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Analysis of Ablation Characteristics of Absorbing Dielectrics Caused by Short Laser Pulses

Samuel George* and Kunal Mitra†
Florida Institute of Technology, Melbourne, Florida 32901

The effect of ablation of absorbing dielectrics by single and two successive ultra short pulses from an excimer laser source is investigated. The numerical model is based on two photon absorption by the molecular chromophores followed by thermal degradation and diffusion, whereas ablation occurs through sublimation of the material from the surface. The numerical analysis involves solving a set of coupled three- or two-level chromophore rate equations, heat diffusion equation, and the transient radiative transport equation, using two techniques: a fully implicit iterative scheme and a predictor corrector technique (Fromm's scheme). Results for the temperature distribution and ablation depth are obtained for different laser parameters such as the delay time between two successive pulses, laser pulse width, laser fluence, and various material properties such as activation energy, relaxation time, thermal conductivity, and absorption cross section of molecules. The results obtained by consideration of the transient radiative transfer equation are compared with the steady-state formulation, and significant differences are observed in the temperature profiles and the ablation depth.

Nomenclature

C_p	=	specific heat
C_0	=	initial chromophore density
c	=	velocity of light in the medium
D_T	=	thermal diffusivity ($\kappa/\rho C_p$)
d	=	ablation depth
E_a	=	ablation activation energy
$\hbar$	=	modified Planck's constant
I	=	intensity
$I_{\max}$	=	maximum intensity of the laser pulse
k_B	=	Boltzmann constant
l_s	=	penetration depth
n_0, n_1, n_2	=	chromophore densities at different levels
R	=	reflectivity of the material
S_0, S_1, S_2	=	energy states
s	=	ratio of absorption cross section of molecules (σ_2/σ_1)
T	=	temperature
T_∞	=	ambient temperature
t	=	time
t_{DT}	=	heat diffusion time
t_d	=	delay time between pulses
t_p	=	pulse width
V	=	velocity of the ablation front
V_a	=	constant and close to sound velocity
z	=	spatial coordinate
ΔH	=	enthalpy for evaporation of the material
κ	=	thermal conductivity
ρ	=	density
σ_1, σ_2	=	absorption cross section of molecules
τ_1, τ_2	=	nonradiative relaxation time
ϕ	=	fluence
ω	=	radiation frequency

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*Graduate Research Assistant, Mechanical and Aerospace Engineering Department, 150 W. University Blvd.; currently Mechanical Engineer-Technical Services, Applied Materials, Santa Clara, CA.

†Assistant Professor, Mechanical and Aerospace Engineering Department, 150 W. University Blvd.

I. Introduction

LASER ablation of dielectrics using ultrashort pulses has opened new frontiers for research in various engineering applications especially in the material processing field. Most of the current research work in pulsed laser ablation of dielectrics deals with two broad varieties: transparent and absorbing dielectrics. Various applications for ablation of transparent materials include thin-film deposition of quartz on silicon wafers,[1] high-precision machining of ceramic glasses with no thermal shock or distortion to the adjoining material,[2,3] optical switches,[4] removal of water from microcircuits and micromachines,[5] and changing the dielectric constants of materials to act as a plasma shutter to prevent damage to photodetectors.[6] Whereas for absorbing type of dielectrics, applications include etching of polyimides,[7] microscale chip packaging, laser cladding, and laser machining.[8] Researchers in the past have addressed the ablation phenomena caused by short-pulse laser interaction with both transparent and absorbing materials, but may not actually perform systematic analysis to determine the effects of the variation of laser parameters and material properties, which influence the ablation phenomenon.[9,10] Depending upon the material considered, various mathematical models such as photothermal or photochemical for absorbing dielectrics can be formulated to analyze and explain the ablation characteristics including ablation depth as a function of the process parameters.[11,12] But most of the previous research studies have been related to experimental observations, and little effort has been made to explain the fundamental phenomenon associated with the ablation caused by short pulse lasers having pulse widths on the order of pico and femto seconds.[13–15] This research work focuses on a parametric study of the laser parameters and the material properties that influence the ablation characteristics of absorbing dielectrics incorporating the transient nature of short-pulse laser propagation phenomena.

For the case of transparent dielectrics, the ablation or damage mechanism is significantly different for lasers having large and short pulse widths. For large-pulse-width laser sources the damage to the defect free dielectrics occurs as a result of the heating of the seed or conduction-band electrons by incident radiation and transfer of this energy to the lattice. The damage to the dielectric occurs because of conventional thermal deposition, which results in melting and boiling of the dielectric.[3,15] As these temperatures are typically very high, the ablation mechanism results in a strong thermal shock to the dielectric, which initiates a crack within the material and leads to uncontrolled material ablation.[16,17]

For the case of short-pulse lasers, there is no need to invoke some arbitrary number of initial seed electrons. Field-induced

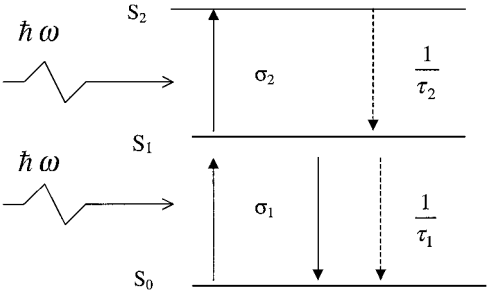

Fig. 1 Schematic of a three-level molecular chromophore system.

