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Overheated metastable states in polymer sublimation by laser radiation

V.I. Mazhukin^a, I. Smurov^b, C. Surry^b, G. Flamant^{c,*}

^a *Institute of Mathematical Modelling, Russian Academy of Sciences, Miusskaya Square 4, 125074 Moscow, Russia*

^b *Ecole Nationale d'Ingénieurs de Saint-Etienne, 58 Rue Jean Parot, 42023 Saint-Etienne Cedex 2, France*

^c *Institut de Science et de Génie des Matériaux et Procédés, CNRS, B.P. 5 Odeillo, 66125 Font-Romeu Cedex, France*

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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 formation of optical disks, are analysed.

1. Introduction

The creation of submicron-sized elements is one of the main tasks of the microelectronics industries and of informatics [1]. Various types of laser techniques are widely used to this aim. One example in this area is related to the fabrication of information-storage devices involving optical recording [2,3]. This is why the phenomenon of controlled shaping of solid matter by means of high-power laser radiation is subject to intensive investigations. The application requires the investigation of laser action on thin organic films with a thickness less than 1 μm .

As a result of experimental observation and from theoretical estimations [2,3], the optimum processing regimes often are in the following range of the

radiation intensity G and the pulse duration τ : $G = 5 \times 10^6 - 5 \times 10^7 \text{ W/cm}^2$ and $\tau = 10^{-8} - 10^{-7} \text{ s}$.

Studied in greater detail by now are the physical phenomena in the laser machining of metals (for example, Refs. [7,10–14]), 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 general mathematical approach is reported in Ref. [15]). 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 the insulators the relation $l_T/l_r \ll 1$ holds.

It is known [4] that the process of material evaporation, in the sub-critical range of pressures, is often accompanied by the creation of overheated metastable

* Corresponding author. Fax: +33-68 30 29 40.

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 the irradiated surface as compared to the saturated vapour pressure at a 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 at giving an analysis of the peculiarities of insulating film destruction (material removal) by means of laser sublimation, provided the film is relatively thin ($l = 0.5\text{--}2 \mu\text{m}$), has low heat conductivity and low radiation absorption coefficient. As it was already mentioned above, such processes lie at the heart 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-vapour phase transition.

2. Mathematical model

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

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

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

The initial and boundary conditions:

$$\begin{aligned} t = 0, \quad T(x, 0) &= T_0, \\ x = 0, \quad \lambda \frac{\partial T}{\partial x} &= 0, \\ x = X_L, \quad G_s &= G_0. \end{aligned} \quad (3)$$

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

The evaporation process is described within the approximation of a 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 (characterizing the nonequilibrium degree of the phase boundary) are used [6]. In the present work evaporation into vacuum is considered, as a result $M = 1$:

$$\begin{aligned} \rho_s V_{sv} &= \rho_v (V_{sv} - u), \\ P_s + \rho V_{sv}^2 &= P_v + \rho_v (V_{sv} - u)^2, \\ -\lambda \frac{\partial T}{\partial x} &= L_v V_{sv} \rho_s, \end{aligned} \quad (4)$$

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

$$\begin{aligned} \frac{\rho_v}{\rho_H} &= \left(\frac{T_s}{T_v} \right)^{1/2} \left[\left(m^2 + \frac{1}{2} \right) \exp(m^2) \operatorname{erfc}(m) \right. \\ &\quad \left. - \frac{m}{\pi^{1/2}} \right] + \frac{1}{2} \frac{T_s}{T_v} \\ &\quad \times \left[1 - \pi^{1/2} m \exp(m^2) \operatorname{erfc}(m) \right], \end{aligned}$$

$$m = u / (2RT_v)^{1/2},$$

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

$$\rho_H = \frac{P_H}{RT_s},$$

$$P_H = P_b \exp \left[\frac{L_v}{RT_b} \left(1 - \frac{T_b}{T_s} \right) \right],$$

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

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 vapour 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; χ coefficient of volumetric absorption of laser radiation; λ coefficient of heat conductivity; ρ density. Subscripts: b boiling point; H saturated vapour; s condensed phase; v gas phase.

3. Results and discussion

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

Yet the experimental and theoretical data available up to now do not allow to make a final conclusion about the character and the mechanism of such a phase transformation.

