t=0 \quad T(x,0)=T_0$$

$$x=0 \quad \lambda \frac{\partial T}{\partial x} = 0 \quad (3)$$

$$x=X_L \quad G_s = G_0$$

Here: X_L - coordinate of the irradiated surface, $x=0$ - the back surface of the slab; x -axis is oriented in the direction of outward normal to the irradiated surface.

The evaporation process is described within the approximation of Knudsen layer, presented as the gas-dynamic discontinuity on the phase boundary at $x=X_L$, where three conservation laws (energy, mass and momentum, respectively) and two additional relations (characterized the nonequilibrium degree of phase boundary) are used [6]. In the present work evaporation into vacuum is considered, as a result $M=1$.

$$\rho_s V_{sv} = \rho_v (V_{sv} - u)$$

$$P_s + \rho V_{sv}^2 = P_v + \rho_v (V_{sv} - u)^2$$

$$-\lambda \frac{\partial T}{\partial x} = L_v V_{sv} \rho_s \quad (4)$$

$$\frac{T_v}{T_s} = \left[\left[1 + \pi \left(\frac{\gamma-1}{\gamma+1} \frac{m}{2} \right)^2 \right]^{1/2} - \pi \frac{\gamma-1}{\gamma+1} \frac{m}{2} \right]^2$$

$$\frac{\rho_v}{\rho_H} = \left(\frac{T_s}{T_v} \right)^{1/2} \left[\left(m^2 + \frac{1}{2} \right) \exp(m^2) \operatorname{erfc}(m) - \frac{m}{\pi^{1/2}} \right] +$$

$$+ \frac{1}{2} \frac{T_s}{T_v} \left\{ 1 - \pi^{1/2} m \exp(m^2) \operatorname{erfc}(m) \right\}$$

$$m = \frac{u}{(2RT_v)^{1/2}}, \quad M = \frac{u}{u_c} = \frac{u}{(\gamma RT_v)^{1/2}} = m \left(\frac{2}{\gamma} \right)^{1/2}$$

$$\rho_H = \frac{P_H}{RT_s}, \quad P_H = P_b \exp \left\{ \frac{L_v}{RT_s} \left(1 - \frac{T_b}{T_s} \right) \right\}$$

$$\operatorname{erfc}(m) = \frac{2}{\pi^{1/2}} \int_m^{\infty} \exp(-v^2) dv$$

Nomenclature: a thermal diffusivity; C_p heat capacity; G energy density flux; L_v latent heat of evaporation; M Mach number; P pressure; R universal gas constant; t time; $T(x,t)$ temperature; T_0 initial temperature; u vapor velocity; V_{sv} velocity of solid - vapour interface; x spatial coordinate; X_L coordinate of solid - vapour interface.

Greek Symbols: γ the ratio of heat capacities; κ coefficient of volumetric absorption of laser radiation; λ coefficient of heat conductivity; ρ density.

Subscripts: b boiling point; H saturated vapor; s condensed phase; v gas phase.

III.METHOD OF THE SOLUTION

Numerical algorithm is based on the method of dynamic adaptation of computational grids for the solution to be determined (specially developed for Stefan type problems [7,23]). This method is used for the solution of the problem (1-4) and allow to analyse both one-dimensional and multi-dimensional tasks [24]. In the dynamic adaptation methods the problem for computational grid construction is formulated at differential level. In the differential problem one part of the equations describes physical processes and the other one the behavior of grid points.

3.1. General Introduction. The main complexity for the solution of Stefan type problems is connected with the presence of moving boundaries, the position of which is determined during the solution. The dynamic adaptation method is based on the procedure of transition to arbitrary transient coordinate system by means of its automatic transformation with the help of the solution to be determined. The transition to transient coordinate system allows to eliminate the problems related to moving boundaries. In this case it is necessary to determine not only grid's functions but also the coordinates of grid points. The grid points behavior is determined by the partial differential equations (their amount is defined by independent variables number) which are added to the initial mathematical model. In the proposed method the adaptation mechanism of computational grids is introduced at differential level and does not depend on the method for numerical realization of mathematical models (finite differences or finite elements). The behavior of the additional equations depends on the dynamics of physical process. The transformation of coordinates by means of the solution to be determined, allows to dislocate grid points depending on the solution peculiarities. Such peculiarities can be as follows: spreading of large gradients, shock waves, contact and phase boundaries. Thickening of points in the regions of strong variation of the solution is done by transformation function, Q , which in general case could be a combination of numerical solution and its derivatives [25,26].