multiphoton ionization produces free electrons, which are then rapidly accelerated by the laser pulse. For these very short, intense pulses, energy is gained by the newly free electrons from the laser field much faster than the transfer of energy from the electrons to the lattice.[15] These electrons gain energy from the laser field until they have sufficient energy to collisionally ionize neighboring atoms thereby producing more free electrons.[18] This process continues until a critical density plasma is reached wherein minimal further energy deposition from the laser occurs. The actual damage occurs after the pulse has passed, when the dense plasma expands away from the surface. Plasma formation is quantitatively described by the time dependence of the electron energy distribution function.[15,19] It has also been experimentally observed that with femtosecond pulses all regions throughout the laser beam profile with sufficient intensity for multiphoton ionization will be removed resulting in extremely fine confinement of the position of material removal. There is no evidence of heat transfer into the surrounding material and no thermal shock-induced cracking.[3,20]

The mechanism of ablation in absorbing dielectrics is different from the transparent dielectrics, as ablation occurs at a fluence, which is smaller than that for transparent materials. Therefore, it is found that avalanche ionization does not initiate the ablation process. Ablation takes place with energy absorption by chromophores either through single-photon or multiphoton absorption depending upon the bond energies of the dielectric.

Figure 1 shows the possible electronic transitions that a chromophore can undergo upon absorbing one or more photons from a monochromatic laser pulse. Three electronic levels are shown and are labeled S_0, S_1, and S_2, where S_0 represents the ground energy level, S_1 the first excited energy level, and S_2 the second excited level. When the second excited level is excluded, the model represents a two-level system having states S_0 and S_1. A two- or three-level system corresponds to the case when the energy absorbed from multiple photons is needed to break the bonds of the absorbing dielectric. At the start of the laser heating process, all of the chromophores are present in the ground-state energy level S_0 caused by thermal equilibrium. With excitation of the chromophores caused by absorption of photons incident from the laser pulse, the density at the higher energy level increases. With absorption of two photons, the chromophores could be excited from the ground energy level to the first excited energy level S_1, as well as excited from the first excited energy level to the second excited state S_2. Because this represents a nonequilibrium condition, the chromophores would relax from the higher energy level to the ground state by radiative relaxation and nonradiative relaxation after a characteristic relaxation time. This particular mechanism can be easily extended for higher energy levels for multiple photon absorption. The nonradiative relaxation contributes to the heating of the material and therefore to the photothermal mechanism of ablation. This energy, absorbed by the dielectric produces changes in the temperature distribution caused by heat diffusion within the material. Hence the nonradiative relaxation time for chromophores τ at different energy levels and the ratio of absorption cross section of molecules ($s = \sigma_2/\sigma_1$) are important parameters in laser heating of absorbing dielectrics. In addition, activation energy E_a also plays an important part in the ablation characteristics for dielectrics. Activation energy implies the minimum energy absorbed by the chromophores in order to initiate ablation. With the increase in the value of the activation energy for a particular dielectric, the ablation process may require two or more photon absorption, depending on the incident wavelength of the laser pulse.

For incident radiation from a short-pulse laser, the absorption mechanism for dielectrics, polymers, and saturable liquids shows a strong deviation from the classical mechanism, which exhibits a constant absorption coefficient.[21,22] Laser ablation in absorbing dielectrics was first explained as a photochemical process[12,23] where the absorption of photons of ultraviolet wavelengths excites the bonding electrons in polymers causing a direct bond break and associated ablation. Although this might be true for some cases, especially when the incident pulse has a lower range of fluence, this model fails to explain the ablation characteristics for organic polyimides, which need large fluence on the order of 30 mJ/cm^2. The photothermal model explains the preceding case for ablation in an absorbing type of dielectric. In this model it is considered that the energy incident on the material is absorbed by chromophores either by a single-photon or multiphoton absorption mechanism. The excited chromophores relax rapidly to the ground state with the absorbed energy being converted into vibrational energy.[24] This vibrational energy is manifested as a change in the temperature of the medium, whereas ablation takes place through material sublimation, that is, change of phase directly from solid to vapor.[25] The ablation depth or the etch depth can be related in an exponential manner to the activation energy. Even though ablation and absorption take place simultaneously, it is reasonable to treat the two processes as independent from a mathematical modeling point of view.

Experimental validation for a purely photothermal model has been demonstrated by obtaining a relation for ablation rate as a function of the incident laser fluence for wavelengths in the range of 193–308 nm.[26] The photon energy lies between 4.0 and 6.5 eV for laser pulses with wavelengths between 193–308 nm. Because the bond energy for the dielectric under consideration varies from 8 to 12 eV, usually a two-photon absorption model is necessary to describe the ablation mechanism.[27]

The present research develops the photothermal model for ablation of absorbing dielectrics caused by two successive short excimer laser pulses having a delay time between them shorter than the heat diffusion time. Although there have been previous experimental results obtained for two successive pulse laser heating, this paper presents a parametric study on the parameters affecting the ablation mechanism in dielectrics caused by heating by two successive short laser pulses. The model chosen here neglects multiphoton ionization because the incident energy fluence is considerably lower than the ionization potential. A coupled set of chromophore rate equations based on Fig. 1, transient radiative transport equation, and the heat diffusion equation are used to calculate the chromophore density at different energy levels and the temperature distribution within the dielectric. Most of the previous studies with short-pulse lasers have neglected the wave nature of the intensity distribution within a medium, thereby neglecting the temporal variation of the laser intensity. However, the preceding is true if the temporal duration of the radiation, that is, the time taken by the pulse to propagate through the medium, is larger than the relaxation time of the chromophores. It has been demonstrated that the hyperbolic radiative transport formulations give significantly different and physically realistic intensity profiles, compared to the commonly used steady-state or the parabolic approximations for analyzing ultrashort laser pulse propagation through a participating medium.[27–29] The results presented in this paper show that there exists a considerable difference in the temperature profiles and the ablation depth between steady-state formulation and transient nature of intensity distribution. Therefore, accurate transient nature of intensity distribution will be used for analysis purposes.