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

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

The rectangular laser pulse of the energy density flux $G_0 = 5 \times 10^6 \text{ W/cm}^2$ and duration $\tau = 40 \text{ ns}$ falls on the surface of the phthalocyanine film of thickness $1 \text{ }\mu\text{m}$ with absorption coefficient $\chi = 10^5 \text{ cm}^{-1}$. By the moment $t = 15 \text{ ns}$ 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 a distance of about $0.01 \text{ }\mu\text{m}$ from the surface (see Fig. 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 is overheated by 55 K (relative to the sublimation temperature of 750 K 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 $V_{sv}(t)$ (Figs. 2 and 3) reveals that these values approach the quasi-stationary regime in a non-monotonous way. Non-monotonous behaviour shows that during volume heating, material in condensed phase stores an excess energy which is later on released by the sublimation process. The release of the excess energy is followed by an increased rate of sublimation V_{sv} , which later, with a small down-

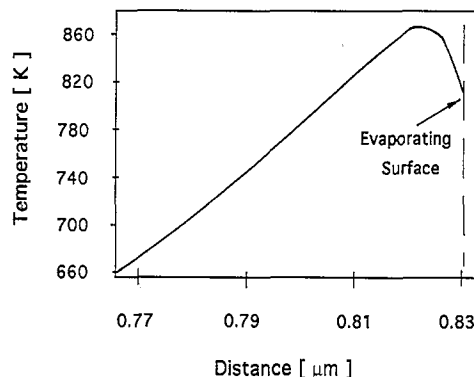


Fig. 1. Spatial temperature distribution in a polymer layer (initial thickness $1 \text{ }\mu\text{m}$) under the action of a rectangular laser pulse ($G_0 = 5 \times 10^6 \text{ W/cm}^2$, $\tau = 40 \text{ ns}$) at the moment $t = 15 \text{ ns}$. The right end of temperature curve corresponds to the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

fall, approaches the stationary level. At relatively low values of the thermal diffusivity coefficient $a = \lambda/\rho C_p$, which is usual for the polymers being considered, the condition of volume heating [11] $V_{sv}/a\chi > 1$ is fulfilled even at a velocity $V_{sv} \approx 1 \text{ m/s}$. The value of the sublimation rate V_{sv} is determined by the surface temperature T_s . For fixed a and χ the temperature T_s rises with an increase of G . Thus, with the growth of radiation intensity the influence of a superheated metastable region on the regime of sublimation becomes more pronounced. This results in the appearance of well-defined peaks on the plots of V_{sv} and P_s (Figs. 2–7). Note that the non-mo-

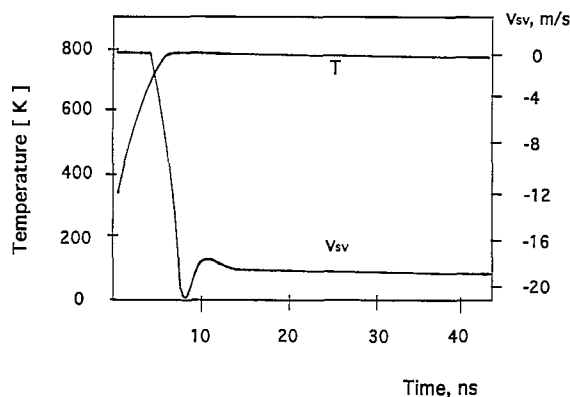


Fig. 2. Transient dependencies of surface temperature T and sublimation front velocity V_{sv} for the pulsed laser action ($G = 5 \times 10^6 \text{ W/cm}^2$, $\tau = 40 \text{ ns}$) on the polymer layer (initial thickness $1 \text{ }\mu\text{m}$, $\chi = 10^5 \text{ cm}^{-1}$).