The problems connected with moving boundaries are eliminated by transition to arbitrary transient system of coordinates in which grid

points and boundaries appear to be unmovable. In this respect the method is similar to Lagrangian methods. However, there is a principal difference. In Lagrangian methods hydrodynamic velocity is fastened for transient system of coordinates. This is not always convenient and considerably narrows the class of the problems to be solved. In the dynamic adaptation methods, the velocity of coordinate system (and, respectively, grid points distribution) is not indicated beforehand. It is defined during the problem solution and depends on the peculiarities of the solution to be determined. It principally allows to obtain any desired points distribution and the application of the method is not limited by the problems of phase fronts dynamics, hydro- and gas-dynamics. More completely, the principles for constructing dynamically adapting algorithms for transient boundary value problems are given in [27].

It is necessary to underline, that different methods of computational grids construction, based on the various adaptation mechanisms are developed (for example, [13 - 16]). Also note should be taken to the fact that the simulation of the Stefan type problems with the volume energy release should be done by the explicit tracking of phase fronts positions.

3.2. Application of dynamic adaptation method to the present problem. Let us formulate the method for numerical solution with dynamic adaptation for the system (1-4). Transition to arbitrary transient system of coordinates is done by substitution of variables of general type

$$x = f(q, \tau), \quad t = \tau,$$

having the reverse transformation

$$q = \Phi(x, t), \quad \tau = t.$$

Partial derivatives of dependent variables are expressed conventionally:

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial \tau} + \frac{\partial q}{\partial \tau} \frac{\partial}{\partial q} = \frac{\partial}{\partial \tau} - \frac{\partial x}{\partial \tau} \frac{\rho}{\Psi} \frac{\partial}{\partial q} = \frac{\partial}{\partial \tau} + \frac{Q}{\Psi} \frac{\partial}{\partial q}$$

$$\frac{\partial}{\partial x} = \frac{\partial q}{\partial x} \frac{\partial}{\partial q} = \frac{\rho}{\Psi} \frac{\partial}{\partial q}, \quad \Psi = \frac{\partial x}{\partial q} \rho \quad (5)$$

where $\frac{\partial x}{\partial \tau} = -\frac{Q}{\rho}$ - velocity of coordinate system, Q - arbitrary function depending on the solution to be determined, Ψ - metric coefficient (or transformation coefficient) indicating how many times the initial area is changed.

Function Q (as it is already noticed, depends on peculiarities of the solution to be determined) permits a great freedom of choice, and it should be chosen by the user. Without entering into details, concerning the choice of Q , (special analysis is done in paper [27]), just note that some typical forms of Q functions will lead to different typical transformations. For example, choosing Q depending on the velocity of the solution variation, it is possible to obtain the thickening of grid points in the region of large gradients [25-27]. As it is shown in practice, for the problem with moving boundaries the most convenient form is $Q = -D \cdot (\partial \Psi / \partial q)$. It provides quasi-uniform grid with fixed number of points at each time step, if the value of coefficient D is optimum. Thus, the problem for moving interface boundaries in computational space leads to the determination of Q_{sv} values .

IV. RESULTS AND DISCUSSION

In a number of laser experiments with organic polymers (for example, [2,3,8,9]), the creation of bubbles at a certain depth under the surface, was observed. It is accompanied by a rapid pressure growth up to 100 bar. After the end of laser pulse, the pressure drops fast, reaching zero in several nanoseconds.

Yet the experimental and theoretical data available up to now do not allow one to make a final conclusion about the character and the

mechanism of such phase transformations.

