

PHOTOPHYSICAL ABLATION

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ABSTRACT

The photophysical mechanism of laser ablation related to the change in activation energy for desorption (or destruction and further elimination) of electronically excited molecules is discussed. Despite the obvious physical reasons, up to now there is no experimental confirmation that this mechanism plays an important role with nanosecond laser ablation where duration of the laser pulse is longer than the corresponding relaxation time (typically, tens of picoseconds). On the other hand there was no special study of this mechanism for Ultra Short Laser Pulses (USLP) with pulse duration significantly shorter than the electronic energy relaxation time. Here we present the theoretical investigation of the photophysical ablation features with USLP and compare predictions which follow for the photophysical and pure thermal models.

Keywords: laser ablation; thermal evaporation; non-thermal ablation, analytical modeling

1. INTRODUCTION

Laser ablation of material by short laser pulses is of great relevance to numerous technological applications and it involves many fascinating aspects on the fundamentals of laser-solid interactions¹⁻³. Although a lot of studies were done in the field during the last 30 years (see e.g. Refs. in¹) some basic problems are still under discussion. One of them is what we have in mind saying that ablation is the effect of «material removal»? It is easy to understand when the sharp boundary separates the bulk material and the vapor products, i.e. the temperature of the material is less than thermodynamic critical temperature, T_c . At this condition material removal can be considered as a motion of the ablation front (sharp boundary). There is no sense to introduce the ablation front in the opposite case, when $T > T_c$ and one can see the continuous density distribution. Nevertheless during the cooling of material soon or later (e.g. after the laser pulse) we arrive to the «normal situation» with sharply separated bulk material and ablation products. At this moment one can find how much material was «removed».

With short intensive laser pulses both situations can be realized. Naturally, the overall ablation kinetics would be different. If one considers the situation with $T < T_c$ than he can introduce the thickness of ablated material as

$$h(t) = \int_0^t v(t_1) dt_1, \quad (1)$$

where $v(t)$ is the velocity of ablation front. At such consideration there is no difference between the «ablation» and

conventional surface evaporation process discussed in many papers (see, e.g. ⁴). The surface evaporation rate v is given by

$$v = v_A e^{-\Delta E/T_s}, \quad (2)$$

where T_s is the surface temperature, v_A is preexponential factor (by the order of sound velocity) and ΔE is the activation energy (in K). This energy represents the height of potential barrier which one should overcome to remove the elementary piece (atom, molecule) from the bulk material. Far from the critical temperature parameters v_A and ΔE can be considered as constants (their values are given in the handbooks).

Formula (2) represents the kinetics of purely thermal evaporation process. At the same time with sufficiently high laser intensity one would expect the non-thermal contributions into the ablation kinetics. For example, species of some materials can be electronically excited under the action of laser radiation. Then one would expect the situation when the activation energy ΔE^* for excited species would be smaller than for the species in the ground state, ΔE (see in Fig. 1). This effect is similar to photo-enhanced desorption.

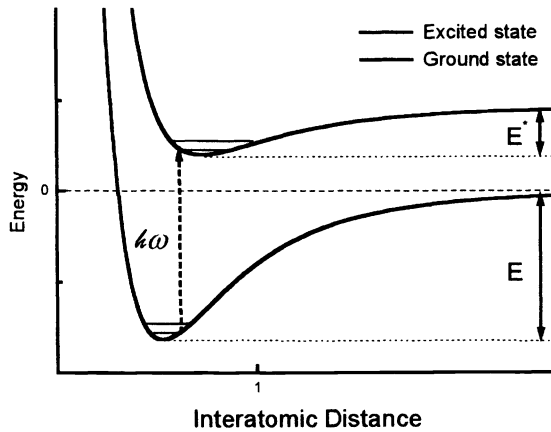


Fig. 1. Schematic for the change in activation energy in the excited electronic state.

