Pulse Duration Dependence of Lithographic Printing Plate Imaging by Near-Infrared Lasers

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Exposure thresholds are measured for laser photothermal imaging materials that can be used as direct writing lithographic offset printing plates, as a function of laser pulse duration in the 30-μs to 1-ps range. The materials studied are based on direct imaging technology developed by Presstek, Inc. By shortening the pulse duration, the exposure threshold can be reduced by a factor of 26 from 0.52 J/cm^2 (30-μs duration) to 0.02 J/cm^2 (1-ps duration). Thermal conduction plays a key role in determining this nonreciprocal behavior. In layered media, thermal conduction is anisotropic and three dimensional, but in many cases simpler treatments of thermal conduction are possible. The conditions under which a one-dimensional model can be used are discussed and shown to apply here. The 1-D thermal conduction model fits the data accurately over a vast range of timescales for exposed spots with radii greater than ~10 μm and provides insights into fundamental mechanisms. The practical implications of mating writing engines to materials with nonreciprocal behavior, where the thresholds decrease with decreasing pulse duration, are discussed.

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Introduction

In this article, we present data on the pulse-width dependence of the threshold for exposing a laser photothermal imaging material. A theoretical model is presented to explain pulse-width dependence, which provides insights into the fundamental mechanisms of the exposure process. The model also is a framework for predicting, understanding, and optimizing the performance of imaging media exposed in writing engines that provide different exposure intensities and pulse widths. The specific system studied here is an imaging medium that when imaged by near-infrared laser pulses can be used as an offset lithographic printing plate. The model system[1] is based on direct imaging technology developed by Presstek, Inc. (Hudson, NH). However, the measurement techniques and theoretical development described in this article can be used to study and model the behavior of a wide range of laser photothermal imaging materials.[2] In fact, we have successfully applied this model to both Presstek media and laser ablation transfer media (Lasermask™) as described elsewhere in a short conference abstract.[2]

The exposure process for laser photothermal materials is fundamentally different from ordinary imaging materials such as silver film or photopolymers.[3,4] These latter materials usually exhibit reciprocity over a wide range of conditions. Reciprocity means if the intensity I of the imaging source is doubled, the time-to-exposure t_p is cut in half. In other words, the fluence J (J/cm^2) needed to expose a reciprocal medium remains constant for any pulse duration t_p. Laser photothermal materials often show large deviations from reciprocity. (We will see below some conditions may exist when reciprocity is obeyed). That is easily illustrated by noting these materials are "light-safe." Even extended exposure to room lights (many hours) has virtually no effect on the media, even if the time-integrated radiation fluence greatly exceeds the fluences used in laser imaging.[3]

The reason that low-intensity sources do not image laser photothermal media is that generally these media need to reach a rather high threshold temperature T_{th} before the chemical or physical processes responsible for image formation begin to occur.[1–5] We will see below that laser heating of the medium must compete with thermal conduction away from the heated region.[1–5] For low-intensity sources thermal conduction wins and T_{th} can never be reached. For higher intensity sources that produce rapid heating, the effects of thermal conduction can be overcome.[6]

As shown in Fig. 1, the direct writing plate is a model system[1] based on PEARL™ Direct Imaging technology developed[7] by Presstek, Inc. (Hudson NH). The medium consists of a transparent substrate, a very thin (~30 nm) absorbing interlayer composed of Ti metal and its oxides and a 2-μm-thick coating of ink adhesive silicone polymer. In usual applications,[1,7] the medium is mounted on an external drum and imaged from the coating side by 10-μs-duration pulses from diode lasers. The exposed region of ink adhesive material is removed by post-imaging physical cleaning. The medium is then suitable for waterless

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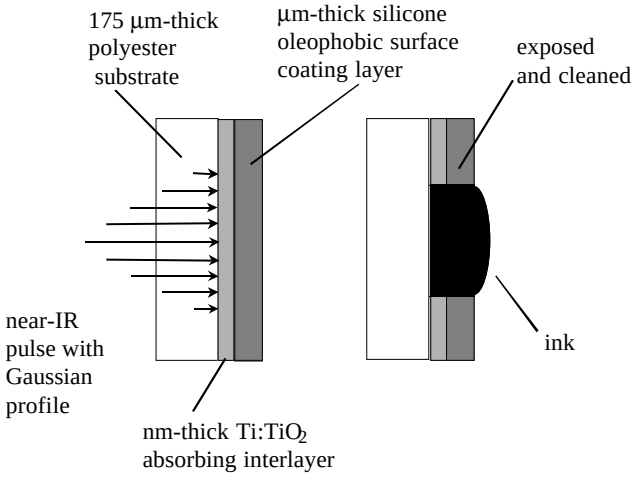

Figure 1. Schematic of the direct imaging computer-to-plate material based on technology developed by Presstek, Inc. The plate consists of a substrate, an absorbing interlayer, and a silicone surface coating layer. Rapid laser heating of the interlayer causes the surface layer to debond. After cleaning, a well is left in the oleophobic silicone coating layer that attracts printer inks.

offset lithographic printing runs of 100,000 copies.[1] In studies at the University of Illinois, the medium is exposed by Nd:YAG lasers, which provide greater flexibility in pulse duration and pulse energy than diode lasers.[1] As we shall see, the Presstek medium can be imaged as well from the substrate side, as if mounted on an internal drum assembly, and it can be imaged with a wide range of pulse durations. Indeed, the exposure fluence threshold drops dramatically when the pulse duration is decreased below 10-μs.