Let us consider some general features of sublimation process as described by the model (1-4), considering rectangular shape of laser pulse.

The simulation was carried out for an organic material with the thermophysical and optical properties close to the properties of phthalocyanes: $\rho = 1.44 \text{ g/cm}^3$, $L_v = 0.384 \text{ kJ/g}$, $\kappa = 10^5 - 10^4 \text{ cm}^{-1}$, $T_b = 750 \text{ K}$, $\lambda = 3.8 \cdot 10^{-3} \text{ W/(cm K)}$, $C_p = 3 \text{ J/(g K)}$.

The rectangular laser pulse of the energy density flux $G_0 = 5 \cdot 10^6 \text{ W/cm}^2$ and duration $\tau = 40 \text{ nsec}$ falls on the surface of the phthalocyan film of thickness $1 \text{ }\mu\text{m}$ with absorption coefficient $\kappa = 10^6 \text{ cm}^{-1}$. By the moment $t = 15 \text{ nsec}$ the quasi steady state regime is established, characterized by the spatial temperature profile that has a maximum value $T_{\text{max}} = 870 \text{ K}$ at the distance of about $0.01 \text{ }\mu\text{m}$ from the surface (see Figure 1). The temperature of the surface (current position $X_s = 0.832 \text{ }\mu\text{m}$) is equal to 805 K , the layer of $0.168 \text{ }\mu\text{m}$ thickness has been evaporated by that time. Thus at the moment when the steady state is established the surface of the solid phase turns out to be overheated by 65 K (relatively the sublimation temperature in normal conditions), while the volume overheating reaches the value of 120 K .

The analysis of the transient dependencies of the reactive pressure of evaporation and the sublimation front velocity $V_{sv}(t)$ (Figures. 2,3) reveals that these values approach the quasi-stationary regime in a non-monotone way. This type of non-monotone behavior is caused by the energy stored in excess of the stationary value. The release of this "spare" energy causes the increase of the sublimation rate. As a result, well-defined peaks appear on the plots of $V_{sv}(t)$ and $P_s(t)$. Note, that the decrease of polymer film thickness corresponds to the negative values of V_{sv} .

The reactive pressure P_s , rising at the surface due to the flux of sublimating matter, mounts up to 4 bar . At the same time the estimations based on the saturated vapor pressure indicate the possibility of the pressure increase up to 130 bar in the region where the temperature maximum is localized.

Under these conditions the thickness of the evaporated layer x_v reaches the value of $0.65 \text{ }\mu\text{m}$ at $t = 40 \text{ nsec}$ (Figure 3).

The time dependencies of the main characteristic values of the

process, namely surface temperature $T(t)$, sublimation rate $v_{sv}(t)$, reactive pressure $P_s(t)$, thickness of evaporated layer $x_v(t)$ during the action of the rectangular laser pulse with duration $\tau=10$ nsec and intensity $G=10^7$ W/cm² are presented in the Figures 4, 5. The curves indicate that the energy stored up causes comparatively slow surface cooling after the heat source is switched off and rather prolonged evaporation.

Affecting most significantly the process as a whole is an important parameter of the medium, namely the radiation absorption, which is characterized by the coefficient κ . The absorption of phthalocyanes is known very approximately, and it varies considerably from one material to another inside of the same family. Moreover the absorption coefficient strongly depends on the radiation wavelength. The absorption coefficients of phthalocyanes lie in the range 10^4 - 10^5 cm⁻¹, at the same time the heat conductivity coefficient varies slightly. Consequently, the region of heat release and of the temperature sharp variation for different materials should differ substantially.

The temporal characteristics of sublimation during irradiation of the phthalocyan film 1 μm thickness by the laser pulse with $G_0=10^7$ W/cm² and $\tau=10$ nsec for different κ values are presented in the Figures 6-9. Reducing κ by one half (down to $\kappa=5 \cdot 10^4$ cm⁻¹, Figures 6-7) results in the temperature maximum localization at a larger depth. The approach to the quasi steady state regime becomes more prolonged with more distinct non-monotone behavior in time. The velocity v_{sv} and the pressure P_s peaks increase by about a factor of two. The thickness of evaporated layer therewith sufficiently decreases.