The excited species can be considered as some kind of “defects” which directly contribute to the ablation kinetics. Under the simplified consideration the ablation rate can be represented as ⁵

$$v = \left(1 - \frac{N_s^*}{N}\right) v_A e^{-\Delta E/T_s} + \frac{N_s^*}{N} v_A^* e^{-\Delta E^*/T_s}, \quad (3)$$

where N_0 and N^* are the number density of chromophores, and $N = N_0 + N^*$ its total number density. The subscript s refers to the ablation front.

Under the photophysical ablation we understand the situation when the contribution of the second attendant in (2) (which describes the «evaporation of excited species») becomes noticeable in ablation kinetics. Naturally, it depends on the difference in ΔE and ΔE^* , and also on the density of N^* , which can be reached during laser ablation. Unfortunately it is extremely difficult to measure directly both characteristics $v(t)$ and $T_s(t)$ during laser ablation with nanosecond (and shorter) laser pulses. Thus, it is not possible to study the ablation kinetics by direct way (i.e. to study the dependence $\text{Log}(v) = f(1/T)$). Instead of it experimentalists study the dependencies related to the thickness of ablated material versus

laser fluence, $h = h(F)$. It is very difficult to analyze these dependencies because of the complexity of the problem and the lack of reliable data on a lot of optical and thermodynamical parameters, relaxation times, etc.

The results of theoretical calculations⁵ show that the photophysical ablation should be clearly pronounced for the materials with a big activation energy, $\Delta E \approx 3-5$ eV. Thus, the suitable materials for the investigations can be some dielectrics and, probably, some organic polymers⁶. Our studies⁷ which were done for the polyimide under the assumption of $\Delta E = 3$ eV (typical for the breaking energy of covalent bonds^{6,8,9}) shows that the necessary relaxation times should be of the order 100-500 ps to explain the experimental data¹⁰. These times are by the order of the magnitude higher than the reported in¹¹. In order to avoid the discrepancy we analyzed the values of the activation energy ΔE for polyimide using the variable laser pulse length¹². These studies show that the true value of ΔE is approximately 1.5 eV which is close to those which can be seen with conventional thermal degradation of polyimide⁸. The consequent calculations¹³ with this small activation energy show that they are in a good agreement with experimental data¹⁰ for ns-laser ablation with 351, 308 and 248 nm radiation wavelengths. At the same time with 193 nm radiation one can see a big enhancement of the ablation rate (compared to the purely thermal process).

Despite the obvious physical reasons, up to now there is no direct evidence that the photophysical mechanism really works (at least with ns laser pulses). The aim of the present communication is to investigate the features of photophysical ablation when the material is irradiated by USLP with pulse duration significantly shorter than the electronic energy relaxation time. We compare predictions of photophysical and pure photothermal models to understand the possibility to recognize the photophysical effects.

2. THE MODEL

We consider the effect of USLP on a dielectric which can be described as a two-level media. The laser frequency is assumed to be in resonance with the electronic transition. We take into consideration that the excited level has a complicated structure, thus the effective band width is larger than the band width of the laser radiation. We assume also that the excited electron changes its energy inside the level in such a way that the transition frequency goes from resonance faster than the pulse duration. Thus, we will not take into account the induced radiation effect. This approximation is not very important and is made only for the sake of simplicity. We consider laser ablation of such a media within the framework of a surface evaporation model^{4,14} in order to compare the predictions of a thermal and photophysical models.

Both of the models describe the material response in a similar way:

$$\frac{\partial N^*}{\partial t} = v \frac{\partial N^*}{\partial z} + (N - N^*) \frac{I\sigma_{01}}{\hbar\omega} - \frac{N^*}{t_T}, \quad (4)$$

$$\frac{\partial I}{\partial z} = -I\sigma_{01}(N - N^*), \quad (5)$$

$$\frac{\partial T}{\partial t} = v \frac{\partial T}{\partial z} + \frac{1}{c_p(T)\rho} \frac{\partial}{\partial z} \left[\kappa(T) \frac{\partial T}{\partial z} \right] + \frac{N^*}{t_T \rho c_p(T)}, \quad (6)$$

