Improved model for the angular dependence of excimer laser ablation rates in polymer materials

J. E. A. Pedder,[1] A. S. Holmes,[1] and P. E. Dyer[2,a)]
[1]*Department of Electrical and Electronic Engineering, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom*
[2]*Department of Physics, University of Hull, Hull HU6 7RX, United Kingdom*

(Received 14 August 2009; accepted 30 September 2009; published online 29 October 2009)

Measurements of the angle-dependent ablation rates of polymers that have applications in microdevice fabrication are reported. A simple model based on Beer's law, including plume absorption, is shown to give good agreement with the experimental findings for polycarbonate and SU8, ablated using the 193 and 248 nm excimer lasers, respectively. The modeling forms a useful tool for designing masks needed to fabricate complex surface relief by ablation. © *2009 American Institute of Physics*. [doi:10.1063/1.3254236]

Great advances have been made in the technological applications of UV laser polymer ablation since this was first reported in 1982.[1] It has become possible to fabricate a variety of microstructures with complex surface relief for use in microelectromechanical systems (MEMS),[2] micro-optoelectromechanical systems (MOEMS),[3] lab-on-chip,[4] as well as surfaces with special physical properties.[5] Whether variable surface height is machined by changing aperture shape, synchronized-image-scanning, mask/workpiece dragging, or half-tone masks,[2] the shaping demanded often means the surface presented for ablation lies well off normal incidence. In such cases knowledge of the angular dependence of ablation rate is needed to facilitate mask design and exposure strategies for producing the desired surface relief.

In previous works, it has generally been assumed that the reduction in ablation rate on inclined surfaces can be accounted for by the geometrical cos θ reduction in the normal component of the fluence, possibly combined with the variation in the reflection loss.[6–9] However, recent experiments have shown that a model based on these assumptions can break down at higher fluence levels.[10] In this paper we present an alternative model for angular dependence, which takes into account the effect of plume absorption. The model is shown to produce good agreement over a wide fluence range for polycarbonate ablated at 193 nm and for SU8 photoresist ablated at 248 nm, both materials being important substrates for fabricating various microdevices.

Polycarbonate and cross-linked SU8 photoresist were ablated at normal and oblique incidence using laser pulses from an Exitech 8001 workstation for 248 nm exposure (30 ns pulse duration) or Exitech 7002 workstation for 193 nm exposure (21 ns pulse duration). An in-line attenuator and a fly's-eye homogenizer were employed to attain a variable, uniform fluence at the sample. Normal incidence data were derived by exposing a special half-tone mask[2] that produced a stepped multilevel fluence at the workpiece. The oblique incidence measurements made use of a rotary stage to accurately control the angle of incidence while ensuring the center of rotation lay in the upper surface of the substrate. Samples were exposed to 30 pulses at 10 Hz and at various fluences, and the depth removed over the 200×200 μm^2 site measured using a surface profilometer, allowing the average ablation rate per pulse to be determined.

Figure 1(a) shows the variation in ablation depth per pulse versus angle of incidence for polycarbonate ablated at 193 nm and fluences of 50, 150, and 350 mJ cm^{-2}. For each fluence value, the ablation depth remains approximately constant out to $\sim$20° and thereafter declines slowly until ablation effectively ceases at some limiting angle that becomes

