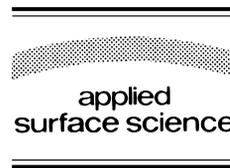




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Bulk model of laser ablation of polymers

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Abstract

The model of laser ablation driven by a bulk photothermal reaction is considered. Stationary wave solutions are obtained and analyzed. In the case of a simple photothermal bond-breaking reaction, it is possible to reduce this bulk ablation model to the surface evaporation model with some apparent activation energy. A more complicated model of laser ablation, taking into consideration a photothermal modification of broken bonds within the bulk of material, is also studied. The existence of the second threshold related to multiple-shot and long pulse irradiation experiments has been demonstrated. It is shown that the effect of modification on the ablation kinetics qualitatively depends on the interrelation between activation energies of two considered bulk reactions. © 1998 Elsevier Science B.V.

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1. Introduction

UV-laser irradiation of polymers leads to various thermal, photophysical, and photochemical processes within the bulk and on the material surface. Bulk processes may lead to incubation effects, facilitate or hinder material removal, and may result in instabilities of the plain ablation front. Their influence can be understood within the framework of two types of models.

In models of the first type [1-7], laser ablation is considered as a thermal surface process similar to surface evaporation (sublimation). This leads to the concept of a moving ablation front whose velocity is

determined by the temperature and, probably, by the material composition at this front. Within this picture, bulk processes modify the chemical and physical properties of the material below the surface, e.g., due to changes in the chemical composition of the polymer. Additionally, bulk chemical reactions may produce volatile species as by-products which induce stresses and thereby influence the ablation rate. As a result, the surface temperature and/or the constants involved in the evaporation law (activation energy, pre-exponential factor) may change. Thereby, bulk processes influence the ablation rate indirectly.

In the present communication, we consider the non-surface thermal models of laser ablation. Features of a photochemical bulk etching process have been studied in Refs. [8,9]. In the case of laser ablation, the interface velocity is not determined by

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the temperature at the ablation front. Here, the position of the moving boundary is directly related to the degree of material modification, e.g., to the critical average chain length of macromolecules. This length is decreased via thermal bond-breaking reactions within the bulk of material. The analysis presented below shows, however, that in some cases, the bulk ablation process may be described as surface evaporation with some apparent activation energy.

In order to demonstrate the crucial role of modification that hinders material removal, as has been observed in recent multiple-pulse and long-pulse experiments [10–12], along with the bond-breaking reaction, we consider the following deep modification reaction. It allows describing qualitatively the existence of the second ablation threshold.

2. The models

We consider the simplest thermally activated reaction:



Here A is associated with elements of initial virgin material, while B denotes the reaction products which, in the context of this paper, can be attributed to broken bonds. In our previous papers, we considered the same reaction as that accompanying thermal evaporation from the surface [5,6]. In the present model, we relate the laser ablation directly to reaction (1) [13] evaluating the position of the moving ablation front from the condition:

$$N_B(0,t) = N^* . \tag{2}$$

Condition (2) is written in a coordinate system fixed with the ablation front $z = 0$. N^* is a parameter, N_A and N_B are concentrations of A and B species, respectively. The set of equations consists of the concentration kinetic equation:

$$\frac{\partial N_A}{\partial t} = V \frac{\partial N_A}{\partial z} - A_1 N_A \exp\left(\frac{-E_A}{T}\right) \tag{3}$$

the heat diffusion equation:

$$\frac{\partial T}{\partial t} = V \frac{\partial T}{\partial z} + D_T \frac{\partial^2 T}{\partial z^2} + \frac{\alpha I}{c_p \rho} \tag{4}$$

and the equation for intensity distribution within the bulk of material:

$$\frac{\partial I}{\partial z} = -\alpha I. \tag{5}$$

Here, V is the ablation front velocity, A_1 is the reaction frequency, E_A is the activation energy, T is the absolute temperature, D_T is the heat diffusivity, I is the light intensity, α is the absorption coefficient, and c_p and ρ are specific heat and density.