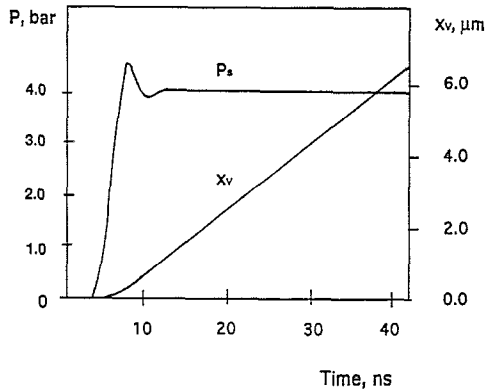


Fig. 3. Transient dependencies of reactive pressure of evaporation P_s and evaporated layer thickness x_v for the pulsed laser action ($G = 5 \times 10^6$ W/cm², $\tau = 40$ ns) on the polymer layer (initial thickness 1 μ m, $\chi = 10^5$ cm⁻¹).

nonotous character of approaching the stationary solution being observed is usual for most of strongly nonlinear systems.

The reactive pressure P_s , rising at the surface due to the flux of subliming matter, reaches 4 bar. At the same time the estimations based on the saturated vapour pressure indicate the possibility of a 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 μ m at $t = 40$ ns (Fig. 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 $\tau = 10$ ns and intensity $G = 10^7$ W/cm² are presented in Figs. 4 and 5. The curves indicate that the energy stored causes a comparatively slow surface cooling after the heat source is switched off and a 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 χ . The absorption of phthalocyanines is known very approximately, and it varies considerably from one material to another within the same family. Moreover, the absorption coefficient strongly depends on the radiation wavelength. The absorption coefficients of phthalocyanine lie in the range 10^4 –

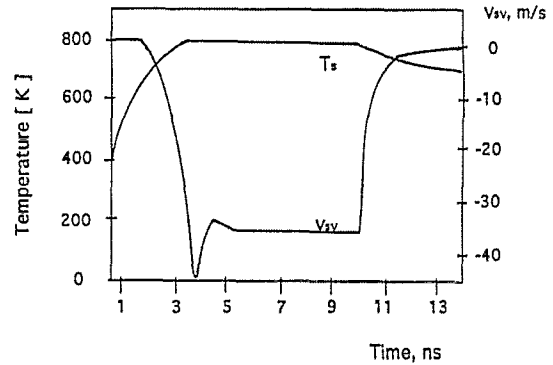


Fig. 4. Transient dependencies of surface temperature T and sublimation front velocity V_{sv} for the pulsed laser action ($G = 10^7$ W/cm², $\tau = 10$ ns) on the polymer layer (initial thickness 1 μ m, $\chi = 10^5$ cm⁻¹).

10^5 cm⁻¹, at the same time the heat conductivity varies slightly. Consequently, the region of heat release and of the sharp variation of the temperature should differ substantially for different materials.

The temporal characteristics of sublimation during irradiation of the phthalocyanine film of 1 μ m thickness by the laser pulse with $G_0 = 10^7$ W/cm² and $\tau = 10$ ns for different χ values are presented in Figs. 6–9. Reducing χ by one half (down to $\chi = 5 \times 10^4$ cm⁻¹, Figs. 6 and 7) results in a temperature maximum located at a larger depth. The approach to the quasi-steady state regime becomes more prolonged with more distinct non-monotonous behaviour in time. The velocity V_{sv} and the pressure P_s

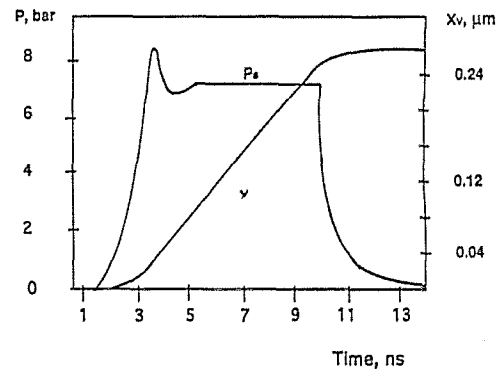


Fig. 5. Transient dependencies of reactive pressure of evaporation P_s and evaporated layer thickness x_v for the pulsed laser action ($G = 10^7$ W/cm², $\tau = 10$ ns) on the polymer layer (initial thickness 1 μ m, $\chi = 10^5$ cm⁻¹).