Reducing the absorption coefficient down to $\kappa=2 \cdot 10^4$ cm⁻¹ at given pulse duration and intensity (Figures 8,9) causes the reduction of heating and insignificant sublimation. The sublimated layer thickness diminishes down to 0.018 μm .

When $\kappa=10^4$ cm⁻¹ the sublimation of the matter is in fact absent, the surface temperature $T_s=500$ K being far below T_v .

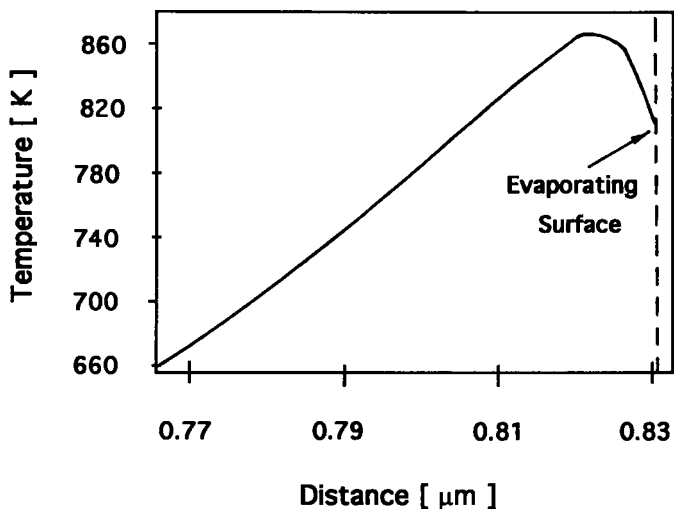


Figure 1. Spatial temperature distribution in polymer layer (initial thickness 1 μm) under the action of a rectangular laser pulse ($G_0 = 5 \cdot 10^6 \text{ W/cm}^2$, $\tau = 40 \text{ nsec}$) at the moment $t = 15 \text{ ns}$. The right end of temperature curve corresponds to the position of the irradiated surface.

V. CONCLUSION

When phthalocyanans are exposed to pulsed laser radiation the region of temperature maximum is formed under the surface due to the volume nature of energy absorption. The matter in this region occurs in a metastable overheated state. The depth of this region, as well as the rate of intensive sublimation strongly dependent on the properties of the material, namely absorption coefficient.

As already mentioned, we assume stability of the metastable state in thermocycles simulation. However, even though its lifetime is unknown, it is always finite. The explosive decay of the metastable phase is possible in reality, caused by the process of volume evaporation. It should necessarily be kept in mind when elaborating and applying laser technologies of the above mentioned type in microelectronics. The explosive decay of the metastable phase on the one hand speeds up the process of materials removal, but also can cause a serious problem when obtaining submicron-sized elements.