with the initial and boundary conditions

$$N^* \Big|_{t=0} = 0, \quad T \Big|_{t=0} = T_\infty, \quad (7)$$

$$I \Big|_{z=0} = I_0(t), \quad N^* \Big|_{z \rightarrow \infty} = 0, \quad T \Big|_{z \rightarrow \infty} = T_\infty, \quad (8)$$

$$\kappa \frac{\partial T}{\partial z} \Big|_{z=0} = \rho \left[\left(1 - \frac{N_s^*}{N} \right) v_A \Delta H e^{-\Delta E/T_s} + \frac{N_s^*}{N} v_A^* \Delta H^* e^{-\Delta E^*/T_s} \right], \quad (9)$$

where I is laser intensity, T temperature, N concentrations of the absorbing groups, N^* is the concentrations of excited species, ΔH and ΔH^* are the corresponding transition enthalpies, $\hbar\omega$ is the photon energy, σ_{01} is the absorption cross-section, t_T is the thermal relaxation time. The thermal conductivity and specific heat are denoted as $\kappa(T)$ and $c_p(T)$. The coordinate system is fixed with the ablation front. The ablation velocity for photophysical model is given by (3) and for thermal model by (2). In the latest case the boundary condition (10) should be rewritten as

$$\kappa \frac{\partial T}{\partial z} \Big|_{z=0} = \rho v_A \Delta H e^{-E/T_s} \quad (10)$$

Hereafter in numerical calculations we use the values of parameters close to those of polyimide¹⁵. For temperature dependencies of $\kappa(T)$ and $c_p(T)$ were used data¹⁰. For the analytical estimations we used the ‘‘averaged’’ values of c_p and heat diffusivity D_T . We take $t_T=30\text{ps}$, $\Delta H = 700\text{mJ/g}$, $\Delta H^* = \Delta H \cdot (E^*/E)$

The system of equations (3) - (10) was integrated by finite difference method.

3. RESULTS AND DISCUSSIONS

Fig. 1a exhibits the time dependence of ablation velocity for photothermal model and for photophysical models with different activation energies for elimination of excited species. Since the pulse duration is essentially shorter than relaxation time, ablation starts after the end of the laser pulse. Relaxation of excited species results in an increase of temperature. The ablation velocity, according to photothermal model, monotonously depends on surface temperature. This leads to relatively rapid increase in velocity resulted from the temperature rise due to electronic relaxation, this rise being followed by the slow decrease of temperature caused by penetration of ablation front into the colder part of the sample and by heat diffusion.

The ablation velocity demonstrates another behavior in photophysical model. The sharp maximum is related to a decrease of concentration of excited species. When excited states vanish, the velocity of the ablation front reaches its pure thermal value. This value is slightly less than the corresponding value for a pure thermal model (see Fig.2a) at the same moment of time. It results from the somewhat smaller value of the surface temperature as can be seen from the Fig.2b.