Experimental

The Presstek medium was exposed by pulses incident on the substrate as in Fig. 1. The exposure fluence threshold was measured using near-IR pulses with durations t_p in the 1-ps to 30-μs range. Presently no single laser exists that can produce pulse durations over such a range. To accomplish these measurements, different lasers were used: a continuous-wave YAG laser with external pulse slicer, a Q-switched YAG laser, a mode-locked and Q-switched YAG laser, and a Ti:sapphire laser. The details of the experimental set up and measurement techniques are described elsewhere.[8]

The Presstek media were exposed and cleaned. The threshold was determined by knowing the laser beam parameters and measuring the size of the exposed spot with a microscope, a digitized video camera, and image analysis software.[8]

Results

The results are shown in Fig. 2. The medium did not produce a satisfactory image for t_p > 30-μs, but imaging quality was fine for all durations $t_p \leq$ 30-μs. As the pulse duration was shortened, the threshold fluence J_{th} decreased dramatically until the pulse duration became about 10^{-9} s. When t_p was below ~10^{-9} s, the threshold became independent of pulse duration. At t_p = 30-μs, the threshold J_{th} = 0.52 J/cm^2, and at t_p = 1 ps, J_{th} = 0.02 J/cm^2. Thus, the threshold could be varied by a factor of 26 by varying t_p.

Theoretical Model

The essential idea of our pulse-duration model is to assume a threshold temperature T_{th} exists that the imaging

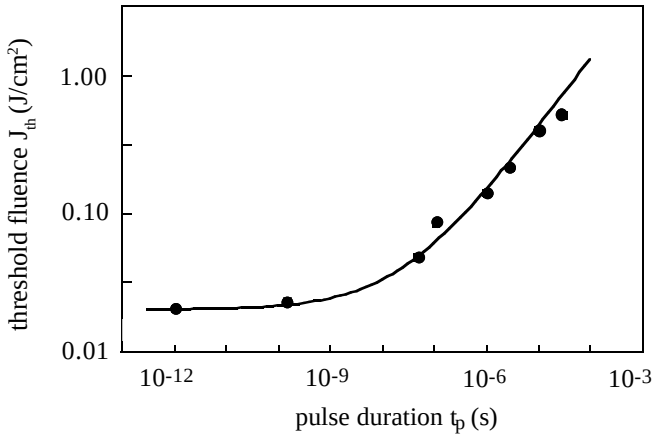

Figure 2. Dependence of the threshold fluence for exposing the direct imaging plates versus optical pulse duration. Starting from the longest exposure time used (30 μs), the threshold decreases by a factor of 26 for pulsewidths down to ~1 ns and then remains constant as the pulse duration is further decreased. The smooth curve is a fit to Eq. 11.

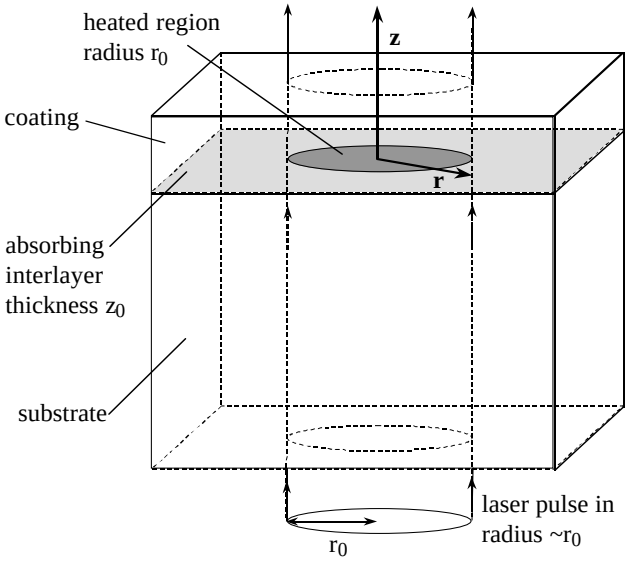

Figure 3. A film with a thin absorbing interlayer irradiated by a laser beam that heats a disk-shaped region of radius r_0. The coating is 2 μm thick, the substrate is 175 μm thick, and the interlayer is 30 nm thick. In this geometry, thermal conduction can be treated as a 1-D model with diffusion along the z-axis.

medium must attain for exposure to occur and that T_{th} is *independent of pulse duration*.[1–4]

One-Dimensional Thermal Conduction: Qualitative Discussion. To derive our model, we assume that heat flow can be approximated by a one-dimensional thermal conduction equation.[1,5] Because this point has caused confusion in the past, we now spend some time describing why thermal diffusion in three dimensions can be modeled as a 1-D process and when this simplifying assumption is accurate.