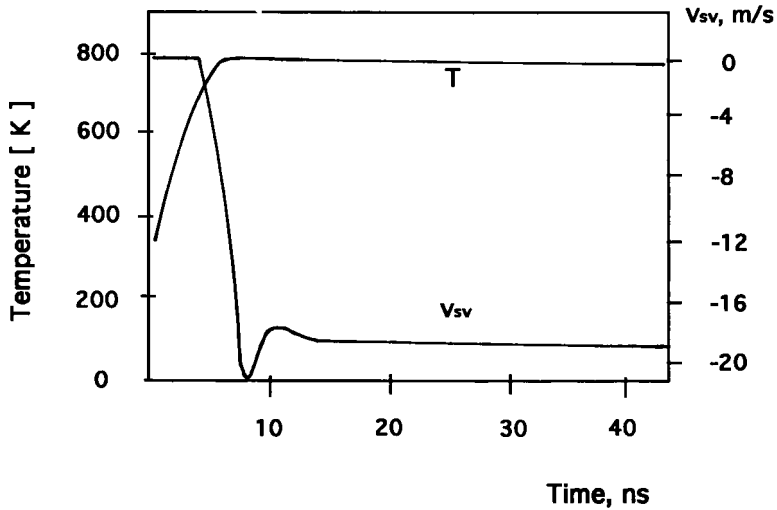


Figure 2. The transient dependencies of surface temperature T and sublimation front velocity V_{sv} for the pulsed laser action ($G=5 \cdot 10^6$ W/cm², $\tau=40$ ns) on polymer layer (initial thickness $1 \mu\text{m}$, $\kappa=10^5$ cm⁻¹).

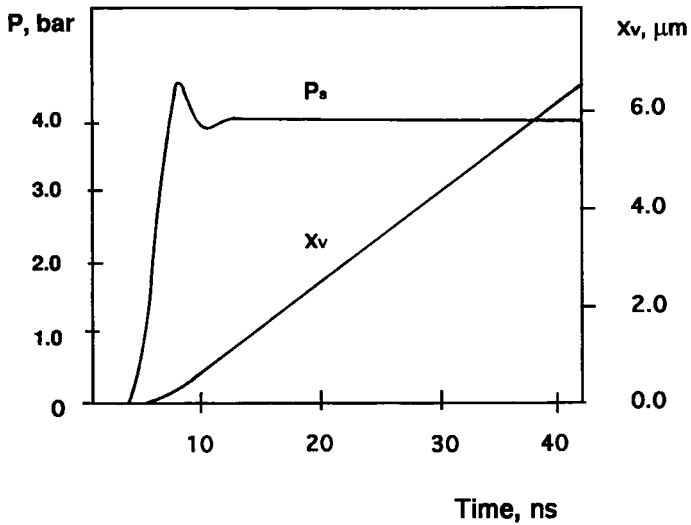


Figure 3. The transient dependencies of reactive pressure of evaporation P_s and evaporated layer thickness x_v for the pulsed laser action ($G = 5 \cdot 10^6$ W/cm², $\tau = 40$ ns) on polymer layer (initial thickness $1 \mu\text{m}$, $\kappa=10^5$ cm⁻¹).

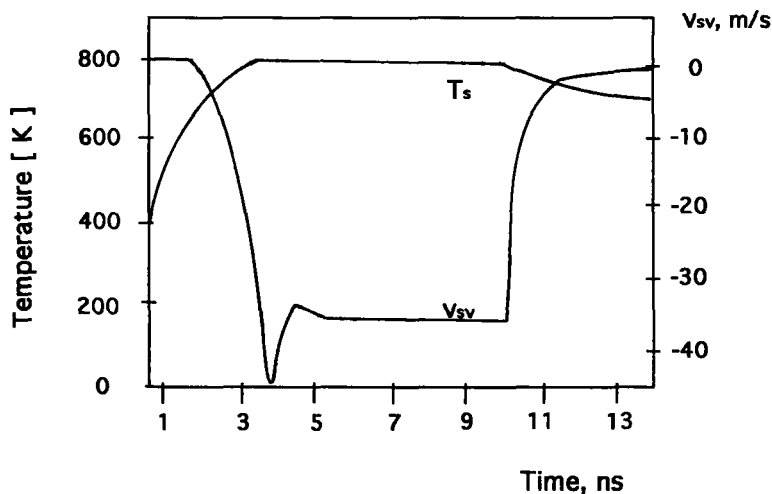


Figure 4. The transient dependencies of surface temperature T and sublimation front velocity V_{sv} for the pulsed laser action ($G=10^7$ W/cm², $\tau=10$ ns) on polymer layer (initial thickness $1\ \mu\text{m}$, $\chi=10^5$ cm⁻¹).