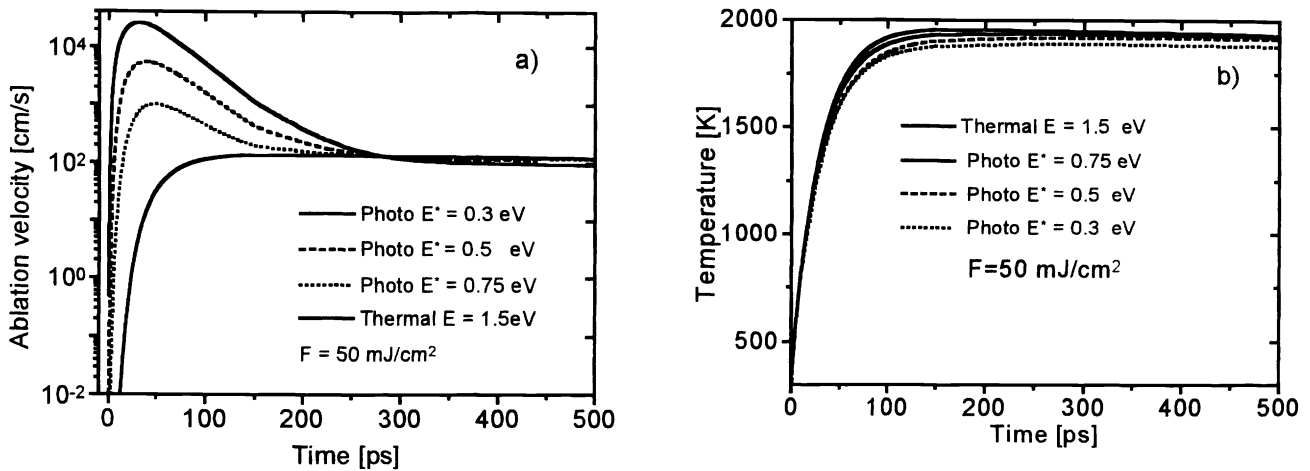


Fig.2. The dynamic of laser ablation under the effect of a single 500 fs laser pulse with fluence $50 \text{ mJ}/\text{cm}^2$. The photophysical ablation with different E^* and pure photothermal ablation. For all the curves $E = 1.5 \text{ eV}$. a). Ablation velocity vs time. b). Surface temperature vs time.

The reason for that can be understood from the Fig.3. Here ablation velocity is displayed versus ablated depth. It is seen that in the considered situation only a small amount of material is ablated photophysically, whereas the main part of ablation proceeds through the thermal mechanism. The difference between dashed and solid curves in Fig.3 results from the fact that photophysical ablation front overtakes the photothermal ablation front. Therefore the temperature at the same point of material at the time when the ablation front comes to it, is higher for the photophysical case because of heat diffusion. It follows from the Fig.3 that in the considered case the difference between the ablated depths in photophysical and thermal ablation is essentially due to heat diffusion.

Fig.3 demonstrates the ablated depth versus fluence for photophysical and thermal models. It is seen that these curves go approximately parallel to each other. Thus, at high fluences the relative input of photophysical mechanism vanishes. The photophysical mechanism influences the ablated depth mainly at small fluences.

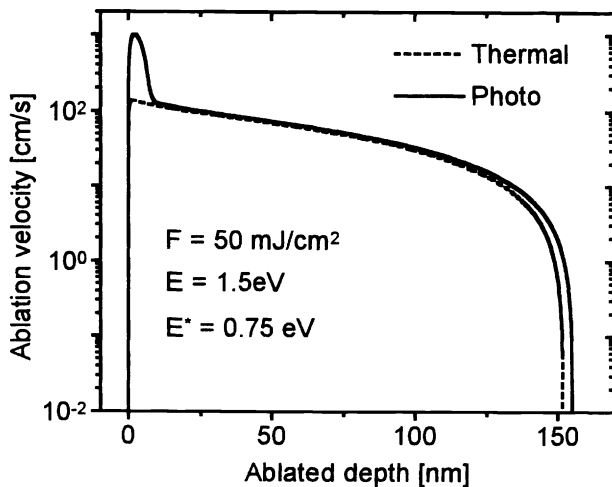


Fig.3. Ablation velocity vs ablated depth for photophysical ablation (solid) and for thermal ablation (dashed).

