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Electronic Supplementary Information

Direct laser write process for 3D conductive graphite circuits in polyimide

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S1 Beam Profiling

To determine the minimum spot size of the beam (ω_0) a wafer of crystalline silicon was ablated at different pulse energies following the technique outlined in reference [1]. This technique expresses the spatial energy distribution of a Gaussian beam as

$$E(r) = E_0 \exp(-r^2/w_0^2). \tag{1}$$

$$r^2 = w_0^2(\ln E_0 - \ln E(r)) \tag{2}$$

Here r is the measured beam radius and E_0 is the peak fluence at the center of the beam. This equation can then be rewritten as (2). From this it is clear that the minimum spot size may be found by measuring the slope of a semi-log plot of beam radius squared versus E_0. The beam radius was measured from the ablation spots in the silicon wafer, which are shown in Fig. S1 (a)-(h). In Fig. S1 (i) the experimental data is fit to equation (2), which returns a minimum spot size of 2.5 μm for the beam.

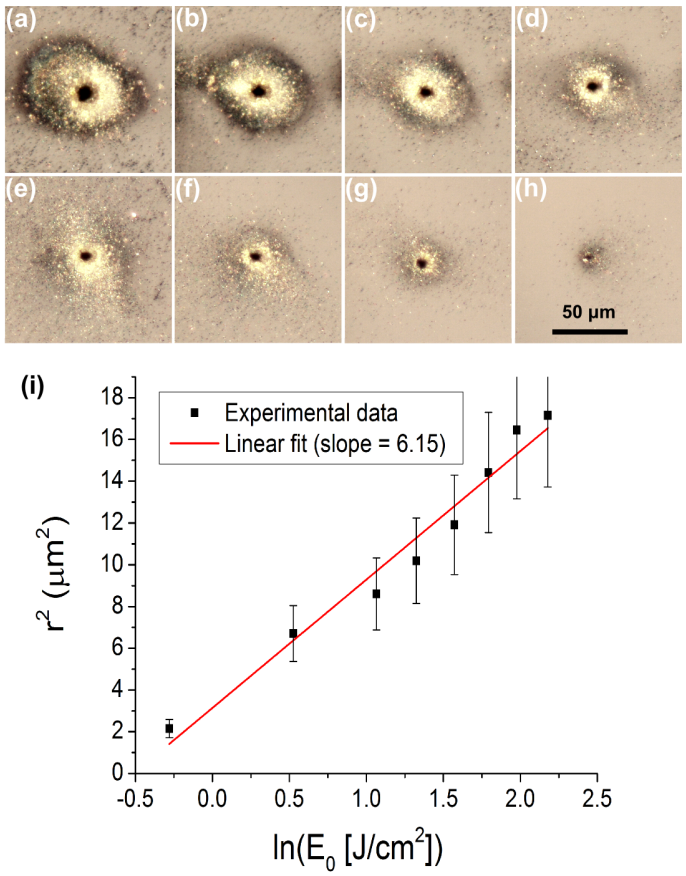

Fig. S1: Microscope images of the ablation of a silicon wafer at pulse energies of (a) 2.22 μJ, (b) 1.82 μJ, (c) 1.51 μJ, (d) 1.21 μJ, (e) 0.95 μJ, (f) 0.73 μJ, (g) 0.43 μJ, (h) 0.19 μJ. (i) a semi-log plot of the squared ablation radius versus E_0.