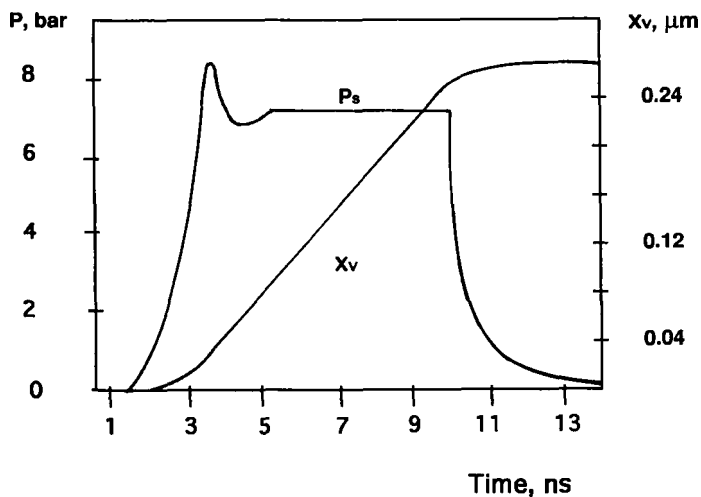


Figure 5. The transient dependencies of reactive pressure of evaporation P and evaporated layer thickness x_v for the pulsed laser action ($G=10^7$ W/cm², $\tau=10$ ns) on polymer layer (initial thickness $1\ \mu\text{m}$, $\chi=10^5$ cm⁻¹).

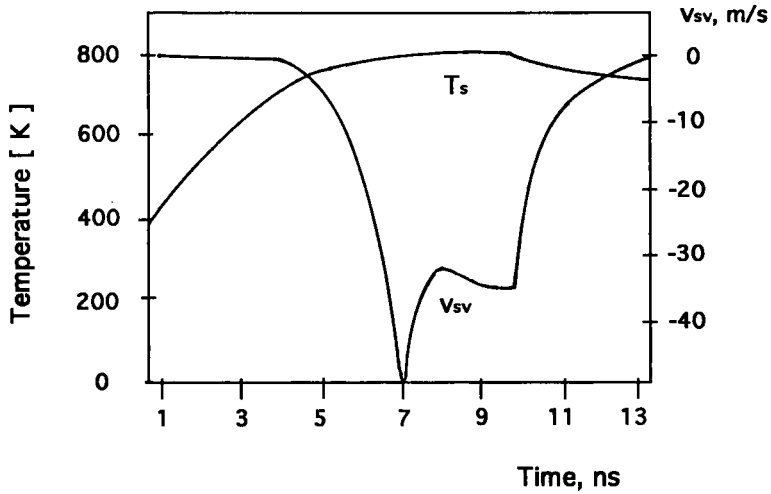


Figure 6. The transient dependencies of surface temperature T and sublimation front velocity V_{sv} for the pulsed laser action ($G=10^7$ W/cm^2 , $\tau=10$ ns) on polymer layer (initial thickness $1 \mu m$, $\alpha=5 \cdot 10^4$ cm^{-1}).

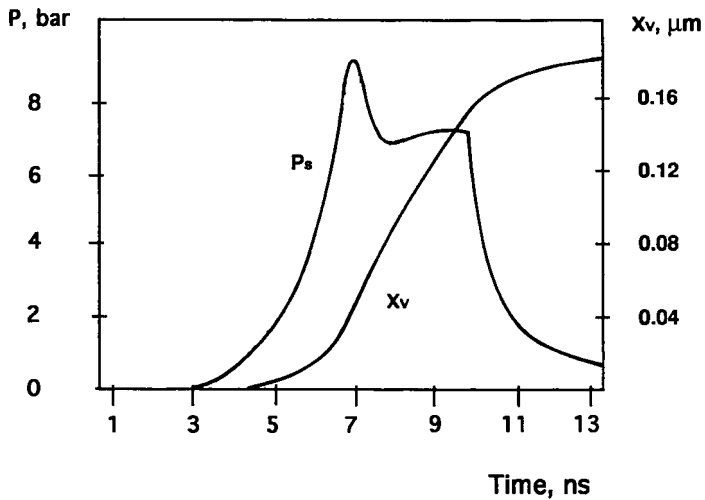


Figure 7. The transient dependencies of reactive pressure of evaporation P_s and evaporated layer thickness x_v for the pulsed laser action ($G=10^7$ W/cm^2 , $\tau=10$ ns) on polymer layer (initial thickness $1 \mu m$, $\alpha=5 \cdot 10^4$ cm^{-1}).