This paper also discusses the effects of the variation of different parameters including laser parameters such as pulse width, fluence, and the delay between two pulses, as well as material properties such as relaxation times, activation energy, thermal conductivity, and absorption cross section of molecules on the temperature distribution and ablation depth of the material. The objectives of this work are

to analyze the results obtained for different cases and determine the influence of the different process parameters on the ablation characteristics of the absorbing dielectric.

II. Mathematical Formulation

The physical case under consideration is the ablation of absorbing dielectrics with two successive ultrashort laser pulses having a delay time between them. Short-pulse laser heating of the dielectric in this particular study is analyzed on the basis of a one-dimensional model because the laser beam diameter is typically much larger than the heat diffusion penetration length. The temporal shape of the laser pulse is assumed to have a Gaussian temporal profile with a full width at half maximum pulse duration t_p and $t = 0$ being the starting point of the pulse. The mechanism of photon absorption for absorbing dielectrics follows closely the transitions between the energy levels of allowable energy states of molecules. Here, we consider a set of rate equations for chromophore level population corresponding to Fig. 1 (Ref. 30). The electronic ground state is given by S_0, whereas S_1 and S_2 represent the first and the second excited states, respectively. The rate equations for a three-level system with a two-photon absorption model are[21,31]

$$\frac{\partial n_0}{\partial t} = V\frac{\partial n_0}{\partial z} - \sigma_1 n_0 \frac{I}{\hbar\omega} + \sigma_1 n_1 \frac{I}{\hbar\omega} + n_1 \frac{1}{\tau_1} \tag{1}$$

$$\frac{\partial n_1}{\partial t} = V\frac{\partial n_1}{\partial z} + \sigma_1 n_0 \frac{I}{\hbar\omega} - \sigma_1 n_1 \frac{I}{\hbar\omega} - \sigma_2 n_1 \frac{I}{\hbar\omega} - n_1 \frac{1}{\tau_1} + n_2 \frac{1}{\tau_2} \tag{2}$$

with the conservation equation of chromophores given by

$$n_0 + n_1 + n_2 = C_0 \tag{3}$$

The first term on left-hand side of Eq. (1) is the rate of change in the chromophore density at the ground energy level. The first term on the right-hand side is the convective term caused by the ablation velocity, the second term represents the loss of n_0 chromophores caused by photon absorption and transition to the higher state, the third term represents the gain caused by radiative relaxation back to the ground state, and the fourth term represents the gain caused by radiationless relaxation from the first excited state to the ground state. Similarly Eq. (2) indicates the rate of increase of n_1 chromophores.

The intensity distribution in the medium caused by the short-pulse laser propagation is analyzed by the transient radiative transport equation by neglecting the scattering effects and is given by

$$\frac{1}{c}\frac{\partial I}{\partial t} + \frac{\partial I}{\partial z} = (-\sigma_1 n_0 + \sigma_1 n_1 - \sigma_2 n_1) I \tag{4}$$

It is evident that Eqs. (1), (2), and (4) form a set of coupled nonlinear partial differential equations, which makes the solution methodology complicated.

Ablation of material follows two mechanisms: surface evaporation and the phase explosion phenomenon.[32] The present formulation considers the surface evaporation phenomena. The heat diffusion equation is used to calculate the temperature distribution in the medium with an added source term [the last term on the right-hand side of Eq. (5)], which is a representation of the energy loss of a chromophore caused by nonradiative relaxation from its excited higher level to lower energy level. The corresponding temperature distribution is then given by

$$\frac{\partial T}{\partial t} = V\frac{\partial T}{\partial z} + \frac{1}{\rho C_p(T)}\frac{\partial}{\partial z}\left[\kappa(T)\frac{\partial T}{\partial z}\right] + \frac{\hbar\omega}{\rho C_p(T)}\left(\frac{n_1}{\tau_1} + \frac{n_2}{\tau_2}\right) \tag{5}$$

A photothermal ablation model is considered in this analysis. The velocity V of the ablation front is given as

$$V = V_a \exp(-E_a/k_B T|_{z=0}) \tag{6}$$

where $T|_{z=0}$ the surface temperature of the material. The preceding ablation model does not take into consideration the effects of physical parameters including pressure or the influence of mechanical stresses.

The initial conditions for the rate equations and the heat diffusion equation are

$$n_1|_{t=0} = n_2|_{t=0} = 0, \qquad n_0|_{t=0} = C_0 \tag{7a}$$

$$T|_{t=0} = T_\infty \tag{7b}$$

The boundary conditions for the rate equations are

$$n_0|_{z\to\infty} = C_0, \qquad n_1|_{z\to\infty} = n_2|_{z\to\infty} = 0 \tag{8a}$$

The boundary condition for the intensity equation is as follows:

$$I(0, t) = (1 - R) I_{\max} \exp[-4\ln 2(t/t_p - 2)^2] \tag{8b}$$

This analysis neglects the effects of shielding by the plume generated during ablation, as this study is primarily relevant for time just before the ablation starts.