Figure 3 is a schematic diagram of an imaging medium where light is absorbed in a thin interlayer. To begin, we present a qualitative discussion of the simplest[1] case where: (1) the laser pulse is instantaneous (e.g., it is 1 ps); (2) the laser beam uniformly heats a disk-shaped region of the absorbing interlayer (top-hat beam profile); (3) the

disk is very thin—its thickness z_0 is much less than its radius r_0 (typically r_0 is 5 to 20 μm and z_0 ~ 30 nm); and (4) the thermal diffusivity D of the material is the same along all directions. Two complications characteristic of real systems, namely, a Gaussian profile for the near-IR laser beam and different thermal diffusivities for different constituents of the imaging medium will be discussed below.

Owing to the cylindrical symmetry of the laser beam (Fig. 3), we need consider only two directions for heat conduction, the radial direction r and the axial direction z. Figure 4(a) shows a slice along the r–z plane. The darkened region is the laser-heated absorbing layer. Note this drawing cannot accurately reproduce the actual aspect ratio of the disk, where the ratio of diameter to thickness is really ~1000:1.

We introduce the thermal diffusion length $\Lambda_D(t)$ (uppercase Greek "lambda"). The value $\Lambda_D(t)$ is an approximate measure of the distance heat can diffuse in time t,

$$\Lambda_D(t) = \frac{1}{2}\sqrt{\pi D t}, \qquad (1)$$

where D is the thermal diffusivity of the material.[9] For polymer components of these imaging media,[1] $D \sim 10^{-3}$ cm^2/s. Table I gives some values for $\Lambda_D(t)$ in a typical polymer. The timescale we need to consider is $t < 30$ μs. The distance heat can diffuse through a polymer in 30 μs, is given by Eq. 1 as $\Lambda_D(30\ \mu s) \sim 1$ μm.

The heavy line in Fig. 4(b) represents the very thin disk in the plane of the absorbing layer, heated to a high temperature by the short pulse. To make the discussion concrete, let us suppose the disk is initially 20 μm in diameter and 50 nm thick. Over the next 30 μs or so, heat diffuses ~1 μm in all directions, causing the volume of the disk of heated material to increase [Fig. 4(b)]. As the volume over which the heat is distributed increases, the temperature drops. Thermal diffusion along the z direction has a much greater effect on the temperature than diffusion along the r direction. If heat diffused only in the radial direction (along r), the diameter of the hot region would increase from 20 to 22 μm. The area (and volume) of the disk would increase by a factor of about 1.2. Therefore the high temperature would drop only slightly, again by about a factor of 1.2. If the heat diffused the same distance, but now only in the axial direction (along z), the thickness of the disk would increase from 50 nm to 2 μm. The volume of the disk would increase by a factor of 40 and the high temperature would drop by a factor of 40. When heat diffusion along one direction has a much greater effect than diffusion along other directions, the heat conduction problem becomes 1-D, where the 1-D axis here is the z direction.[1,2,5]

TABLE I. Diffusion Lengths $\Lambda_D(t)$ for Different Times, in Typical Polymer Media