The photophysical addition to the ablated depth (compare to pure thermal model) can be estimated from the following considerations. For considering two-level model fluence $F \cong 15 \text{ mJ/cm}^2$ is a saturating one. Above this value the maximal surface temperature practically does not depend on the fluence. Fluence influenced only the width L_s of the absorbed laser energy within the material. The maximal surface temperature roughly may be estimated to be

$$T_{\max} \cong \frac{\hbar\omega N}{c_p \rho} + T_{\infty}. \quad (11)$$

Then the photophysically ablated length may be crudely approximated as

$$L_{ph} \approx v_A^* t_T \exp\left[-\frac{E^*}{T_{\max}}\right]. \quad (12)$$

More accurate estimation yields

$$L_{ph} = \int_0^1 v_A^* \cdot N \cdot t_T \exp\left[-\frac{E^* c_p \rho}{\hbar\omega y + c_p \rho \cdot T_{\infty}}\right] dy. \quad (13)$$

It is seen that this quantity does not depend on fluence. Of course, it is assumed that $L_{ph} \leq L_s$. In its turn the L_s value can be roughly estimated as

$$L_s \approx \frac{F}{\hbar\omega N} \quad (14)$$

After the end of the relaxation an ablation proceeds as a purely thermal process. This qualitatively explains the behaviour of the curves in Fig.4 which demonstrates the ablated depth versus fluence for photophysical and thermal models. It is seen that these curves go approximately parallel to each other. Thus, at high fluences the relative input of photophysical mechanism vanishes. The photophysical mechanism influences the ablated depth mainly at small fluences.

The role of photophysical ablation increases with increase in relaxation time. It can be seen e.g. from the estimation (12), (13). In contrast, the purely thermal model yields a decrease in resulting ablated depth with an increase in relaxation time. It can be seen in Fig.5 where the ablated depth is represented as a function of relaxation time for pure thermal and photophysical models. This principal difference in thermal and photophysical models unfortunately can hardly be observed experimentally since it is difficult to change relaxation time in a media without changing the other parameters.

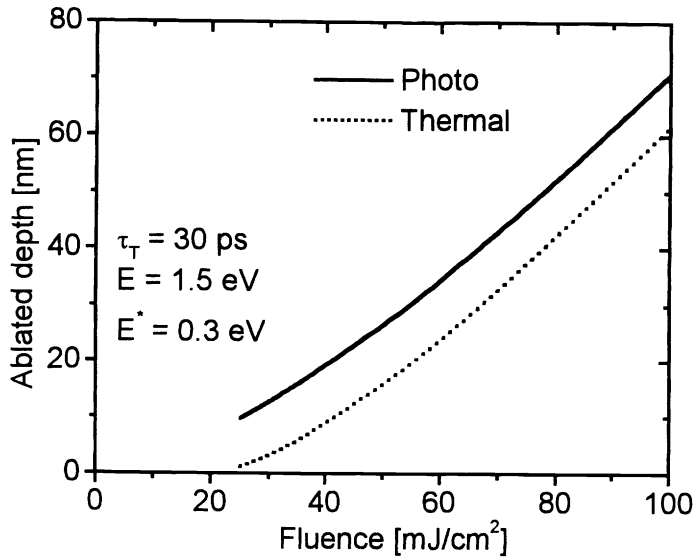


Fig. 4. Ablated depth vs single pulse fluence for photophysical (upper curve) and thermal ablation.

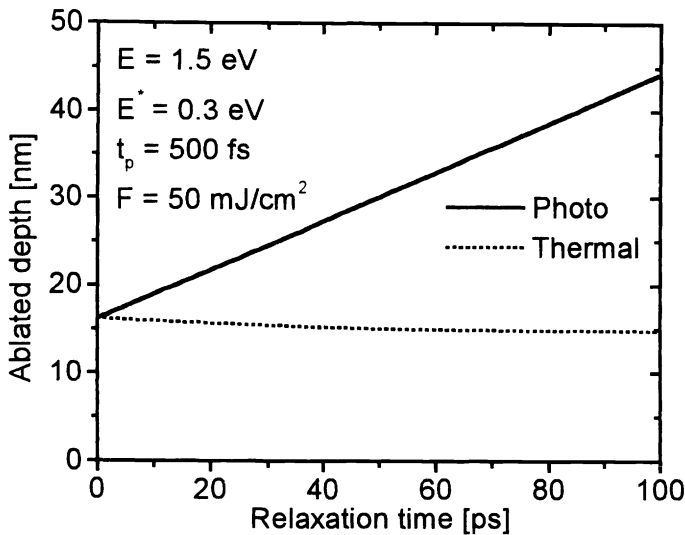


Fig.5. Ablated depth vs relaxation time. Fluence is 50 mJ/cm^2 .