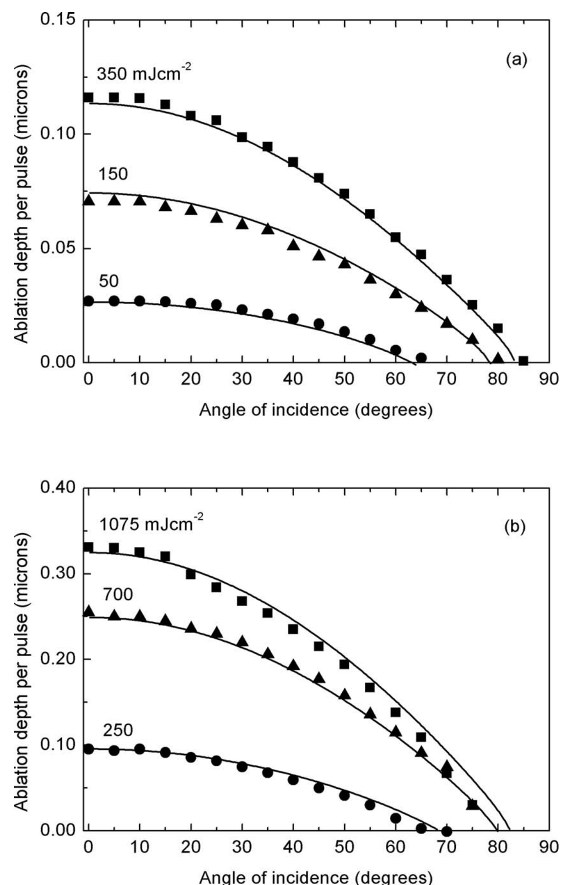

FIG. 1. Ablation depth per pulse versus angle of incidence. (a) Polycarbonate at 193 nm and fluences of 50, 150, and 350 mJ cm^{-2}. Solid lines calculated using Eq. (6) assuming $F_{T0}=25$ mJ cm^{-2}, $n=1.35$, $\kappa=0.32$ and $\mu/\mu_p=1.35$. (b) SU8 at 248 nm and fluences of 250, 700, and 1075 mJ cm^{-2}. Solid lines calculated using Eq. (6) with $F_{T0}=96$ mJ cm^{-2}, $n=1.8$, $\kappa=0.145$ and $\mu/\mu_p=2.8$.

[a)]Electronic mail: p.e.dyer@hull.ac.uk.

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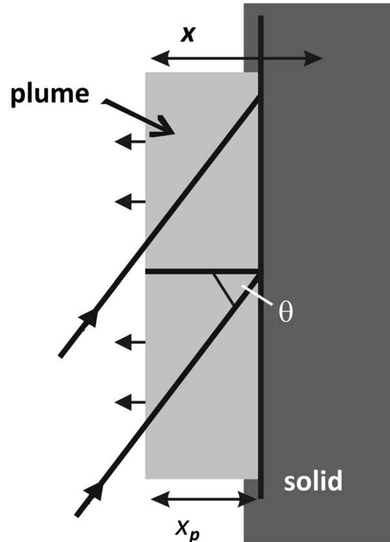

FIG. 2. Geometry of oblique irradiation.

progressively smaller as the fluence falls. A similar behavior is seen in Fig. 1(b) for SU8 exposed at 248 nm and 250, 700, and 1075 mJ cm^{-2}, and was characteristic of other material-wavelength combinations that were investigated.

To model oblique surface irradiation we took specific account of the plume absorption in a manner first outlined by Schildbach[11] and independently reported in Ref. 12. Mass absorption coefficients $\mu = \alpha_o/\rho$ for the solid polymer, where α_o is the absorption coefficient and ρ is the density, and $\mu_p(x) = \alpha_p(x)/\rho_p(x)$ for the plume of ablation products, where $\alpha_p(x)$ is the linear absorption coefficient and $\rho_p(x)$ is the density at x (Fig. 2) are defined. As a simplification it is assumed that $\mu_p(x)$ has a constant value μ_p, independent of the position x in the plume. This allows for a change in the concentration of absorbing chromophores in the transition from solid to vapor but neglects further changes, if any, brought about by secondary photolysis, thermolysis, or plasma initiation in the vapor phase. This simplification should be reasonable for strongly absorbing polymers exposed using ultraviolet lasers with pulse duration in the range of nanoseconds and above where ablation occurs at modest irradiance and laser-produced plasma is not a significant component of the plume.[13] With subnanosecond UV pulses, this is no longer the case as time-dependent plasma absorption and reflection become increasingly important,[14] and more detailed plume modeling is needed.

For a one-dimensional expansion, the depth x_d of solid removed by ablation and the plume thickness x_p at time t are related by

$$\int_0^{x_p} \rho_p(x)dx = \int_0^{x_d} \rho dx' = \rho x_d \tag{1}$$

and the normal component of irradiance just inside the solid surface is

$$I(t) = I_o(t)\cos\,\theta(1 - R_\theta)\exp - \mu_p \int_0^{x_p} \rho_p(x)\frac{dx}{\cos\,\theta} = dF_n/dt. \tag{2}$$

Here $I_0(t)$ is the laser irradiance, θ is the angle of incidence, R_θ is the surface reflection coefficient, and F_n is the normal component of fluence. To perform the integration in Eq. (2), a strictly one-dimensional geometry is assumed, so that edge effects related to the decreasing optical path in the plume near its lower edge[11] in Fig. 2 are neglected. The lateral extent over which this produces changes in the local ablation rate will depend on θ and on the plume width, which will increase during the laser pulse. Given typical plume expansion speeds normal to the surface are $\sim 5 \times 10^3$ ms^{-1}, as an estimate w_p is ≈ 50 μm at the end of a 10 ns duration laser pulse. This expansion will result in the plume density being significantly lower than the solid and its refractive index quite close to unity. Hence neglecting refraction in the plume, as is the case here, is taken to be reasonably well justified.