Time	Λ_D
1 ps	0.3 nm (3Å)
1 ns	10.0 nm
1 μs	0.3 μm
1 ms	10.0 μm

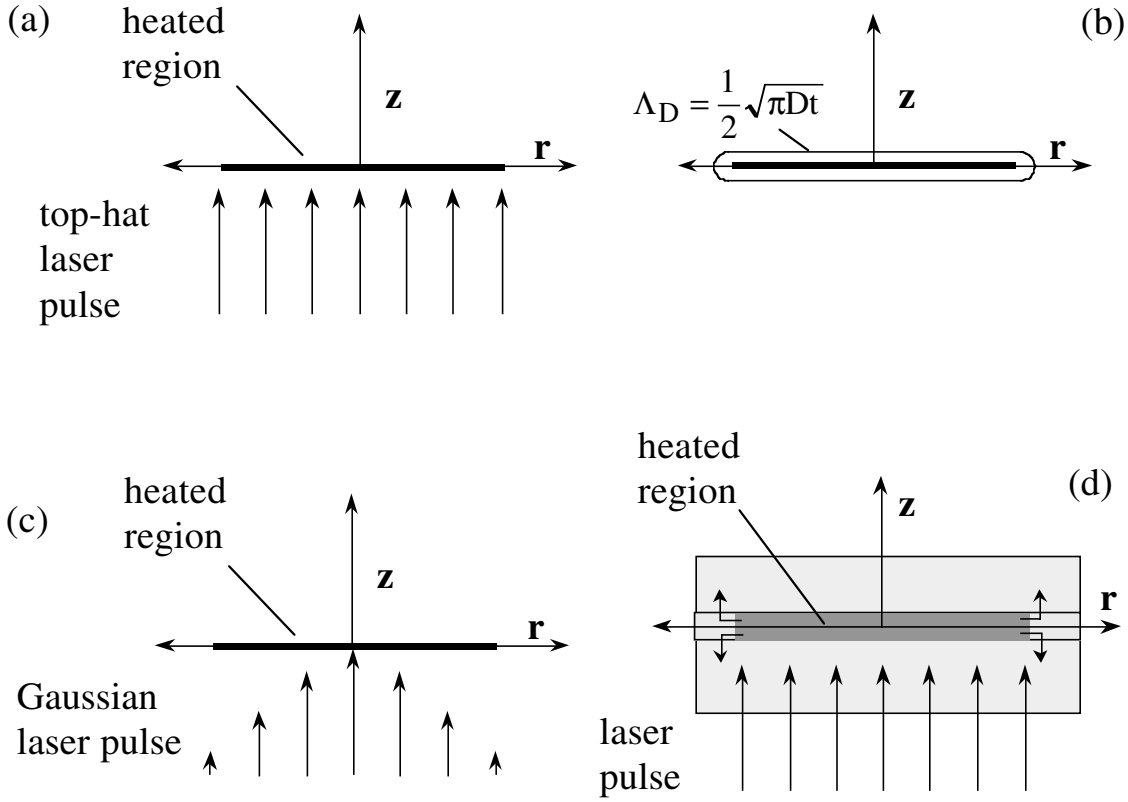

Figure 4. A thin interlayer perpendicular to the z-axis, at $z = 0$, is heated by a laser pulse. The ratio of the radius of the heated region to its thickness, ~1000:1, is much larger than appears in the figure. (a) Interlayer heated by a pulse with a uniform (top-hat) profile. (b) After a time t, heat has moved a distance Λ_D in all directions. Thermal diffusion along z has a much greater effect on the interlayer temperature than diffusion along r. (c) Interlayer heated by a pulse with a Gaussian radial intensity distribution. (d) The thermal diffusivity D' of the interlayer (light gray) is much greater than the diffusivity D in the surrounding polymer (shaded). Heat from the laser-irradiated region (darker gray) can diffuse rapidly through the interlayer, but when the interlayer is very thin, the heat leaks into the polymer before it can diffuse very far.

TABLE II. Parameters Used for Temperature Calculations

	Density ρ	Heat capacity C_p	Thermal conductivity κ	Diffusivity D
Silicone*	0.98 g/cm^3	1.53 Jg^{-1}deg^{-1}	1.5×10^{-3} Js^{-1}cm^{-1}deg^{-1}	0.98×10^{-3} cm^{2}s^{-1}
Polyester*	1.49 g/cm^3	1.13 Jg^{-1}deg^{-1}	2.8×10^{-3} Js^{-1}cm^{-1}deg^{-1}	1.86×10^{-3} cm^{2}s^{-1}
Ti†	4.5 g/cm^3	0.52 Jg^{-1}deg^{-1}	2 $\times 10^{-1}$ Js^{-1}cm^{-1}deg^{-1}	8.49×10^{-2} cm^{2}s^{-1}
TiO^{2} †	4.2 g/cm^3	0.59 Jg^{-1}deg^{-1}	6.5×10^{-2} Js^{-1}cm^{-1}deg^{-1}	2.5×10^{-2} cm^{2}s^{-1}

* Reference 10
† Reference 11

One-Dimensional Thermal Conduction: Quantitative Discussion. The temperature $T(r,z,t)$ at any time t can be computed using the two-dimensional diffusion equation in cylindrical coordinates.[9] In the case of interest,[1] the laser pulse is absorbed only in the interlayer located at $z = 0$. We ignore complications such as thermal equilibration between electrons and phonons in the interlayer,[1,6] which introduce no significant errors for times longer than 1 ps. In the case where the thickness of the interlayer $z_0 \to 0$,

$$\left[\frac{\partial}{\partial t} - D_{eff}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) - D\frac{\partial^2}{\partial z^2}\right]T(r,z,t) = \frac{\eta}{C\rho}\delta(z)I(r,t). \quad (2)$$

In Eq. 2, $D = \kappa/\rho C$ is the thermal diffusivity of polymer, where κ, ρ, and C are its thermal conductivity, density, and heat capacity. Numerical values of these parameters for silicone and polyester are given in Table II. The corresponding symbols for the interlayer parameters are D', κ′, ρ′ and C'. The interlayer is a nanostructured material containing Ti and its oxides, and it is a better thermal conductor then the polymer layers. Because we do not know the interlayer's thermal properties very accurately, for comparison's sake, values for bulk Ti and TiO_2 are given in Table II. The quantity D_{eff} is the effective thermal conductivity in the interlayer plane. As discussed below in conjunction with Eq. 6, D_{eff} ranges between the larger value D' and the smaller value D, depending on the thickness z_0 of the interlayer. In the Presstek media, the thermal diffusivities of the polyester substrate and silicone coating are about equal, so in Eq. 2 we ignore the small correction needed to account for these differences.[1] The parameter η is the fraction of incident light absorbed in the interlayer. The $\delta(z)$ is the Dirac δ-function, which localizes all laser heating at the interlayer. To account for the finite thickness of the interlayer, which matters only at short times (≤ 1 ns), analytical approximations for the δ-function can be used[9] to spread the heating over a 30-nm-thick layer. The value $I(r,t)$ is the instantaneous intensity of the laser pulse. For example, for a laser of power P where the laser beam has a Gaussian spatial profile and the pulse duration is t_p (the laser is turned on at time $t = 0$ and turned off at $t = t_p$),

$$I(r,t) = \frac{2P}{\pi r_0^{\,2}}\exp\left(\frac{-2r^2}{r_0^{\,2}}\right) \quad (0 \le t \le t_p). \quad (3)$$

Using well-known mathematical techniques, we can derive closed-form analytical solutions[1] to Eq. 2 for relatively simple laser pulses such as the one described by Eq. 3. If the laser pulse has a more complicated form, Eq. 2 can be solved by standard numerical methods, as described in Ref. 5. We will reserve the details for a later publication. Instead, we will concentrate on outlining the specific conditions when a 1-D approximation is accurate.