The boundary conditions for the heat diffusion equation are given by[25]

$$\kappa(T)\left.\frac{\partial T}{\partial z}\right|_{z=0} = \rho \Delta H V \tag{9a}$$

$$T|_{z\to\infty} = T_\infty \tag{9b}$$

A simple relation between fluence ϕ and the maximum intensity $I_{\max}$ is given by[33]

$$\phi = 2 I_{\max} t_p \tag{10}$$

The ablation depth d can be calculated using the following relation:

$$d \cong t_{\mathrm{DT}} V \tag{11}$$

The heat diffusion time t_{DT} is given by[25]

$$t_{\mathrm{DT}} = 2 l_s^2 / D_T \tag{12a}$$

$$l_s = 2\phi/\hbar\omega C_0 \tag{12b}$$

III. Results and Discussion

This study investigates the effects on the temperature distribution and ablation depth of absorbing dielectrics caused by its interaction with ultrashort laser pulses. It also presents a parametric study of different laser parameters and material properties to analyze the ablation characteristics of the material. In this paper the effects of fluence ϕ or the total energy incident on the material, delay time between the pulses t_d, pulse width t_p, chromophore nonradiative relaxation times from higher to lower energy level τ_2, ablation activation energy E_a, thermal conductivity κ, and ratio of absorption coefficients s are considered. The effects of a single laser pulse compared to two successive laser pulses and level of excitation, that is, two- and three-level system, are also analyzed. The values of the material parameters are chosen to represent a wide variety of absorbing dielectrics.[25] The laser and material parameters, which are varied, are as follows: $\phi = 2.5$, 25, 50 mJ/cm^2; $t_p = 500$ fs, 5, 50 ps; $t_d = \infty$, 0, 5 ps; $E_a = 0.75$, 1.5 eV; $\tau_2 = 20$ fs, 10 ps; $\kappa = 0$, 1.55×10^{-4}, 1.55×10^{-3}, 1.55×10^{-2} W/cm · K; and $s = 2$, 4, 10. The parameters that are kept constant are $\sigma_1 = 5 \times 10^{-17}$ molecules/cm^2, $\tau_1 = 50$ ps, and $T_\infty = 300$ K. The thermal constants are assumed to be independent of temperature. The heat flux at the boundary ($z = 0$) is equal to zero in this paper, though the form of boundary condition given by Eq. (9a) can be easily implemented. The values of the parameters that are varied are mentioned while discussing the figures. The temperature in the medium will rise even after the pulse passes through the medium. The temperature distributions are determined at a time instant, which is several times larger than the laser pulse width, in which it does not vary

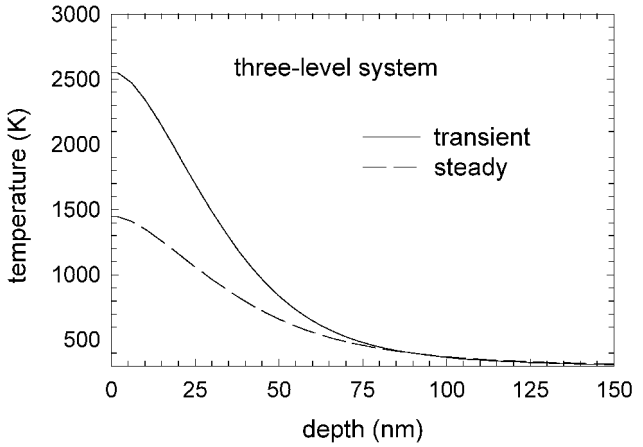

Fig. 2 Comparison of the temperature distribution between transient and steady-state analysis: $E_a = 0.75$ eV, $t_d = 0$, $t_p = 500$ fs, $\sigma_1 = 5 \times 10^{-17}$ cm^2, $\sigma_2 = 50 \times 10^{-17}$ cm^2, $\tau_1 = 50$ ps, $\tau_2 = 10$ ps, $\phi = 25$ mJ/cm^2, and $\kappa = 1.55 \times 10^{-3}$ W/cm · K.

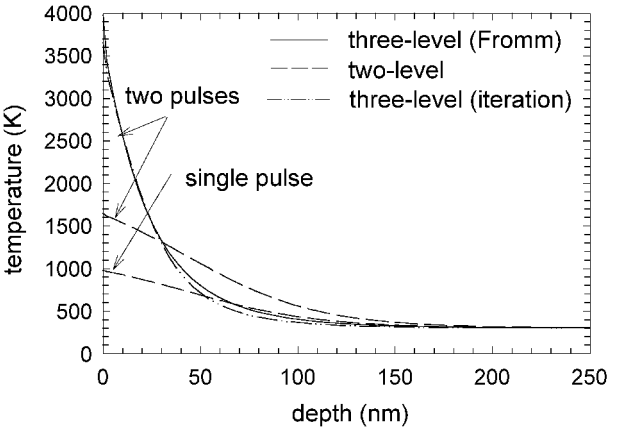

Fig. 3 Comparison of the temperature distribution between single and two successive laser pulses; two- and three-level chromophore system; iterative technique and Fromm's scheme: $t_d = \infty$, $t_p = 500$ fs, $\sigma_1 = 5 \times 10^{-17}$ cm^2, $\sigma_2 = 50 \times 10^{-17}$ cm^2, $\tau_1 = 50$ ps, $\tau_2 = 10$ ps, $\phi_{\text{two}} = 25$ mJ/cm^2, $\phi_{\text{single}} = 50$ mJ/cm^2, and $\kappa = 0$.

at each point in the medium with the change in the values of time instant. Results are obtained by selecting various time instants in order to determine the appropriate time instant for a given pulse width and delay time between pulses.