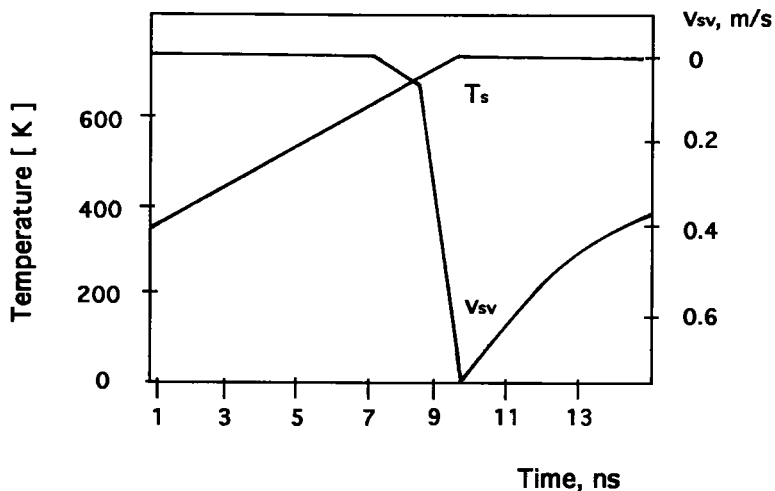


Figure 8 . The transient dependencies of surface temperature T and sublimation front velocity V_{sv} for the pulsed laser action ($G=10^7$ W/cm², $\tau=10$ ns) on polymer layer (initial thickness $1 \mu\text{m}$, $\kappa=2 \cdot 10^4$ cm⁻¹).

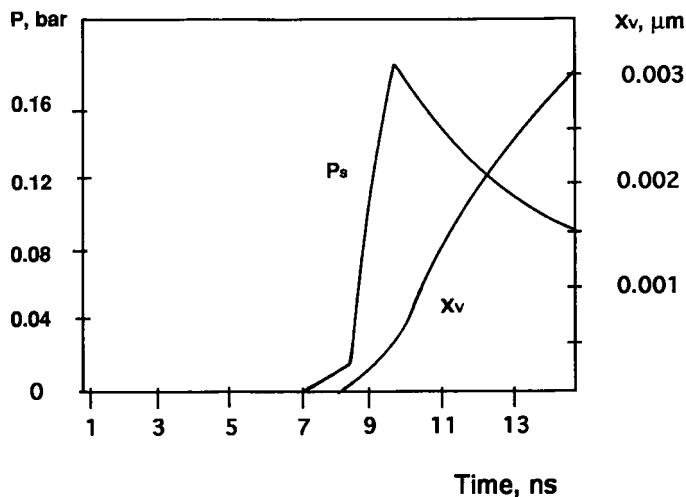


Figure 9 . The transient dependencies of reactive pressure of evaporation P and evaporated layer thickness x_v for the pulsed laser action ($G=10^7$ W/cm², $\tau=10$ ns) on polymer layer (initial thickness $1 \mu\text{m}$, $\kappa=2 \cdot 10^4$ cm⁻¹).