In the previous section, we briefly discussed the case [see Fig. 4(a)] where the laser pulse has a top-hat spatial profile and $D = D'$, that is, the thermal diffusivity of the polymer layers was equal to the diffusivity of the interlayer material. Then the 1-D approximation is valid when,

$$r_0 >> z_0$$

and (4)

$$\Lambda_D(t) << r_0.$$

Equation 4 show the laser beam radius r_0 must be much greater than the thickness z_0 of the interlayer. Then at short times when $\Lambda_D(t) << r_0$, a 1-D treatment is valid. For example, Fig. 4(b) represents the situation where time is short enough that the 1-D model is still valid. At very long times (say a few ms), the volume heated by thermal conduction away from the disk of radius r_0 becomes approximately spherical in the model. However, that volume becomes a flattened sphere in the real imaging material because of the nearby coating-air interface (Fig. 3), just 2 μm above the interlayer.[1]

Another important case occurs when $D = D'$ as above and the laser pulse has a Gaussian, rather than a top-hat profile [Fig. 4(c)]. The 1-D approximation is valid when,

$$r_0 >> \sqrt{\frac{2}{\pi}}z_0,$$

and (5)

$$\frac{4}{\sqrt{\pi}}\Lambda_D(t) << r_0.$$

The factors $(2/\pi)^{1/2}$ and $4/(\pi)^{1/2}$ in Eq. 5, which are the only differences between Eqs. 4 and 5, are close enough to unity that essentially the same conditions prevail whether the pulse has a top-hat or Gaussian profile. In fact Eq. 4 works well for any pulse profile that is smooth and slowly varying with no sharp hot spots or cold spots.

The case relevant to Presstek media studied here and other media with metallic interlayers is when $D' >> D$, that is, the thermal diffusivity of the interlayer material is much greater than the diffusivity of the polymers (see Table II). Fast diffusion in the interlayer is a complication whenever the diffusion length in the interlayer becomes comparable to the spot radius r_0. Because the diffusion length in the interlayer is a function of pulse duration, for a given pulse duration the 1-D approximation breaks down when the beam radius r_0 becomes sufficiently small. When that occurs, we can no longer use the simpler 1-D solution and instead need to solve Eq. 2 to obtain a considerably more complicated solution.

Even though it is highly conducting because the interlayer is very thin, heat does not diffuse very far through it. As shown in Fig. 4(d), when heat starts to diffuse through the interlayer, it quickly leaks from the interlayer where the diffusivity is the larger value D' into the polymer where the diffusivity is the smaller value D. Radial heat diffusion in the plane of the interlayer

is approximated by an effective radial thermal diffusivity, D_{eff},

$$D_{eff} = \frac{\kappa'}{\rho' C' + \frac{\rho C}{z_0}\sqrt{\pi D t}}. \tag{6}$$

Equation 6 is valid only if it yields a value of $D_{eff} > D$. When Eq. 6 yields a value of $D_{eff} < D$, then D_{eff} should be set equal to D. Thus, D_{eff} ranges between the larger value D' when the interlayer is thick (z_0 is large) and the smaller value D when the interlayer is thin ($z_0 \to 0$). Therefore, when $D' >> D$, the 1-D approximation can still be valid as long as Eq. 4 is satisfied and one additional condition is met, namely, the effective diffusion length $\Lambda_{eff}(t)$ in the interlayer must be small compared to r_0, that is,

$$\Lambda_{eff}(t) << r_0, \tag{7}$$

where

$$\Lambda_{eff} = \frac{1}{2}\sqrt{\pi D_{eff} t}.$$

In our experiments with the Presstek media, it turns out that the 1-D approximation is very accurate. Equation 6 can be used to show that for the longest pulse durations used here, 30 μs, Λ_{eff} is at most 3 μm. That value is computed for pure Ti, which probably overestimates the thermal diffusivity of the actual interlayer. Thus, theory shows the 1-D approximation to be valid for spot radii much larger than 3 μm. In all our experiments, the exposed spot radii were much larger than 3 μm, in fact, they were in the 15 to 40-μm range. An experimental check can be made to verify that the 1-D approximation is valid in our experiments. It must be shown that the exposure threshold fluence J_{th} is independent of the spot radii used in exposure threshold measurements. We have previously shown there is no spot size dependence of J_{th} for Presstek media[1,8] using 10-μs-duration pulses, when r_0 is in the 15 to 40-μm range.[1] In some preliminary measurements with smaller spots, we have seen that the 1-D approximation starts to break down with 10-μs pulses (30% error) when the spot radius is below about 5 μm. The thermal conduction model developed here predicts that for pulses shorter than 10 μs, the 1-D approximation should remain valid for spots even smaller than 5 μm in radius.