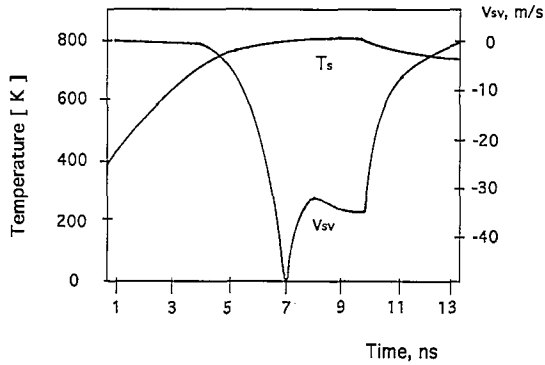


Fig. 6. Transient dependencies of surface temperature T and sublimation front velocity V_{sv} for the pulsed laser action ($G = 10^7$ W/cm², $\tau = 10$ ns) on the polymer layer (initial thickness 1 μm , $\chi = 5 \times 10^4$ cm⁻¹).

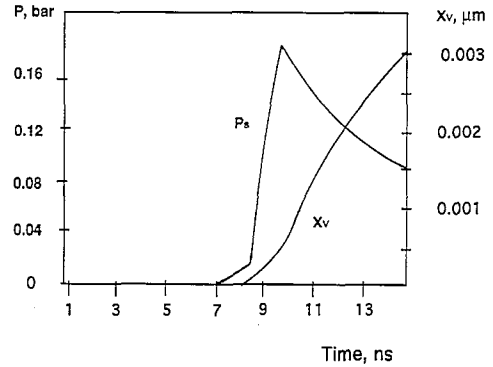


Fig. 9. Transient dependencies of reactive pressure of evaporation P_s and evaporated layer thickness x_v for the pulsed laser action ($G = 10^7$ W/cm², $\tau = 10$ ns) on the polymer layer (initial thickness 1 μm , $\chi = 2 \times 10^4$ cm⁻¹).

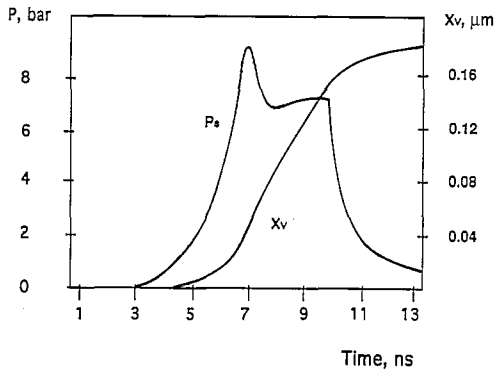


Fig. 7. Transient dependencies of reactive pressure of evaporation P and evaporated layer thickness x_v for the pulsed laser action ($G = 10^7$ W/cm², $\tau = 10$ ns) on the polymer layer (initial thickness 1 μm , $\chi = 5 \times 10^4$ cm⁻¹).

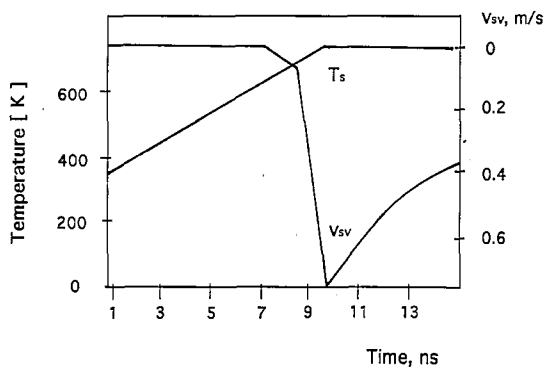


Fig. 8. Transient dependencies of surface temperature T and sublimation front velocity V_{sv} for the pulsed laser action ($G = 10^7$ W/cm², $\tau = 10$ ns) on the polymer layer (initial thickness 1 μm , $\chi = 2 \times 10^4$ cm⁻¹).

peaks increase by about a factor of two. The thickness of the evaporated layer decreases.

Reducing the absorption coefficient down to $\chi = 2 \times 10^4$ cm⁻¹ at a given pulse duration and intensity (Figs. 8 and 9) causes the reduction of heating and insignificant sublimation. The sublimed layer thickness diminishes down to 0.003 μm .

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

4. Conclusion

When phthalocyanines are exposed to pulsed laser radiation the 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 are strongly dependent on the properties of the material, namely the absorption coefficient.

As already mentioned, we assume stability of the metastable state in the thermocycle 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.

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