Sets (2)–(5) should be completed by the boundary conditions:

$$\left. \frac{\partial T}{\partial z} \right|_{z=0} = 0; \quad T(\infty) = T_\infty \tag{6}$$

$$I(0,t) = I_0(t) \tag{7}$$

and the initial conditions:

$$N_A(z,0) = N_0; \quad N_B(z,0) = 0 \tag{8}$$

$$T(z,0) = T_\infty. \tag{9}$$

Here, $I_0(t)$ is the laser light intensity. We choose the boundary conditions in the simplest form (Eq. (6)), neglecting the heat flux on the surface due to difference in enthalpies. We do not need a differential equation for N_B since the relation holds:

$$N_A + N_B = N_0. \tag{10}$$

Therefore, the boundary condition (2) can be overwritten:

$$N_A(0,t) = N_0 - N^* . \tag{11}$$

Along with the model (1)–(11), we consider the other model with the subsequent reaction:



It can be interpreted as production of hard-ablated material C, such as ‘glassy’ carbon investigated in Ref. [10]. The set of equations describing the chain of reactions (Eqs. (1) and (12)) will contain Eqs.

(2)–(9) completed by the equation for concentrations of species B:

$$\frac{\partial N_B}{\partial t} = V \frac{\partial N_B}{\partial z} + A_1 N_A \exp\left(\frac{-E_A}{T}\right) - A_2 N_B \exp\left(\frac{-E_B}{T}\right). \quad (13)$$

Here A_2 and E_B are frequency and activation energy of reaction (12). Eqs. (10) and (11) do not hold now. Instead of Eq. (10), we have:

$$N_A + N_B + N_C = N_0 \quad (14)$$

3. Stationary wave analysis I

The aim of this paper is to consider the stationary solutions of above models, i.e., the solutions which correspond to the constant light intensity I_0 and propagate with the constant velocity. The role of such solutions in the theory of laser ablation is well-understood, see, e.g., Refs. [1,3,4]. The stationary wave solution obeys the equations and conditions of the previous chapter when all the time derivatives are taken to be zero. In what follows, we take $T_\infty = 0$. Hence, the stationary solutions have to obey the conditions at infinity:

$$T|_{z \rightarrow \infty} \rightarrow 0, \quad N_A|_{z \rightarrow \infty} \rightarrow N_0, \quad N_B|_{z \rightarrow \infty} \rightarrow 0. \quad (15)$$

For stationary solutions set of Eqs. (4) and (5) is known to have the first integral. Thus, instead of Eqs. (4) and (5), we can write:

$$D_T \frac{\partial T}{\partial z} = \frac{I}{c_p \rho} - VT. \quad (16)$$

Let us first consider the problem when only the reaction (Eq. (1)) is essential while the transition (Eq. (12)) can be neglected. For convenience, we introduce the dimensionless concentrations $n_{A,B,C} = N_{A,B,C}/N_0$. The stationary wave in this case obeys Eqs. (16) and (17):

$$V \frac{\partial n_A}{\partial z} = A_1 n_A \exp\left(\frac{-E_A}{T}\right) \quad (17)$$

and conditions (6) with $T_\infty = 0$ and (18), (19):

$$n_A(\infty) = 1 \quad (18)$$

$$n_A(0) = 1 - n^* \quad (19)$$

Eqs. (17)–(19) yield:

$$\frac{V}{A_1} \ln \frac{1}{1 - n^*} = \int_0^\infty \exp\left(\frac{-E_A}{T(z)}\right) dz. \quad (20)$$

The integral in the right-hand side of Eq. (20) can be estimated using the saddle point method, taking into account that $E_A/T(0)$ is a large number, and, as it can be obtained from Eqs. (6) and (16):

$$T(0) = \frac{I_0}{c_p \rho V}; \quad (21)$$

$$\left. \frac{\partial^2 T}{\partial z^2} \right|_{z=0} = -\frac{I_0 \alpha}{D_T c_p \rho}; \quad \left. \frac{\partial T}{\partial z} \right|_{z=0} = 0$$

Eq. (20) thus becomes:

$$V = \left(\frac{A_1}{\ln \frac{1}{1 - n^*}} \right)^{2/3} \left(\frac{T(0) D_T \pi}{2 E_A \alpha} \right)^{1/3} \times \exp\left(-\frac{2E}{3T(0)}\right). \quad (22)$$