4. ABLATION BY TWO SUCCESSIVE LASER PULSES.

The effect of successive USLP of the same fluence on material is widely used for investigation of laser ablation peculiarities¹⁶. The important part of these studies is the possibility to vary the delay time between the pulses (it can be less or comparable to relaxation time). Recently the sequence of USLP of relatively low irradiance has been used for optical 3D information storage¹⁷.

Let us consider pair pulse response curve i.e. the dependence of ablated depth on delay time between two USLP. The single pulse fluence is chosen to be somewhat less than the threshold one while the summary fluence (doubled single pulse fluence) is somewhat higher than the threshold.

This curve has been obtained experimentally in ¹⁶ for polyimide (KrF laser, pulse duration 500 fs, single pulse fluence $25\text{mJ}/\text{cm}^2$). Theoretically this “delay curve” has been studied in¹⁵ for the pure thermal model and in¹² for the photophysical model. The examples of such delay curve are shown in Fig.6. We consider here the situation when induced bleaching takes place. This bleaching results from the saturation effect. It is quite evident for two-level model. It was shown in¹⁵ that it is rather general case for highly absorbing dielectrics near the ablation threshold.

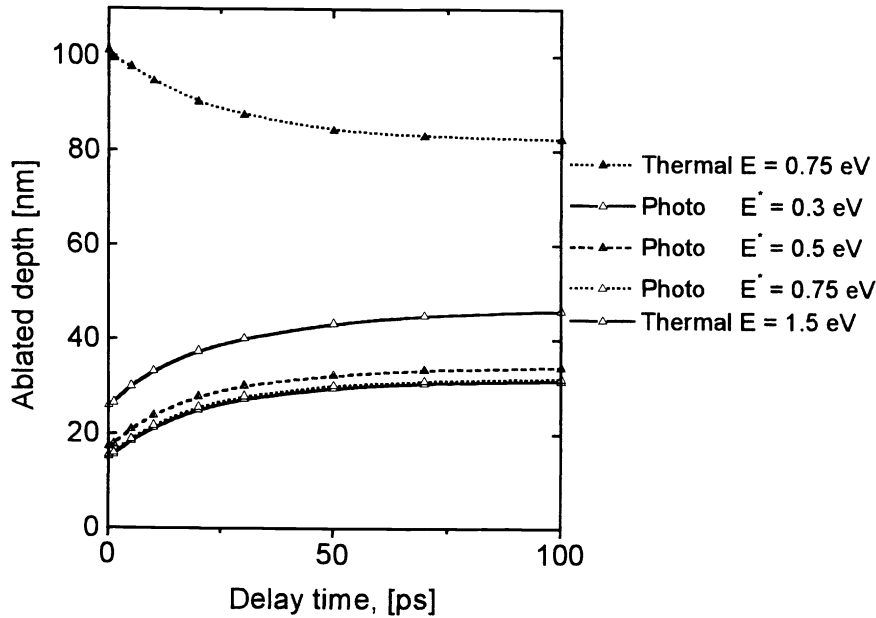


Fig.6. Pair pulse laser ablation. Ablated depth vs delay time. Delay curve. The fluence of each pulse is $25\text{mJ}/\text{cm}^2$. Relaxation time is 30 ps. For all the photophysical curves $E=1.5\text{eV}$.

In order to understand the main features of delay curves we should consider the distribution of the absorbed laser energy inside the material after the end of the second pulse. This distribution is bell-shaped and can be characterized by its width, L_s , and by the maximum value of the absorbed energy which is situated at the surface. The absorbed energy can be directly recalculated to the temperature after the end of thermal relaxation. The integral value of absorbed energy does not depend on delay time and it is equivalent to the sum of fluences of both incoming pulses.