The set of coupled radiative transport equation, the rate equations, and the heat diffusion equation are solved using two different techniques: an iterative scheme[28] and a predictor corrector method called Fromm's scheme.[21,34] Time-step size of $\Delta t = 1.38 \times 10^{-17}$ s and spatial-step size $\Delta z = 4 \times 10^{-7}$ cm are used in the Fromm's scheme, which is second-order accurate in space and first-order accurate in time. A predictor step advances the solution from t to $(t + \Delta t/2)$, followed by a corrector step from $(t + \Delta t/2)$ to $(t + \Delta t)$. The iteration technique, on the other hand, uses a fully implicit scheme with an order of accuracy of Δt and Δz similar to Fromm's scheme. In the iterative technique when the percentage difference between the current value of a parameter and its previous iteration value is less than 0.3%, the convergence criterion is met. The values of the spatial grid size and temporal node size for both techniques are varied by one order in either direction, and the results are found to be stable and converging.

One of the key features in this study is consideration of the transient nature of the intensity distribution within the dielectric for laser ablation caused by multiple laser pulses. Figure 2 represents the difference in the temperature distribution obtained for the transient and the steady-state analysis having $t_p = 500$ fs, $\phi = 25$ mJ/cm^2, $\tau_2 = 10$ ps, $t_d = 0$, $E_a = 0.75$ eV, $\sigma_2 = 50 \times 10^{-17}$ molecules/cm^2 ($s = 10$), and $\kappa = 1.55 \times 10^{-3}$ W/cm · K. The transient analysis is required for the case of short-pulse lasers when the pulse width is in the same order as the time required for the laser pulse to propagate within the medium.[27,29] The retention of the transient term in Eq. (4) affects the temperature distribution in the medium at large times compared to the laser pulse width. The steady-state results are obtained by dropping the transient term (first term) on the left-hand side of Eq. (4). There is a significant difference in the temperature distribution between steady-state and transient cases particularly closer to the surface, as seen in Fig. 2. The steady-state or parabolic formulation underpredicts the temperature particularly at the surface. Because the surface temperature is directly related to ablation depth, this has wide impact in the analysis of ablation characteristics of dielectrics. The use of accurate transient radiative transport formulation implies that less energy is required to ablate a certain amount of the material for a particular pulse width compared to the steady-state analysis. Without the correct model one could use higher fluence or energy than the required threshold value to ablate a given volume of the material.

In pulsed laser heating of dielectrics, the concept of two heating regimes, namely, the length scale regime and the insufficient heating regime arises. Many parameters such as activation energy, excitation level of chromophores upon photon absorption, and thermal conductivity determine the heating regime. Depending upon the heating regime, there exists a relation between ablation depth and other ablation characteristics, namely, the penetration depth (or the heat affected region within the material) and the surface temperature. In the length scale regime the ablation depth is dictated by the penetration depth, which implies that the higher the penetration depth the greater the ablation depth. On the other hand, in the insufficient heating regime the maximum surface temperature is the dominant parameter, and a higher temperature would imply greater ablation depth.

To ensure accuracy of the Fromm's scheme formulation, the temperature distributions in the medium are first obtained for the steady-state formulation using the Fromm's scheme by neglecting the ablation front velocity [i.e., by dropping the first term on the right-hand side of Eqs. (1), (2), and (5)] and compared with the existing results in the literature.[25] The temperature profiles overlap each other. This matching with the existing results is critical in order to test the accuracy of the Fromm's scheme.

Figure 3 presents the comparison between the two computational techniques used, namely, Fromm's scheme and the iteration scheme. The parameters used are $t_p = 500$ fs, $\tau_2 = 10$ ps, $E_a = 0.75$ eV, $\phi = 25$ mJ/cm^2, $\sigma_2 = 50 \times 10^{-17}$ molecules/cm^2 ($s = 10$), and $\kappa = 0$. The results are found to match closely for the two schemes. Therefore the results from Fromm's scheme are only presented henceforth, as it is computationally faster than the fully implicit iterative scheme. The figure also presents the comparison between the temperature distribution for a single pulse and two successive laser pulses, having a delay time between pulses t_d equal to infinity. Delay time $t_d = \infty$ implies it is greater than the maximum relaxation time for the chromophores, but much shorter than the heat diffusion time. A two-level energy absorption model is considered with the fluence for a single pulse being double that of the case for two successive pulses. The results show a higher surface temperature for the two pulses than the single pulse. The figure also shows the temperature distribution for the case where two successive laser pulses excite the molecules to the second excited level as shown in Fig. 1 and which corresponds to a three-level system. It is evident from the figure that in the two-level system the microscopic energy transfer increases the penetration depth of the laser radiation and reduces the peak surface temperature significantly. This implies that the heat affected zone for a two-level system would be greater than that for a three-level system. This in turn signifies that the ablation depth for a two-level system is greater than that for a three-level system in the length scale regime. On the other hand, the surface temperature for a three-level system is much higher than the two-level system. Therefore, in the insufficient heating regime the ablation depth for the three-level system is greater than that of the two-level system. The emphasis of this paper is on a three-level system for the case of insufficient heating regime as it is of more practical significance.[25]