S2 Absorption spectroscopy

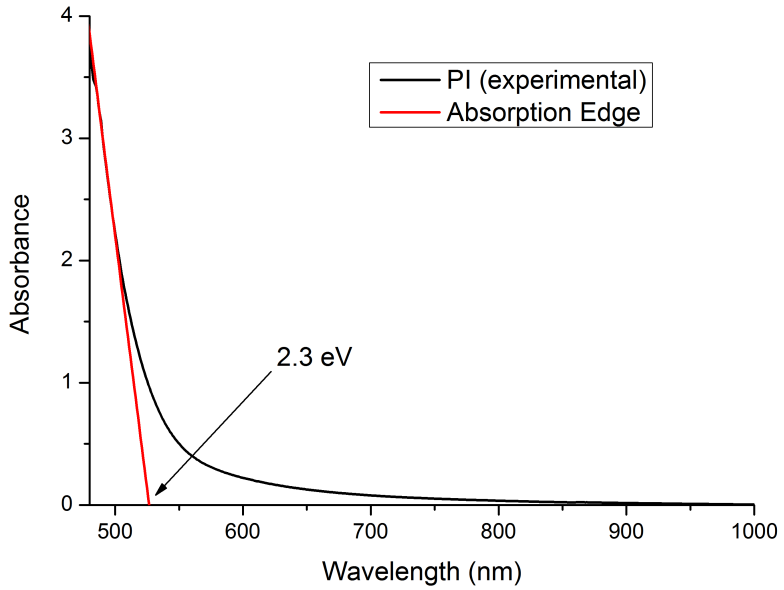

Fig. S2: The absorbance of PI measured on a PerkinElmer Lambda 1050 UV/Vis/NIR Spectrophotometer. The absorption edge was determined to be 2.3 eV.

S3 Pulse energy dependence

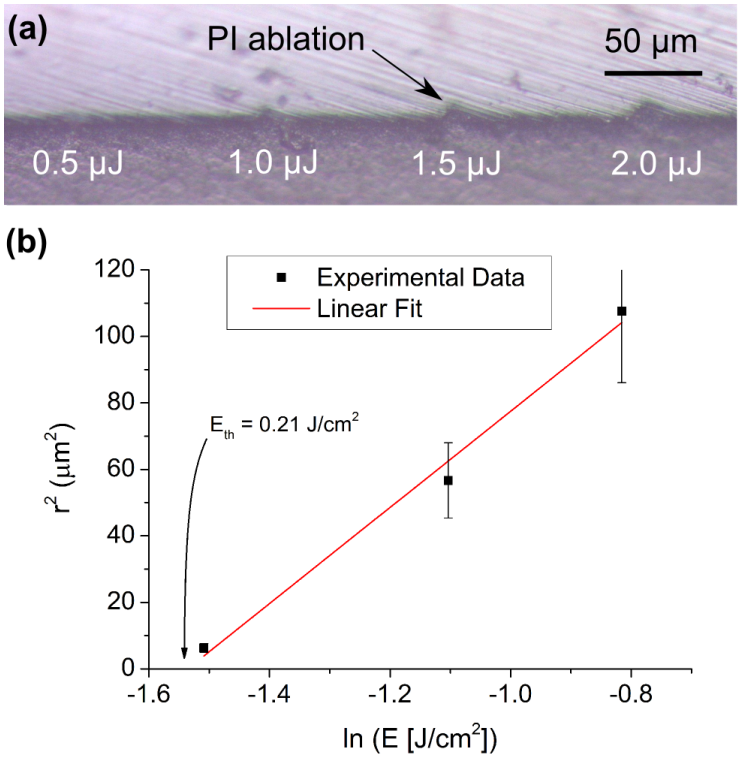

Fig. S3: The pulse energy dependence for ablation of a PI film during DLW at a focus depth of 50 μm below the surface and a scan speed of 10 pulses/μm. Figure (a) illustrates the surface ablation in the sample cross-section at various pulse energies. In (b) the measured ablation area is plotted as a function of laser fluence. The ablation threshold for the PI film is determined from the X-intercept of a linear fit to this data, which corresponds to a 0.95 μJ pulse energy under these conditions.