Pulse-Duration Dependence: Qualitative Discussion. Figure 5 is a simple sketch of how pulse duration affects exposure thresholds. The curves in the figure represent temperature T as a function of distance z from the plane of the interlayer at $z = 0$. The areas under the curves are proportional to the fluence J of the pulse. The shaded regions represent the absorbing regions of the media.

When a medium where heat is absorbed only in a thin interlayer is irradiated by a very short pulse right at threshold the heat is localized very near the plane of the absorbing layer. When the pulse fluence is equal to the threshold fluence, the maximum temperature, occurring at the end of the pulse and located at the interface between the interlayer and the coating,[1] is just exactly T_{th}. When a longer duration pulse with the same fluence is used, the temperature maximum is less than T_{th}, owing to the dissipative effects of thermal conduction. The longer duration pulse needs more fluence to bring the temperature to T_{th}. Thus, the fluence threshold increases as the pulse duration increases.

Pulse-Duration Dependence: Quantitative Discussion. Consider the system in Fig. 4(a), where the laser pulse heats a thin interlayer. Diffusion carries heat out of the interlayer into the surrounding polymer. Threshold is reached when the temperature at the interface between the interlayer and the coating just reaches T_{th}. When the laser pulse duration t_p is very short, essentially no thermal conduction occurs, and the threshold fluence is given by,[6]

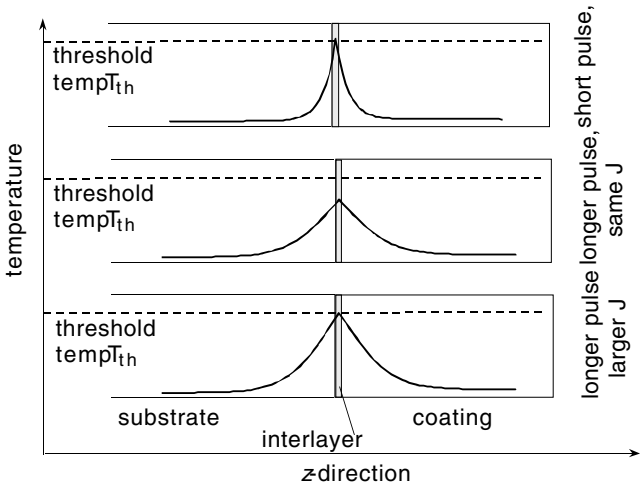

Figure 5. Heat distribution in the imaging medium (solid curves; the areas under the curves are proportional to pulse fluence J). (Top) A short-duration pulse that causes the peak temperature at the interface between the absorbing interlayer and the coating to just attain the threshold temperature T_{th}. (Middle) A longer duration pulse with the same fluence does not attain T_{th} owing to dissipative effects of thermal conduction. (Bottom) A longer duration pulse needs more fluence to reach T_{th}. Thus, the exposure threshold fluence increases with increasing pulse duration.

$$J_{th} = \frac{T_{th}\rho' C' z_0}{\eta}. \tag{8}$$

In Eq. 8 and what follows, we neglect[1,5,12] the temperature dependence of the heat capacity. Equation 8 shows J_{th} is linear in the interlayer thickness z_0. It takes more fluence to heat a thicker interlayer to T_{th}.

When the laser pulse duration t_p becomes longer, heat deposited in the interlayer by the pulse diffuses during the pulse into the polymer a distance roughly equal to the thermal conduction length $\Lambda_D(t_p)$. This length increases with $(t_p)^{1/2}$. When the mass of heated polymer becomes much greater than the mass of heated interlayer, the threshold fluence becomes independent of z_0. That occurs with longer duration pulses when the diffusion length $\Lambda_D(t_p) >> z_0$. In that case we can solve the 1-D thermal diffusion equation to obtain,[1]

$$J_{th} = \frac{T_{th}\rho C}{\eta}\left(\sqrt{\pi D t_p}\right) = \frac{2T_{th}\rho C}{\eta}\Lambda_D(t_p). \tag{9}$$

Equation 9 shows that for longer duration pulses the threshold fluence increases as $(t_p)^{1/2}$. A complete solution combining the models represented by Eqs. 8 and 9 can be obtained that is quite complicated and we will not give it here. Instead, we derived a quite simple approximate solution that is nearly correct at all times $t_p > 0$,

$$J_{th} = \frac{2T_{th}\rho C}{\eta}\sqrt{\pi D t_p} = \frac{T_{th}\rho' C' z_0}{\eta}. \tag{10}$$

Equation 10 shows that for longer pulses, J_{th} still increases as $(t_p)^{1/2}$ as in Eq. 9, but for very short pulses J_{th} becomes independent of t_p.