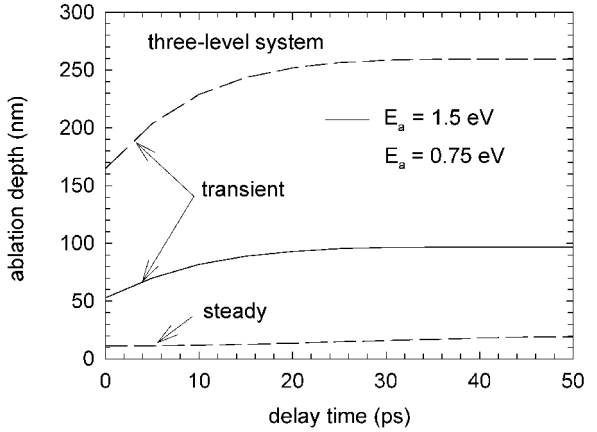

Fig. 4 Ablation depth for various delay times between pulses: t_p =500 fs, $\sigma_1 = 5 \times 10^{-17}$ cm^2, $\sigma_2 = 50 \times 10^{-17}$ cm^2, $\tau_1 = 50$ ps, $\tau_2 = 10$ ps, $\phi = 25$ mJ/cm^2, and $\kappa = 1.55 \times 10^{-3}$ W/cm · K.

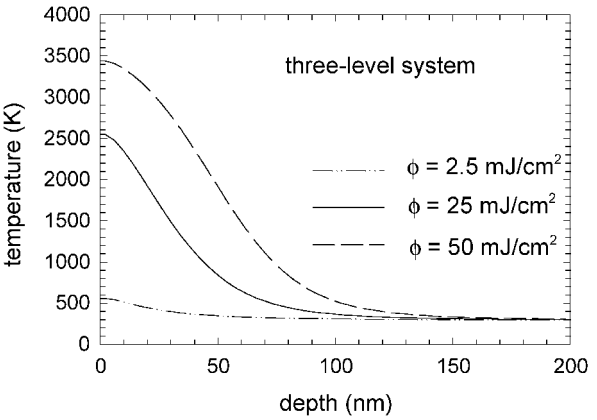

Fig. 5 Temperature distribution for various laser fluence: E_a = 0.75 eV, $t_d = 0$ ps, $t_p = 500$ fs, $\sigma_1 = 5 \times 10^{-17}$ cm^2, $\sigma_2 = 50 \times 10^{-17}$ cm^2, $\tau_1 = 50$ ps, $\tau_2 = 10$ ps, and $\kappa = 1.55 \times 10^{-3}$ W/cm · K.

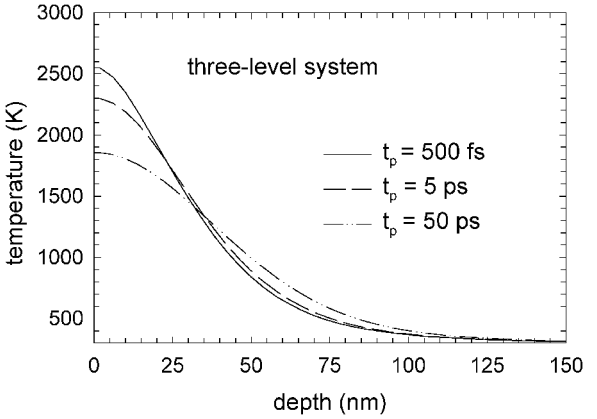

Fig. 6 Temperature distribution for various laser pulse width: E_a = 0.75 eV, $t_d = 0$ ps, $\sigma_1 = 5 \times 10^{-17}$ cm^2, $\sigma_2 = 50 \times 10^{-17}$ cm^2, τ_1 = 50 ps, $\tau_2 = 10$ ps, $\phi = 25$ mJ/cm^2, and $\kappa = 1.55 \times 10^{-3}$ W/cm · K.

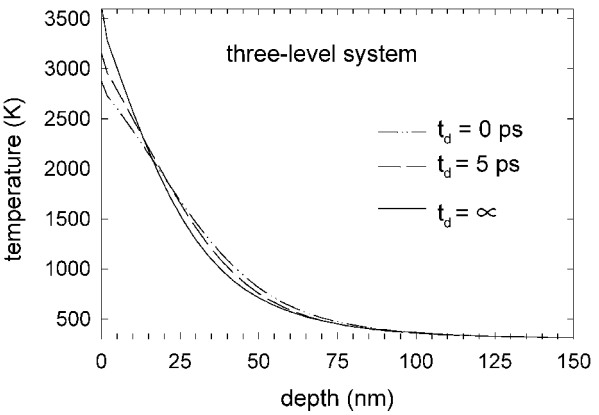

Fig. 7 Temperature distribution for various delay times between pulses: $E_a = 0.75$ eV, $t_p = 500$ fs, $\sigma_1 = 5 \times 10^{-17}$ cm^2, $\sigma_2 = 50 \times 10^{-17}$ cm^2, $\tau_1 = 50$ ps, $\tau_2 = 10$ ps, $\phi = 25$ mJ/cm^2, and $\kappa = 0$.