It is now assumed that ablation commences if the absorbed energy density exceeds a threshold value γ, and that when this is satisfied the surface recession rate is

$$\frac{dx_d}{dt} = \frac{1}{\gamma}\frac{dF_n}{dt}. \tag{3}$$

Combining Eqs. (1)–(3) and performing the integration, we obtain

$$\gamma \frac{\exp\left(\frac{x_d \mu_p \rho}{\cos\,\theta}\right) - 1}{\mu_p \rho} = (1 - R_\theta)(F - F_{T\theta}), \tag{4}$$

where $F_{T\theta}$ corresponds the threshold fluence for ablation at angle of incidence, θ. $F_{T\theta}$ and the threshold F_{T0} at normal incidence are related by

$$(1 - R_o)\alpha_o F_{T0} = (1 - R_\theta)\alpha_\theta F_{T\theta}\cos\,\theta = \gamma, \tag{5}$$

where α_θ is the effective absorption coefficient of the polymer along x for angle of incidence θ, as determined from its complex refractive index $n_c = n + in\kappa$.[15] From Eqs. (4) and (5), we finally obtain

$$x_d = \frac{\mu\cos\,\theta}{\mu_p \alpha_o}\ln\left[1 + \frac{\mu_p(1 - R_\theta)F}{\mu(1 - R_0)F_{T0}} - \frac{\mu_p \alpha_o}{\mu \alpha_\theta \cos\,\theta}\right], \tag{6}$$

relating the ablation depth x_d produced by a beam of fluence F incident at angle θ on the polymer, to the normal incidence ablation threshold F_{T0}, and the ratio of solid and plume mass absorption coefficients μ/μ_p. For normal incidence, $\theta=0$, and with $\chi = \mu/\mu_p = 1$, this reduces to the commonly used form, $x_d = 1/\alpha_o \ln F/F_{T0}$. Here, in addition to the basic $\cos\,\theta$ reduction in fluence, three other factors influence the etch rate as θ increases. These are the longer beam path in the plume and increasing surface reflection loss, both generally leading to a reduction in the fluence coupled to the surface. Off-setting this, there is an increase in α_θ as θ grows larger.

In Fig. 1(a) the solid lines correspond to the ablation rate obtained using Eq. (6) with $F_{T0} = 25$ mJ cm^{-2}, $\mu/\mu_p = 1.35$, and $n = 1.35$, and $\kappa = 0.32$ giving $\alpha_o = 28$ μm^{-1}. Reflection loss was calculated from n_c (Ref. 15) assuming the beam to be randomly polarized. The fit provided by Eq. (6) is seen to be remarkably good, given that refraction in the plume is neglected, and that μ/μ_p, n, and κ are taken to be constant, whereas in reality these likely vary with time and exposure conditions. Neither does the model allow for a possible expansion of the energy deposition zone through thermal diffusion during the pulse, which could be significant as α_o is large. The optical constants used are lower than values of

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$n=1.53$ and $\kappa=0.554$ derived from conventional optical characterization of Lexan polycarbonate.[16] This difference possibly stems from the fact that under ablation conditions, the solid surface interface is no longer sharply defined because of the presence of the plume. An ablation threshold of 25 mJ cm^{-2} is consistent with the measured onset of significant etching, although a small level of removal ($\sim$1 nm/pulse) was perceptible at as low as 15 mJ cm^{-2}. A fit of the model to the experimental results for SU8 exposure at 248 nm, is seen in Fig. 1(b), where $F_{T0}=96$ mJ cm^{-2} is used, together with $\mu/\mu_p=2.8$, $n=1.8$, and $\kappa=0.145$, giving $\alpha_o=13$ μm^{-1}. Again the fit is generally good, although there is a tendency to overestimate the etched depth at higher angles for larger fluence. The ablation threshold of 96 mJ cm^{-2} agrees well with that derived from etch rate-fluence plots for SU8 in the present work, but is higher than a value of $\sim$50 mJ cm^{-2} reported previously for ablation at 248 nm.[17]

In summary, the model reported is based on simple physical principles and is shown to provide a good description of the oblique incidence ablation rate over a wide fluence range, improving over earlier approaches. It should prove useful in helping understand various angle-dependent ablation effects in polymers exposed using ultraviolet lasers with pulse duration in the nanosecond range. It should, in many instances, be sufficiently accurate to aid the design of the complex masking needed to fabricate MEMS, MOEMS, and other structures in polymers where large angle relief is to be produced by ablation.

A.S.H. and J.E.A.P. acknowledge Exitech Ltd. for providing access to their facilities and EPSRC for an industrial CASE studentship. P.E.D. thanks Dr. C. D. Walton for help preparing the figures.

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