In deriving Eq. 10, we assumed the imaging medium became exposed when the interface between the interlayer and coating reached T_{th}. The interface is taken to have zero thickness, which is not realistic. When the laser pulse duration is very short, the exposure process involves very short (nanometer) length scales. To account for the possibility of an interfacial region of finite extent, we introduce a phenomenological parameter Λ_0 with units of length. To maintain consistency with the definition of $\Lambda_D(t)$ in Eq. 1, Λ_0 is defined so that the imaging medium becomes exposed when a region of thickness (along the z axis) $2\Lambda_0$ is heated to T_{th}. In terms of Λ_0, the threshold fluence is,

$$J_{th} = \frac{2T_{th}}{\eta}\left[\rho C\Lambda_D(t_p) + \rho' C' \Lambda_0\right] = \\ = \frac{T_{th}}{\eta}\left[\rho C\sqrt{\pi D t_p} + \rho' C' \sqrt{\pi D t_0}\right]. \quad (11)$$

In Eq. 11 we introduce a time parameter $t_0 = 4\Lambda_0^2/\pi D$. The pulse-width dependent exposure of the imaging material undergoes a fundamental transition near time t_0. For pulse durations shorter than t_0, J_{th} is independent of t_p, and for pulse durations longer than t_0, J_{th} increases as $(t_p)^{1/2}$.

A useful relation[2] can be derived for the power P of the laser and the duration of the pulse needed to expose an area A on an imaging medium that obeys Eq. 11. When $t_p << t_0$, the fluence threshold is independent of pulse duration, a reciprocity relation holds and

$$\frac{P}{A}t_p = \text{const.}, \quad \left(t_p << t_0\right). \quad (12a)$$

When $t_p >> t_0$, the fluence threshold increases as pulse duration increases, reciprocity does not hold, and

$$\left(\frac{P}{A}\right)^2 t_p = \text{const.}, \quad \left(t_p >> t_0\right). \quad (12b)$$

Discussion

In Fig. 2, the smooth curve is the fit to Eq. 11. It is clear the fit to this equation is extremely good. Keep in mind the data in the figures are shown on a log–log plot, so both the pulse duration t_p and threshold fluence J_{th} vary over wide ranges. The ability to fit data over extremely wide ranges is a critical test of the validity of the model.

The parameters obtained by fitting the data to Eq. 11 were T_{th} = 550 (±50)°C and Λ_0 = 30(±5) nm. Because the imaging material consisted of one layer of polyester and one of silicone, these results were obtained by taking the values of D, ρ, and C for silicone and for polyester (Table II) and averaging them. The fraction of light absorbed by the interlayer in the Presstek medium was measured[1] to be η = 0.49. The interlayer was assumed to consist of bulk Ti. The same results (within the cited error bounds) would be obtained if we instead used the values for PET and bulk TiO_2. Of course, the interlayer is neither bulk Ti nor TiO_2. That uncertainty introduces a systematic error in the determination[1] of T_{th}, that we believe is within the cited error bounds. It has no effect on the determination of Λ_0.

In another brief paper,[2] we compared the pulse-width dependence of the Presstek media to Lasermask. Lasermask differs from the Presstek media in several fundamental ways.[2] In Lasermask, the absorbing layer is also the imaging layer.[13,14] In this ~0.5-μm-thick layer are submicrometer graphite particles that act as volume absorbers, embedded in a phenolic polymer binder.[13,14] We found[2] that Eq. 11 also fit the Lasermask pulse-width dependent data very well. The value of T_{th} = 550°C was the same as obtained for the Presstek media, but the value of Λ_0 = 200 nm for Lasermask was much greater than the 30-nm value for Presstek.

The value of T_{th} = 550°C is striking and highly suggestive, because essentially the same threshold temperature has been observed for several other laser photothermal imaging polymers when heated by short-duration near-IR laser pulses. These other materials include Lasermask,[13] color laser ablation transfer media developed by Rexham graphics,[5] and a simple model system[12] consisting of near-IR absorbing dye in poly-methyl methacrylate (PMMA). Why are all of these values of T_{th} nearly identical? Why are these values, measured at very high heating rates on the order of 10^8 to 10^{12} deg/s, far greater than thermal decomposition temperatures determined by conventional experiments[5,15] at low heating rates of a few degrees per second?

We do not yet know the answers to these questions, and the reoccurrence of the 550°C value might simply be a coincidence. This value of T_{th} presumably represents some sort of vaporization temperature for the polymer constituents of the imaging media (silicone, phenolic resins, nitrocellulose, PMMA) when they are being heated at extremely high rates. But it seems likely that T_{th} ~ 550°C could be taken as a reasonable estimation for a wide variety of polymers used in photothermal imaging media.

What does the phenomenological parameter Λ_0 mean? Our simplest model is represented by Eq. 10. In the simplest model, the imaging medium becomes exposed when the zero-thickness interlayer-coating interface (Fig. 1) just attains[1] T_{th}. Because we believe the silicone polymer begins to decompose at a lower temperature than the melting temperature of the titanium interlayer, when the interface attains T_{th}, the silicone polymer at the interface begins to decompose into volatile thermochemical reaction products. When enough decomposition has occurred, the cohesion between the coating and the interlayer is greatly decreased. If that were the case we would expect (see discussion of definition of Λ_0 above Eq. 11) the value of $2\Lambda_0$ to be equal to the thickness of the interlayer, $2\Lambda_0 \simeq$ 30 nm. Because the experimental result gives $2\Lambda_0$ = 60 nm, about twice the expected magnitude, it appears the simple zero-thickness interface model of Fig. 1 is not correct and we should consider the possible effects of an interfacial region of finite thickness, as depicted in Fig. 6.