S4 Pulse length dependence

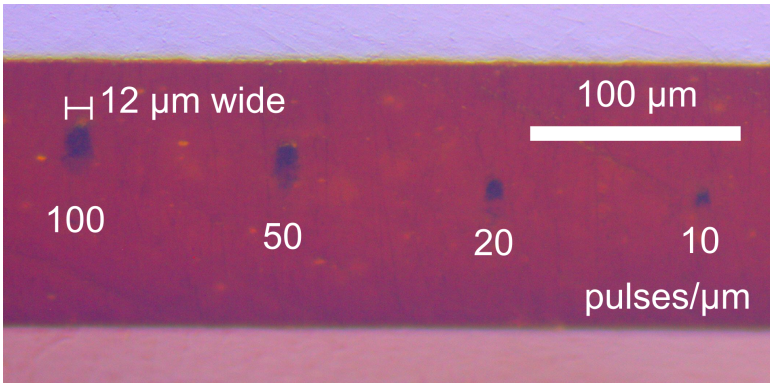

Fig. S4: A microscope image of a cross-sectioned PI film after laser modification at a focal depth of 40 μm using 1.5 ps pulses and several scan speeds.

S5 Mathematical foundation for the thermal model

The temperature rise inside of PI due to the non-linear absorption of femtosecond laser radiation was solved using the three-dimensional heat diffusion equation with a source, which is presented in (3). Here D is the heat diffusivity of the PI, ρ is the density, and C_p is the heat capacity.

$$\frac{\partial T(x,y,z,t)}{\partial t} = D\nabla^2 T(x,y,z,t) + \frac{Q(x,y,z,t)}{\rho C_p} \tag{3}$$

$$Q(x,y,z,t) = Q_0 \exp\left(\frac{-(x-vt)^2 - y^2}{\omega_0^2} + \frac{-z^2}{\omega_z}\right) \sum_{n=1}^{N} \delta(t - n/f) \tag{4}$$

$$Q_0 = \frac{E\alpha}{\omega_0^2 \omega_z \pi^{3/2}} \tag{5}$$

Q(x,y,z,t) represents the laser heat source [2], which has been expressed in (4). The variable v represents the speed of the laser scan, f the number of pulses per second, and N the number of pulses simulated. The constant Q_0 is the peak power of the beam at the center, which has been solved for in (5) by integrating (4) over all space and equating it to the pulse energy (E) multiplied by the non-linear absorbency of the sample (α). The length of the pulses are considered to be infinitely small compared to the time-scale for heat diffusion, therefore the time dependant arrival of the pulses is represented using the Dirac delta function, δ.

$$\omega_z \simeq z\left(\left[\frac{\tan(\sin^{-1}(\mathrm{NA}/n_1))}{\tan(\sin^{-1}(\mathrm{NA}/n_2))}\right] - 1\right) \tag{6}$$

Variables ω_0 and ω_z represent the size of the beam focus perpendicular and parallel to the beam direction, respectively. In this model the stretching of the focus due to spherical aberrations was accounted for by calculating the refraction of the marginal rays at the air/PI interface [3], as shown in (6). In this equation NA is the numerical aperture of the focusing lens, z is the nominal focusing depth, n_1 is the refractive index of the initial medium (air), and n_2 is the refractive index of the new medium (PI).

The equation in (3) was solved using the Green's function method [4]. The boundary condition for the problem is that we assume the initial temperature of the sample to be uniform and equal to the room temperature, $T(x,y,z,0) = T_0$. The advantage of the Green's function method is that the formula can

be broken down and solved for each dimension independently first, then combined:

$$G(x,y,z,t|x',y',z',t') = G_x(x,t|x',t')G_y(y,t|y',t')G_z(z,t|z',t'). \tag{7}$$

$$\frac{\partial T(x,t)}{\partial t} = D\nabla^2 T(x,t) \tag{8}$$

$$T(x,t) = \frac{T_0}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} \exp\left(\frac{-(x-x')^2}{4Dt}\right) \mathrm{d}x' \tag{9}$$

To begin, one must first solve a homogeneous heat diffusion equation in one-dimension [4], as illustrated in (8). The solution to this differential equation is (9).