The length scale regime and the insufficient heating regime produce two types of ablation characteristics, which correspond to the relation between ablation depth and pulse delay. The two different types of ablative mechanisms observed are *bleaching* and *darkening*. In the sufficient heating regime, if the ablation depth increases with the increase in delay time, and in the length scale regime, if the opposite trend is observed, the mechanism for ablation is said to be bleaching. Whereas for darkening phenomena, the ablation depth decreases with the increase of delay time in the insufficient heating regime, and the opposite characteristics are observed in the length scale regime.

Figure 4 presents the ablation depth as a function of the delay time for $t_p = 500$ fs, $\tau_2 = 10$ ps, $E_a = 0.75$ and 1.5 eV, $\phi = 25$ mJ/cm^2, $\sigma_2 = 50 \times 10^{-17}$ molecules/cm^2 ($s = 10$), and $\kappa = 1.55 \times 10^{-3}$ W/cm · K. The lower the activation energy, the higher the ablation depth for the same fluence for both steady and hyperbolic cases. Also the ablation depth increases with the increase in the delay time, which implies a bleaching phenomenon for the insufficient heating regime. The ablation depth for $E_a = 1.5$ eV is negligibly small for the steady-state case and hence not shown in the figure. Thus the use of the steady-state formulation instead of the physically realistic hyperbolic or transient formulation of the radiative transport equation will underpredict the ablation depth of the material for given laser and material properties, and this will have wide impact in analyzing laser-material processing applications.

The threshold fluence necessary to ablate the material also has an impact on the ablation characteristics as already indicated. Figure 5 shows the parametric study of fluence ϕ for $t_d = 0$, $t_p = 500$ fs, $\tau_2 = 10$ ps, $E_a = 0.75$ eV, $\sigma_2 = 50 \times 10^{-17}$ molecules/cm^2 ($s = 10$), and $\kappa = 1.55 \times 10^{-3}$ W/cm · K. Different values used are $\phi = 2.5$ mJ/cm^2, 25 mJ/cm^2, and 50 mJ/cm^2. The results show a considerable variation in the surface temperature for different values of fluence. Increase in the fluence causes a significant rise in surface temperature as evident from the figure.

Figure 6 depicts the temperature variation within the dielectric for different pulse widths keeping the fluence constant. The parameters used are $E_a = 0.75$ eV, $\phi = 25$ mJ/cm^2, $\tau_2 = 10$ ps, $t_d = 0$, $\sigma_2 = 50 \times 10^{-17}$ molecules/cm^2 ($s = 10$), and $\kappa = 1.55 \times 10^{-3}$ W/cm · K. Shorter pulse width implies higher peak intensity of the laser pulse. The results indicate shorter laser pulses yield a higher temperature at the surface, with a reduction in the heat-affected region.

Figure 7 shows the temperature distribution in the medium for three different delay times between pulses. The parameters used are $E_a = 0.75$ eV, $\phi = 25$ mJ/cm^2, $t_p = 500$ fs, $\tau_2 = 10$ ps, $\sigma_2 = 50 \times 10^{-17}$ molecules/cm^2 ($s = 10$), and $\kappa = 0$. It is seen as the delay time is increased from 0 to ∞ it results in an increase in the maximum surface temperature. The higher the surface temperature the higher the ablation depth, and this corresponds to bleaching phenomena in the insufficient heating regime.

The relaxation time for transition of chromophores from a higher excited level to a lower energy level τ_2 also has impact on the bleaching and darkening phenomena. Figure 8 shows the effect of variation of the relaxation time τ_2 on the nondimensional temperature distribution within the medium for $E_a = 0.75$ eV, $\phi = 25$ mJ/cm^2, $t_p = 500$ fs, $\sigma_2 = 50 \times 10^{-17}$ molecules/cm^2 ($s = 10$), and $\kappa = 0$ for two different delay times between pulses, i.e., ∞ and 0 ps. The figure depicts that for $\tau_2 = 10$ ps the maximum surface temperature and

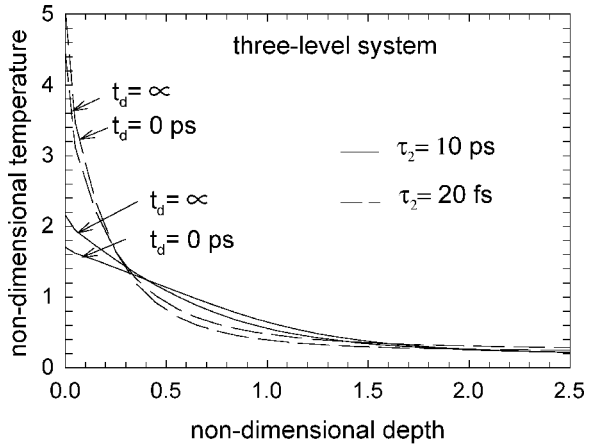

Fig. 8 Temperature distribution for various material relaxation times and delay times between pulses: $E_a = 0.75$ eV, $t_p = 500$ fs, $\sigma_1 = 5 \times 10^{-17}$ cm^2, $\sigma_2 = 50 \times 10^{-17}$ cm^2, $\phi = 25$ mJ/cm^2, and $\kappa = 0$.