The real interface between interlayer and coating is not smooth and flat as in Fig. 1. A variety of analytical methods show the interlayer has a corrugated landscape that varies on the nanometer length scale. Thus, the parameter z_0 should be taken to be the mean thickness of the interlayer. Similarly, the coating material consists of a complicated network of cross-linked polymer chains physically and possibly chemically bonded to the interlayer material. The coating layer loses cohesion with the interlayer when enough of the bonds between polymer chains and interlayer are broken by thermochemical decomposition of polymer chains near the interface. A crude sketch to represent this picture is shown in Fig. 6.

The experimental result is that an interfacial region of thickness $2\Lambda_0$ ~ 60 nm, which is about twice as thick as the mean thickness z_0 of the interlayer, must be heated to temperature T_{th} before the imaging medium becomes exposed. In the picture represented by Fig. 6, some of this interfacial region corresponds to the crevices in the landscape and possibly some corresponds to the polymer network near the interlayer. This interpretation suggests that experiments with very short laser pulses, which intrinsically probe very

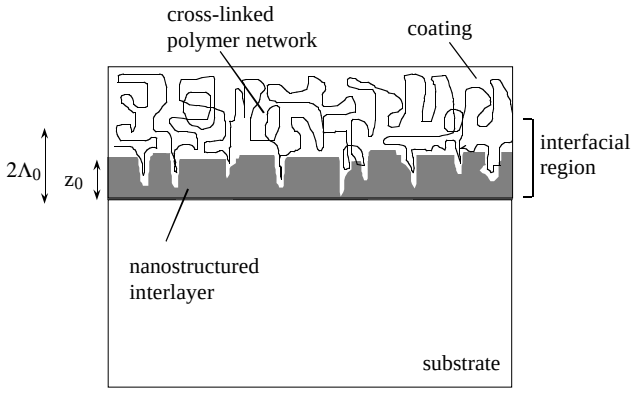

Figure 6. (a) Schematic diagram of the possible role of a nanostructured interface in determining the exposure fluence for very short laser pulses. The mean thickness of the absorbing interlayer is $z_0 \sim 30$ nm. The exposure results using short-duration pulses indicate an interfacial layer of thickness $2\Lambda_0 \sim 60$ nm must be heated before the imaging medium becomes exposed.

short spatial scales, may provide insights into the role of the nanostructure of the imaging medium in determining the imaging properties and the fluence threshold.

Practical Consequences of Pulse-Width Dependence. A hypothetical example is now presented of how the pulse-width dependence effect can be exploited, by matching[4] the properties of a writing engine to the imaging medium. Consider an engine that could expose the medium studied here using as the exposure source a bank of 10 laser diodes, each producing 1 W of power. Each diode exposes a spot of area A with a pulse duration of t_p = 10 μs. The bank of 10 lasers can, thus, expose 1 M spots per second. Now consider replacing the bank of 10 1 W lasers with a single diode-pumped solid state laser producing 10 W, which is focused to the same area on the imaging medium. Now the power delivered by the 10 W on the area A is 10 times that of any single diode laser. If reciprocity held (Eq. 12a), this 10 W laser would operate at a pulse duration one-tenth that of the smaller diode lasers (i.e., 1 μs), and it would expose the medium with exactly the same writing speed as the bank of 10 diode lasers. There would be no practical advantage to this replacement. But in the microsecond regime, the imaging media studied here have a threshold that decreases with decreasing pulse duration. Therefore, with the 10 W laser, Eq. 12(b) shows the pulse duration can be reduced by a factor of 10^2. The 10 W laser could operate at a writing speed 100 times greater than a single 1 W diode laser and 10 times greater than the 10 W bank of 10 diode lasers. Even though the total power incident on the imaging material is 10 W in both cases, having a higher power beam from the 10 W laser allows the writing speed to be increased by a factor of 10. We are of course, assuming that the rest of the engine (scanning, controlling, pulsing, etc.) can keep up with this increased writing speed, and the cost of the engine does not become prohibitive.[4] Alternatively, the 10 W bank of 10 diode lasers could be replaced by a single 3.2-W ($10^{1/2}$ W) solid state laser that would theoretically write at the same speed as the entire 10 W diode laser bank.

Conclusion

The threshold fluence can be made to vary by a factor of 26 in the Presstek medium and by at least an order of magnitude in other media[2–4,6] by changing the pulse width. We are very pleased by the success of our theoretical model in predicting this pulse-width dependence. Moreover, the model is not limited solely to materials that have the structure of the Presstek media as our successful application to Lasermask[2] has shown.

With the model, the effects of using different lasers with different powers and pulse properties can be predicted in advance. The need to introduce the Λ_0 parameter to understand what happens at very short time and length scales seems to offer some very interesting and possibly deep insights into the nature of the exposure process and how to optimize it. For example, if an imaging engine were designed to produce very short laser pulses, this discussion indicates it might be advantageous to control the nanostructure of the interfacial region near the absorbing layer.

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