Eqs. (22) and (21) give a closed set to determine the ablation velocity. This set is much similar to that corresponding to a stationary wave in a simple laser surface evaporation problem (see, e.g., Refs. [1,4]). There, along with Eq. (21), we have the velocity equation in the form:

$$V = V_0 \exp\left(-\frac{E_s}{T(0)}\right). \quad (23)$$

The comparison of Eqs. (22) and (23) leads us to the conclusion that a stationary wave in considered $A \rightarrow B$ ablation model is similar to the stationary laser surface evaporation wave with the activation energy which is about two thirds of the reaction activation energy:

$$E_s = \frac{2E_A}{3}.$$

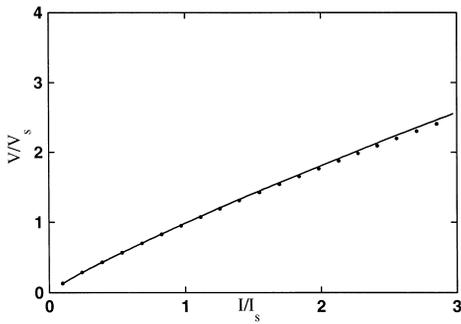


Fig. 1. Validity of the approximate formula (Eq. (22)) for stationary wave velocity. A → B model. Ablation velocity vs. laser intensity. $n^* = 0.4$. Points – numerical solution of corresponding eigenvalue problem. Solid line – solution of the set of transcendental equations (Eqs. (20) and (21)). $A_1 = 10^{13} \text{ s}^{-1}$; $E_A = 3 \text{ eV}$.

Fig. 1 shows the dependence of the stationary ablation velocity on the intensity calculated using numerical solution of the nonlinear eigenvalue problem (Eqs. (16)–(19)) and by the numerical solution of Eqs. (21) and (22). It is seen that the correspondence is quite good.

Here and in what follows, we use parameters close to those of polyimide: $\rho = 1.42 \text{ g/cm}^3$, $c_p = 2 \text{ J/g} \cdot \text{K}$, $D_T = 10^{-3} \text{ cm}^2/\text{s}$, $\alpha = 3 \times 10^5 \text{ cm}^{-1}$, $N_0 = 6 \times 10^{21} \text{ cm}^{-3}$.

We represent values of the variables in relative units: I/I_s , V/V_s , z/z_s , T/T_s . Scale values are chosen to be: $I_s = 10^7 \text{ J/cm}^2 \cdot \text{s}$; $V_s = 10^3 \text{ cm/s}$; $z_s = 1/\alpha = 0.33 \times 10^{-5} \text{ cm}$; $T_s = I_s/C_p \rho V_s = 3521 \text{ K}$.

4. Stationary wave analysis II

In this chapter, we discuss properties of stationary wave solutions of the model A → B → C (Eqs. (2)–(9), (13) and (14)). The corresponding eigenvalue problem consists of Eq. (16) with the conditions $T|_{z \rightarrow \infty} \rightarrow 0, \partial T/\partial z|_{z=0} = 0$ for temperature and Eqs. (17) and (24):

$$V \frac{\partial n_B}{\partial z} = -A_1 n_A \exp(-E_A/T) + A_2 n_B \exp(-E_B/T) \quad (24)$$

for concentrations. These equations are completed by the boundary conditions:

$$n_B(\infty) = 0 \quad (25)$$

$$n_B(0) = n^* \quad (26)$$

and by the boundary condition (Eq. (18)). The appropriate solution of Eq. (16) for the coordinate temperature distribution looks as follows:

$$T = \frac{I_0}{c_p \rho V (1 - D_T \alpha / V)} \times \left(e^{-\alpha z} - \frac{D_T \alpha}{V} \exp\left(-\frac{V}{D_T}\right) z \right). \quad (27)$$

Let us drop for a while Eq. (24) and conditions (25), (26) and fix $n_A(0)$. Then we return to the problem that has been discussed in Section 3. For each fixed $n_A(0)$, we can find the stationary velocity V , $n_A(z)$, and $T(z)$. Then, we can return to Eq. (24) to find, by means of the exhaustive search, the boundary value $n_B(0)$ which gives the solution of Eq. (24) with the asymptotic equation (25). Thus, we obtain $n_B(0)$ as a function of $n_A(0)$, $n_B(0) = f(n_A(0))$. Knowing this function and solving the equation:

$$n^* = f(n_A(0)) \quad (28)$$

we find an appropriate value $n_A(0)$, the value of the stationary velocity, V , and then all the coordinate distributions relating to the desired solution of the problem.