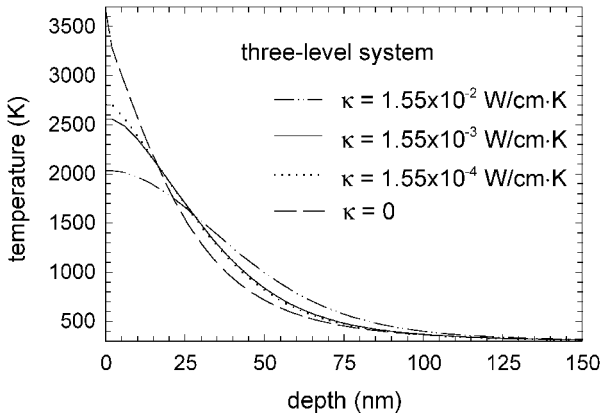

Fig. 9 Temperature distribution for various material thermal conductivity: $E_a = 0.75$ eV, $t_d = 0$ ps, $t_p = 500$ fs, $\sigma_1 = 5 \times 10^{-17}$ cm^2, $\sigma_2 = 50 \times 10^{-17}$ cm^2, $\tau_1 = 50$ ps, $\tau_2 = 10$ ps, and $\phi = 25$ mJ/cm^2.

hence the ablation depth corresponding to $t_d = \infty$ is greater than that for $t_d = 0$, which corresponds to the bleaching phenomenon. On the other hand, for $\tau_2 = 20$ fs the opposite behavior of the decrease of the surface temperature with increase in delay time is noticed, which corresponds to the darkening characteristics for insufficient heating regime. This study reveals that for darkening to occur, fast relaxation for the higher energy level chromophores should take place, i.e., τ_2 should be in the order of 0 to $0.01t_p$ (Ref. 25).

Figure 9 presents the plot of the temperature distribution within the dielectric for different values of thermal conductivity equal to 1.55×10^{-2} W/cm · K, 1.55×10^{-3} W/cm · K, 1.55×10^{-3} W/cm · K, and 0. The other parameters used are $t_p = 500$ fs, $\phi = 25$ mJ/cm^2, $\tau_2 = 10$ ps, $t_d = 0$, $E_a = 0.75$ eV, and $\sigma_2 = 50 \times 10^{-17}$ molecules/cm^2 ($s = 10$). For $\kappa = 0$ the material behaves as a perfect insulator. This results in an increase of the surface temperature because of localized heat deposition within the medium. For lower values of thermal conductivity, the temperature profiles show a higher value at the surface as well as a smaller heat affected zone. This characteristic is desirable in some cases.

The effect of the variation of the absorption cross section of molecules on the temperature distribution is shown in Fig. 10. The absorption cross section of molecules at the first excited level that causes transition to the second excited level is varied and that at the ground state is kept constant. The different values of s used are 2, 4, and 10. Other values of parameters used are $t_p = 500$ fs, $\phi = 25$ mJ/cm^2, $\tau_2 = 10$ ps, $t_d = 0$, $E_a = 0.75$ eV, and $\kappa = 1.55 \times 10^{-3}$ W/cm · K. The higher the value of s, the higher the

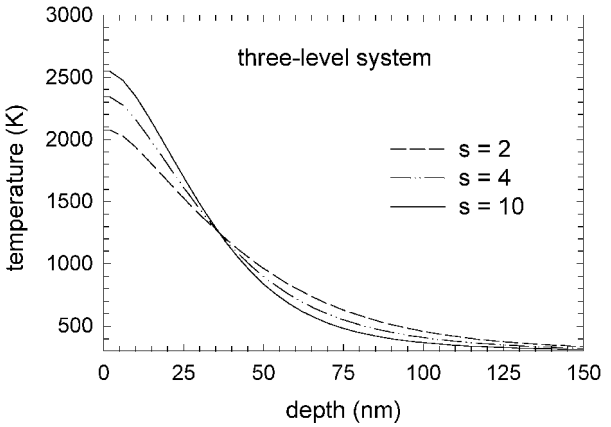

Fig. 10 Temperature distribution for various absorption cross section of molecules: $E_a = 0.75$ eV, $t_d = 0$ ps, $t_p = 500$ fs, $\sigma_1 = 5 \times 10^{-17}$ cm^2, $\sigma_2 = s^* \sigma_1$, $\tau_1 = 50$ ps, $\tau_2 = 10$ ps, $\phi = 25$ mJ/cm^2, and $\kappa = 1.55 \times 10^{-3}$ W/cm · K.

concentration of the chromophores in the second excited state. This results in a higher surface temperature with the increase in the value of s.

IV. Conclusions

This research is one of the first studies, where the effect of two successive short laser pulses on the ablation characteristics for absorbing dielectrics is analyzed using the transient radiative transport equation. Because of the rapid deployment of short-pulse lasers in various engineering applications particularly material processing, this study could be used to determine the optimum process parameters needed for ablation of material. It is demonstrated that the different material properties and the laser parameters considered in this paper affect the temperature distribution within the dielectric and the ablation depth of the material. Further research work is needed to investigate the effects of temperature dependent thermal constants and use of phototphysical model, which assumes a decrease in ablation activation energy of the material caused by photon absorption, instead of a photothermal model, where the activation energy is assumed constant. Direct comparison of the numerical results with the experiments, which are currently being conducted, will be also undertaken.

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