In the case of induced bleaching the absorbed energy penetration depth increases with decrease in delay time between USLP. In contrast, the surface value of the density of absorbed energy increases with increase in delay time.

It is shown in¹⁵ that there are two regimes of pair pulse ablation. These regimes essentially influence the shape of delay curve. If the ablation velocity is high enough we have “the scale length regime” where the ablation front propagates through the essential part of energy penetration depth. In this regime ablation efficiency should decrease with increase in delay time (greater penetration depth, L_s , leads to the greater ablated depth).

In the opposite case, when the ablation time is greater than the time of heat diffusion, we have “the insufficient heating regime”. Here the resultant ablated depth increases with the increase in delay time.

Both regimes are illustrated in Fig.6. Here the thermal delay curve with $\Delta E = 1.5\text{eV}$ is of insufficient heating regime whereas the thermal curve with $\Delta E = 0.75\text{eV}$ is one of scale length regime. It has been shown that insufficient heating regime is more reliable for parameters of material close to those of polyimide. In this sense the photophysical model (see in Fig.6) also demonstrates the insufficient heating behaviour.

Let us consider now the evolution of delay curves with variation of single pulse fluence. As it has been discussed above the pure photophysical ablation depth does not depend on fluence if the latter is sufficiently high. On the other hand L_s is proportional to fluence. Thus, the increase in fluence results in increase of L_s compared to L_{ph} .

We can characterize the delay curve by its contrast i.e. by ratio $\left[h_{\infty} - h_0 \right] / h_{\infty}$. Here $h(t_d)$ designates the ablated depth at delay time t_d . “Infinity” here case is approximately 200 ps (t_d should be significantly smaller than the heat diffusion time). In the case of insufficient heating regime the contrast is positive, while in the case of length scale regime it is negative. For photophysical ablation the contrast would increase with fluence (see in Fig.7). Here the increasing curve corresponds

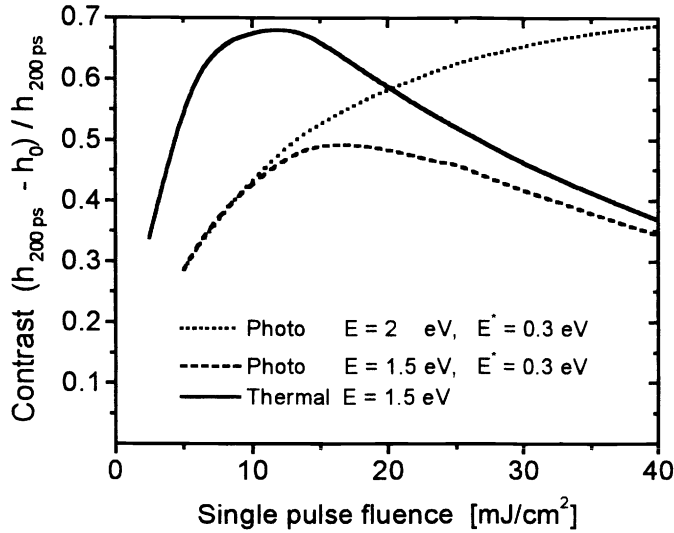


Fig. 7. Different dependence of contrast of delay curve (see text) on single pulse fluence for pure photothermal and photophysical ablation mechanism.

to the photophysical model with $E = 2 \text{ eV}$, $E^* = 0.3 \text{ eV}$.

In the case of pure thermal ablation the ablated depth is approximately proportional to the heat diffusion time and can be roughly estimated to be¹⁵

$$L_{th} \approx v_A \exp \left[-\frac{E}{T_{\max}} \right] 2 L_s^2 / D_T \quad (15)$$

One can see that $L_{th} \propto F^2$ while $L_s \propto F$. Thus, with increasing fluence we get close to the scale length regime and contrast should decrease. Fig.7 illustrates such behavior of delay curve for thermal model for fluences higher than the saturating one.