This method of numerical solving of the relevant eigenvalue problem is illustrated in Fig. 2. We consider two sets of parameters. Fig. 2a is related to the case $E_A < E_B$, whereas Fig. 2b concerns the opposite case $E_A > E_B$. It is seen that the discussed function $n_B(0) = f(n_A(0))$ has a maximum dependent on the intensity. In Fig. 2a, the maximum value of $n_B(0)$ as a function of $n_A(0)$ decreases with increasing intensity, whereas Fig. 2b demonstrates the opposite behavior.

Thus, Eq. (28), for fixed n^* , can admit two solutions, a single solution or no solution depending on the intensity. This is exhibited in Fig. 3. It can be seen in Fig. 3 (curve 1) that if the activation energy of the bond-breaking, E_A , is smaller than the activation energy of the following modification, E_B , then

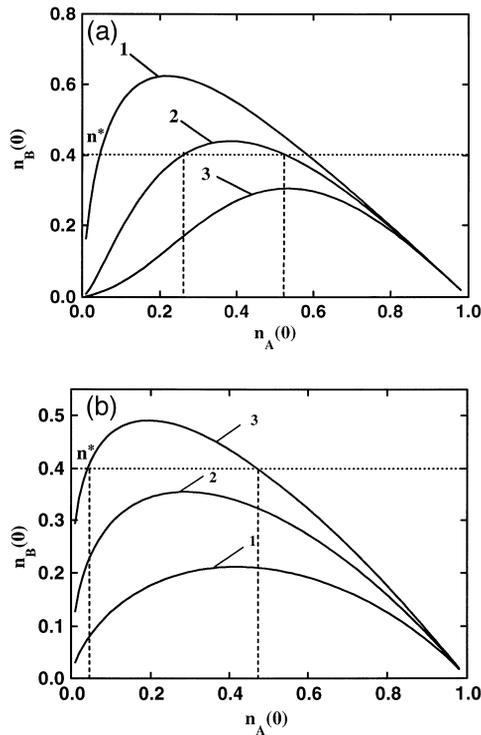


Fig. 2. A → B → C model. Dependence of $n_B(0)$ on $n_A(0)$, $n_B(0) = f(n_A(0))$ (see text). For given $n_B(0) = n^*$ the problem admits two, single or no solutions depending on intensity. (a) $E_B > E_A$; $E_A = 1.5$ eV, $E_B = 3$ eV, $A_1 = 10^{11}$ s⁻¹, $A_2 = 10^{13}$ s⁻¹. No solution at high intensities. (b) $E_B < E_A$; $E_A = 3$ eV, $E_B = 1.5$ eV, $A_1 = 10^{13}$ s⁻¹, $A_2 = 10^{11}$ s⁻¹. No solution at low intensities. (1) $I/I_s = 0.3$; (2) $I/I_s = 1$; (3) $I/I_s = 3$.

the problem admits two stationary solutions at relatively low intensities and no solutions at high intensities. Curve 2 in Fig. 3 corresponds to the case where the bond-breaking activation energy is larger than the modification one. Here, we have no solution at low intensities and two solutions at high intensities. These interrelations can be understood if we take into account that the higher activation energy process dominates at higher temperature.

Two branches of stationary solutions demonstrated in Fig. 3 are not equivalent. It is illustrated in Fig. 4 providing coordinate distributions of temperature and concentrations in stationary waves of different branches. In Fig. 4b, the concentration distribution of species B has a maximum at $z \neq 0$. It allows treating this solution as unstable, since the conditions

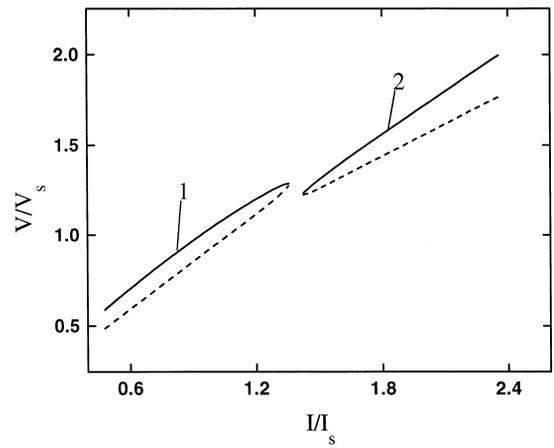


Fig. 3. A → B → C model. Stationary ablation velocity vs. intensity. (1) $E_B > E_A$; $E_A = 1.5$ eV, $E_B = 3$ eV, $A_1 = 10^{11}$ s⁻¹, $A_2 = 10^{13}$ s⁻¹; (2) $E_B < E_A$; $E_A = 3$ eV, $E_B = 1.5$ eV, $A_1 = 10^{13}$ s⁻¹, $A_2 = 10^{11}$ s⁻¹. Solid curve – stable branch. Dashed curve – unstable branch.