REFERENCES

1. Valiev K.A. *Physics of Submicron Litography*. M.:Nauka, 1990., 528 p.
2. Broer D.J., Vriens L. Laser-Induced Optical Recording in Thin Films. *Appl. Physics A.*, 1983, v.32, pp. 107-123.
3. Kivits P., Bont R.D., Jacobs B., Zalm P. The Hole Formation Process in Tellurium Layers for Optical Data Storage. *Thin Solid Films*, 1982, No 82, pp, 215-231.
4. Samohin A.A. The action of laser radiation on strongly absorbing condensed matter. Trudi IOFAN, M.: Nauka, vol.13, p. 120.
5. Iskoldskij A.M., Nesterihin Y.E., Patashinskij A.Z., Pipus V.K., Epelbaum Ya.G. About nonstability of gradient explosion. *DAN SSSR*, 1977, vol.236, No 6, pp. 1346-1349.
6. Knith C.J., Theoretical Modeling of Rapid Surface Vaporization With Back Pressure. *AIAA J.*, 1979, vol.17, pp.519-523.
7. P.V.Breslavskij, V.I. Mazhukin, Mathematical Modeling of Pulse Melting and Evaporation of Metals with Explicit Tracking of Phase Fronts. *Inzhenerno- fizicheskii zhurnal*, vol.57, No 1, pp. 107-114, 1989.
8. Koren G., Oppenheim U.P. Laser Ablation of Polymers in Pressurized Gas Ambients. *J. Appl. Phys.*, 1987, vol. 42, No. 1, pp. 41-43.
9. Dyer P.E., Srinivasan R., *Appl Phys Lett.*, 1986, v.48, pp. 445-448.
13. J.F.Thompson, Grid Generation Technique in Computation Fluid Dynamics, *AJAA J.*,vol.22, No 11, pp.1505-1523, 1984.
14. J.G.Verner, J.G.Blom, J.M.Sanz-Serna, An Adaptive Moving Method for One-Dimensional Systems of Partial Differential Equations, *J.Comput.Phys.*, vol.82, pp.454-486, 1989.
15. M.Lacroix. Numerical Solution of Phase Change Problems: an Eulerian-Lagrangian Approach. *Num.Heat Transfer, Part*

- B*, vol. 19, pp.57 - 78, 1992.
16. A.J.Wathen, Optimal Moving Grids for Time-Dependent Partial Differential Equations. *J.Comput.Phys.* vol. 101, pp. 51-54, 1992.
 18. A.Lashin, I.Smurov, A.Uglov, P.Matteazzi, V.Tagliaferri, Heat Process in Pulse Laser Treatment of Metallic Materials, *Int. J. Heat and Technology*, vol.7, No 2, pp.60-73, 1989.
 19. I.Smurov, A.Uglov, A.Lashin, P.Matteazzi, V.Tagliaferri, Modelling of Pulse-Periodic Energy Flow Action on Metallic Materials, *Int. J. Heat and Mass Transfer*, vol. 34, No 4/5, pp.961-971, 1991.
 20. A.Uglov, I.Smurov, A.Lashin, A.Guskov, *Modeling of Thermal Processes under Pulse Laser Action on Metals*, Moscow, Nauka, 1991.
 21. *Laser Treatment of Materials*, ed by B.L.Mordike, Proceedings of ECLAT'92, DGM Informationsgesellschaft, Verlag, Oberursel, 1992.
 22. *Laser Materials Processing*, vol.75, ed by D.Farson, W.Steen, I.Miyamoto, Proceedings of ICALEO'92, Laser Institute of America, Orlando, 1992.
 23. N.A.Dar'in, V.I.Mazhukin, Mathematical modeling of Stefan problem using adaptive grids. *Differenzialnue uravnenija*, vol. 23, No 7, pp. 1154-1160, 1987.
 24. V.I.Mazhukin, Mathematical modeling of Stefan problems by means of adaptive grids. *Teplomassoobmen - MMF/HEAT/MASS TRANSFER-MIF/*, Minsk, 1988, pp.125-139.
 25. N.A.Dar'in, V.I.Mazhukin, About one approach to construct the adaptive difference grids. *DAN SSSR*, vol. 298, No 1, pp. 64-68, 1988.
 26. V.F.Vasilevskij, V.I.Mazhukin, Numerical calculation of temperature waves with weak break by dynamic adaptive grids. *Differenzialnue uravnenija*, vol. 25, No 7, pp. 1188-1193, 1989.
 27. V.I.Mazhukin, L.Ju.Takojeva, The construction principles of the grids dynamically adapted to the solution. *Mathematischeskoe modelirovanie*, vol. 2, No 3, pp. 101- 118, 1990.