Fig.7 also illustrates that the photophysical model with $E = 1.5 \text{ eV}$ yields the intermediate results. The reason is that the photophysical ablation here is followed by the thermal ablation which gives the significant input to the resultant ablated depth.

Thus, the experimental investigation on the dependence of the contrast of delay curve on single pulse fluence can give the information about the dominating mechanism of laser ablation.

5. CONCLUSIONS

The dynamics of single USLP ablation that proceeds photophysically is essentially different from dynamic of pure thermal ablation. Nevertheless, the resulted ablated depths can be close if the activation energy of the pure thermal process is not essentially high.

The electronic relaxation time significantly influences the effectiveness of photophysical ablation. Increase in relaxation time results in essential increase of resultant etch depth in the case photophysical ablation and slightly decreases the efficiency of pure thermal ablation.

The experimental investigation of pair pulse laser ablation can give the information about the dominating mechanism. The contrast of delay curve will increase with increasing single pulse fluence in the case of pure photophysical ablation and demonstrates the opposite behavior in the case of thermal mechanism.

The photophysical ablation mechanism can be better recognized in materials with long relaxation time and big activation energy for the purely thermal ablation.

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References

1. D. Bäuerle, "Laser Processing and Chemistry", 2nd ed. Springer-Verlag, Berlin, Heidelberg, 1996.
2. E. Fogarassy, D. Geohegan, M. Stuke (Eds.), "Laser Ablation", North-Holland, Amsterdam, 1996.
3. E. Fogarassy, S. Lazare (Eds.), "Laser Ablation of Electronic Materials", North-Holland, Amsterdam 1992.
4. S. I. Anisimov, Ya. A. Imas, G. S. Romanov, Yu. V. Khodyko, "Action of High -Power Radiation on Metals", National Technical Information Service, Springfield, Virginia, 1971.
5. B. Luk'yanchuk, N. Bityurin, S. Anisimov, D. Bäuerle: *Appl. Phys. A* **57**, p. 367 (1993)
6. R. Srinivasan: In "Interaction of Laser Radiation with Organic Polymers", Ed. by J. C. Miller, Springer Series in Materials Science **28** Springer-Verlag, 1994, p.107
7. B. Luk'yanchuk, N. Bityurin, S. Anisimov, N. Arnold, D. Bäuerle: *Appl. Phys. A* **62**, p. 397 (1996)
8. M. I. Bessonov, "Polyimides - a Class of Thermally Stable Polymers", NASA Technical Memorandum, Washington DC 20546, 1986
9. J. Guillet: "Polymers - Photophysics and Photochemistry. An Introduction to the Study of Photoprocesses in Macromolecules", Cambridge University Press, 1985
10. S. Küper, J. Brannon, K. Brannon: *Appl. Phys. A* **56**, p. 43 (1993)
11. J. K. Frisoli, Y. Hefetz, T. F. Deutsch: *Appl. Phys. B* **52**, p. 168 (1991)
12. B. Luk'yanchuk, N. Bityurin, M. Himmelbauer, N. Arnold: *Nucl. Instrum. Meth. B* **122**, p.347 (1997)
13. N. Arnold, B. Luk'yanchuk, N. Bityurin, D. Bäuerle: *Proc. SPIE* (1998) (paper in this volume)
14. S. I. Anisimov, V. A. Khokhlov, "Instabilities in Laser-Matter Interaction", CRC Press, Boca Raton 1995.
15. N. Bityurin, A. Malyshev: *Applied Surface Science*, v.**127**, p.199, (1998)

16. S. Preuss, M. Späth, Y. Zhang, M. Stuke: *Appl. Phys. Lett.* **62**, p.3049 (1993)
17. A. I. Korytin, N. M. Bityurin, A. P. Alexandrov, N. A. Babina, L. A. Smirnova, A. M. Sergeev: «High-contrast bitwise three dimensional optical data storage in doped polymers», *Optical memory & Neural networks*, (1998)

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