Femtosecond-Laser-Induced Nanoscale Blisters in Polyimide Thin Films through Nonlinear Absorption: Supplementary

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I. DERIVATION & FULL SUMMARY OF CALCULATION

This section provides the complete details and set of parameters used for the calculations shown in the main paper. These calculations were performed using Mathematica version 11.1. The advantages of using femtosecond lasers to induce material breakdown are two-fold. Femtosecond pulses deposit energy with minimal heat dissipation, and because amplified femtosecond pulses are extremely intense, nonlinear absorption processes are easily accessible. These two factors, when combined, lead to deposition of energy with much greater confinement than other methods.

We demonstrate this in the following calculation of femtosecond-laser-induced breakdown through linear, two-photon, and three-photon absorption (henceforth 1PA, 2PA, and 3PA) in a polymer film. Each mechanism was considered separately, as is typical by material selection in LIFT experiments using polymer films, and which naturally highlights the main features of energy deposition from each absorption order. We model the film to have the density, heat capacity and decomposition temperature of polyimide [**?** **?**]. The linear absorption coefficient was chosen to match experiments involving blister formation through linear absorption of 355 nm light in polyimide [**?**]. Since nonlinear absorption coefficients of undoped polymers are not reported, we chose two- and three-photon absorption cross sections to be those reported for zinc oxide, a material with a similar band gap [**?**]. In all three scenarios, laser pulses were taken to have durations of $\tau = 50$ fs with square envelopes and Gaussian spatial intensity profiles with focal spot diameters of $2\omega_0 = 3$ µm at their waists. These values are summarized in **Table I**. The focal spot was placed at the surface of the modelled polymer films in all cases; this is equivalent to focussing on the underside of a polymer film in our experimental conditions.

Since femtosecond pulses are much shorter than timescales of heat dissipation, absorption is approximated to be instantaneous. Thus, pulse intensities incident on the polymer are taken to be $I_0(r) = I_{peak}\cdot\exp\left(-2r^2/\omega_0^2\right)$ where peak intensity in space and time is defined as $I_{peak} = \left(2/\pi\omega_0^2\right)(E_{pulse}/\tau)$. Pulse energies were chosen separately for the cases of 1PA, 2PA, and 3PA, such that the peak temperature in the material reached 10000K in all cases; these pulse energy values were 42 nJ, 31 nJ, and 2.5 nJ respectively. This was done to compare the confinement of similar levels of breakdown for each absorption order. The intensity attenuation from each absorption mechanism was calculated and converted into energy deposition proportional to $-dI/dz$ where z is the direction of propagation into the polymer film. Circular symmetry was used to simplify these calculations. In particular, the energy absorbed within a small annular cylinder of thickness with an inner radius of r, outer radius of $r + \Delta r$, and a height of Δz at a distance z into the film is given by the equation below.

$$E_{abs}(z,\Delta z, r, \Delta r) = 2\pi\tau \int_r^{r+\Delta r} r' \cdot [I(z,r') - I(z+\Delta z, r')]dr' \quad (1)$$

The function $I(z,r)$ represents the intensity at each point in the material, given by the below equations in the cases of 1PA, 2PA, and 3PA.

$$I(z,r) = I_0(r)\cdot\begin{cases} e^{-\alpha z} & \text{for 1PA} \\ (1+\beta\cdot I_0(r)\cdot z)^{-1} & \text{for 2PA} \\ (1+2\gamma\cdot I_0^2(r)\cdot z)^{-1/2} & \text{for 3PA} \end{cases} \quad (2)$$

To obtain local temperature increase ΔT, we equated the energy absorbed to heat energy as given by $Q = c\rho V\Delta T$ where $V = \pi\Delta z\Delta r[2r+\Delta r]$ is the volume of each annular cylindrical region. Therefore, the local temperature increase is given by:

$$\Delta T(z,\Delta z, r, \Delta r) = \frac{E_{abs}(z,\Delta z, r, \Delta r)}{c\rho\Delta z\Delta r[2r+\Delta r]} \quad (3)$$

Using Equation (3), we generated plots of the temperature distributions induced by 1PA, 2PA, and 3PA respectively. These plots are shown in **Fig. 1** of the main paper.

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Symbol	*Definition*	*Value*	*Reference*
ρ	Density of polyimide	1.42 g cm^{-3}	[1]
c	Specific heat capacity of polyimide	1.09 J g^{-1} K^{-1}	[2]
T_{decomp}	Decomposition temperature of polyimide	550C	[2]
α	1PA absorption coefficient of polyimide at $\lambda = 355$ nm	1.3×10^4 cm^{-1}	[3]
β	2PA absorption coefficient of ZnO at $\lambda \sim 550$–750 nm	$\sim$1 cmGW	[4]
γ	3PA absorption coefficient of ZnO at $\lambda \sim 850$–950 nm	$\sim10^{-3}$ cm^3/GW^2	[4]
τ	Duration of pulse, square envelope	50 fs	chosen
ω_0	Radius of beam waist	1.5 µm	chosen
E_{pulse}	Pulse energies used in each case (1PA, 2PA, 3PA)	42, 31, 2.5 nJ	chosen

TABLE I. Summary of simulated polymer and laser parameters used in calculation. 'Chosen' denotes parameters that were selected to model typical values in experiment.

II. BLISTER RUPTURE AT HIGH PULSE ENERGIES

In blister fabrication experiments, excessive pulse energies result in mechanical failure of the film. This is caused by excessive laser penetration into the film and/or pressure built up beneath the film. AFM data of ruptured blisters in a 1.3 µm polyimide film are shown in **Figure 1**. Between 215 nJ and 360 nJ of pulse energy, blisters were no longer left intact; rupture was seen as infrequent cracking and reduction in blister height. At higher energies, blisters show consistent cracking and in extreme cases, partial removal of the film. As seen in Fig. 4 of the main paper, blisters made with large pulse energies show slight asymmetry from the outer low-intensity portions of the pulse profile.

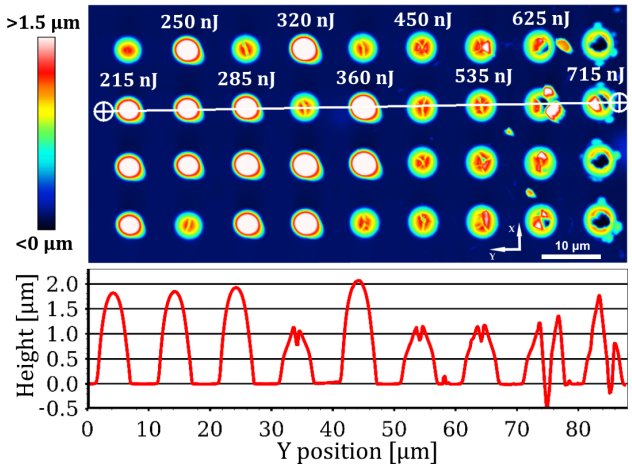

FIG. 1. (color online) An AFM image of blisters fabricated in 1.3 µm polyimide using a 0.4 NA objective with excessive pulse energies. The AFM line profile displayed (bottom) corresponds to the cross-section denoted by the black line in the 2D image. From 215 nJ to 360 nJ, structures show occasional cracking and diminished height. As pulse energy is increased further, blisters show consistent cracking of material, and then material removal.