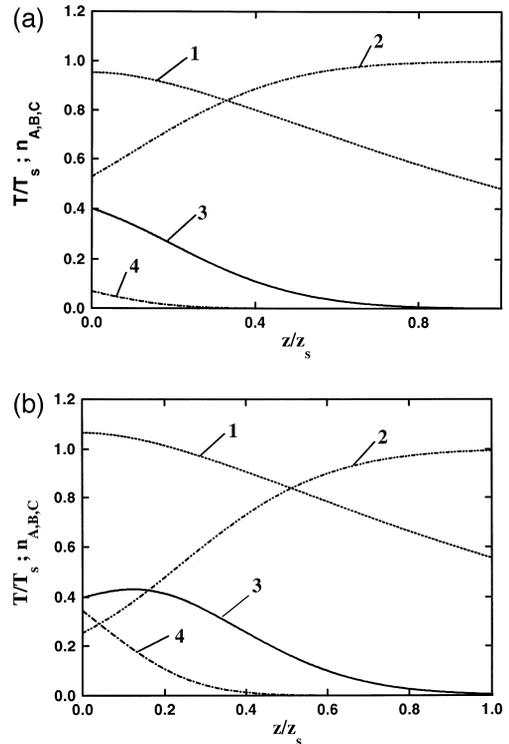


Fig. 4. Coordinate concentrations and temperature distributions. (1) $T/T_s(z/z_s)$, (2) $n_A(z/z_s)$, (3) $n_B(z/z_s)$, (4) $n_C(z/z_s)$ ($I/I_s = 1$, $n^* = 0.4$), (a) stable branch; (b) unstable branch.

for ablation appeared to be more favorable within the bulk of material than on its surface. Such regime cannot be achieved within the considered model starting from any real initial conditions. In Fig. 3, the unstable branches are shown by the dashed curves. It should be noted that the surface temperature in the solution of an unstable branch is higher than that of a stable one at the same intensity value.

5. Discussions

In the present communication, we consider only stationary solutions of the non-surface photothermal model of laser ablation. Nevertheless, some features of these solutions seem to be promising for describing a real experimental situation.

It has been shown in recent experimental publications [10–12] that during multiple-shot irradiation of polyimide by a KrF excimer laser, the increase in etch depth slows down and stops if the fluence is smaller than some ‘second threshold’ one. Several ways to explain these phenomena have been suggested in Refs. [10–12]. The simple model developed above can be treated as one more possible interpretation of these experimental findings.

The absence of stationary solutions can be interpreted as if in these regimes, the deep modification causes the ablation front velocity to decrease, preventing the achievement of stationary motion. The second threshold here can be assigned to the lower limit of the intensities, whereby the ablation velocity is high enough to eliminate the heated region before the deep modification occurs. This assignment is evident in Fig. 3 (curve 2).

However, since both the breaking bonds and the following deep modification processes are thermally activated, appropriate interrelation between their parameters should exist to provide such simple picture. Otherwise, the intensity increase may cause the ablation to stop as it can be seen in Fig. 3 (curve 1).

The analogy between stationary waves of the simplest non-surface model and the surface evaporation model of laser ablation, with the activation energy about two thirds of the bond-breaking energy, allows to consider bulk reactions between other

mechanisms diminishing the apparent activation energy of laser ablation compared to the bond-breaking energy.

6. Conclusions

The model of laser ablation with a moving ablation front is considered in which the ablation is associated with the bulk reaction resulting in bond-breaking. The stationary wave solutions have been studied.

The analysis of this model reveals that the *bulk* ablation process may be described by an *apparent* activation energy for *surface* evaporation with the value of about two thirds of the bond-breaking energy.

A subsequent reaction of the broken bond modification resulting in hindering of ablation process provides more complicated dependence of ablation velocity on laser intensity.

It is shown that if the activation energy of bond-breaking is larger than the activation energy of modification, there is no stationary solution at relatively low laser intensity. In contrast, at intensities higher than some threshold one, there are two stationary solutions, one of that is unstable.

This behavior can be associated with the existence of the second ablation threshold in multiple shot ablation of polymers recently investigated experimentally in Refs. [10–12].

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