$$G(x,t|x',t') = \frac{1}{\sqrt{4\pi D(t-t')}} \exp\left(\frac{-(x-x')^2}{4D(t-t')}\right) \tag{10}$$

$$\begin{aligned} T(x,y,z,t) = &\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} G(x,y,z,t|x',y',z',t')T_0 \,\mathrm{d}x' \,\mathrm{d}y' \,\mathrm{d}z' + \\ &\frac{1}{\rho C_p}\int_0^t \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} G(x,y,z,t|x',y',z',t')Q(x',y',z',t') \,\mathrm{d}x' \,\mathrm{d}y' \,\mathrm{d}z' \,\mathrm{d}t' \\ &= T_0 + \sum_{n=1}^{N} \frac{E\alpha}{\rho C_p \pi^{3/2}(\omega_0^2 + 4D(t-n/f))\sqrt{\omega_z^2 + 4D(t-n/f)}} \\ &\qquad \exp\left(\frac{-(x-tv)^2 - y^2}{\omega_0^2 + 4D(t-n/f)} - \frac{z^2}{\omega_z^2 + 4D(t-n/f)}\right) \end{aligned} \tag{11}$$

Comparing (9) to the definition for the Green's function, one can determine the one-dimensional Green's function (10). Using this same format for the y and z components and substituting them into (7), the final solution to (3) can be expressed as (11).

The constants used to solve (11) for the bulk irradiation of PI are summarized in Tab. S1.

Tab. S1: Constants used to solve the heat diffusion model in PI.

Variable	Value	Source
v	10 and 5 mm/s	set in stage
f	10 000 Hz	set in laser source
E	0.5 μJ	set using optical attenuator
T_0	300 K	room temperature
α	0.57 ± 0.06	measured during DLW
ρ	1420 kg/m^3	taken from DuPont^{TM} Kapton® HN Technical Data Sheet [5]
C_p	1090 J/kg K	taken from DuPont^{TM} Kapton® HN Technical Data Sheet [5]
D	7.75E-7 m^2/s	taken from DuPont^{TM} Kapton® HN Technical Data Sheet [5]
ω_0	2.5 μm	measured through beam profiling
ω_z	50 μm	calculated using (6) and confirmed experimentally in Fig.1
n_1	1.0	refractive index of air
n_2	1.7	taken from DuPont^{TM} Kapton® HN Technical Data Sheet [5]

S6 Via IV measurements

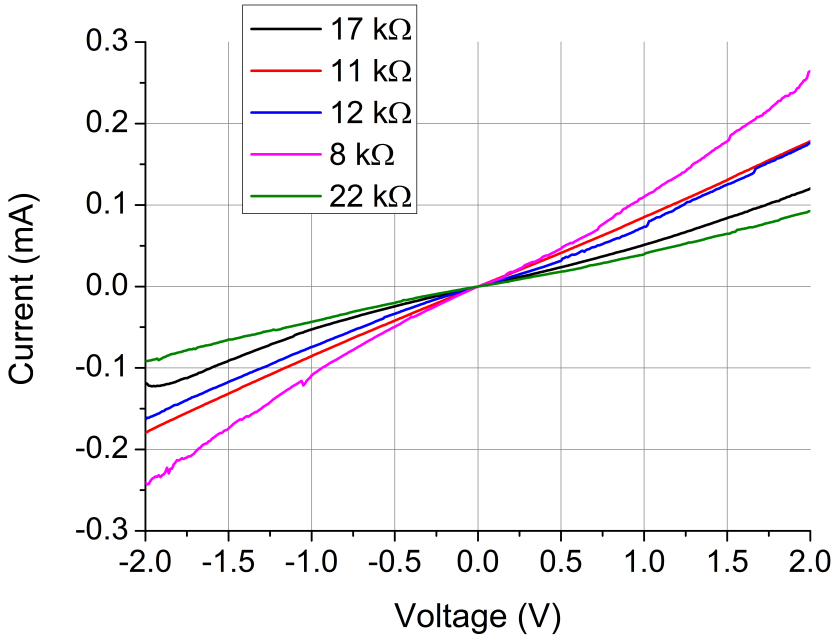

Fig. S5: The IV curves for 5 vias fabricated at 10000 pulses/μm.

S7 Electrical turn-on procedure

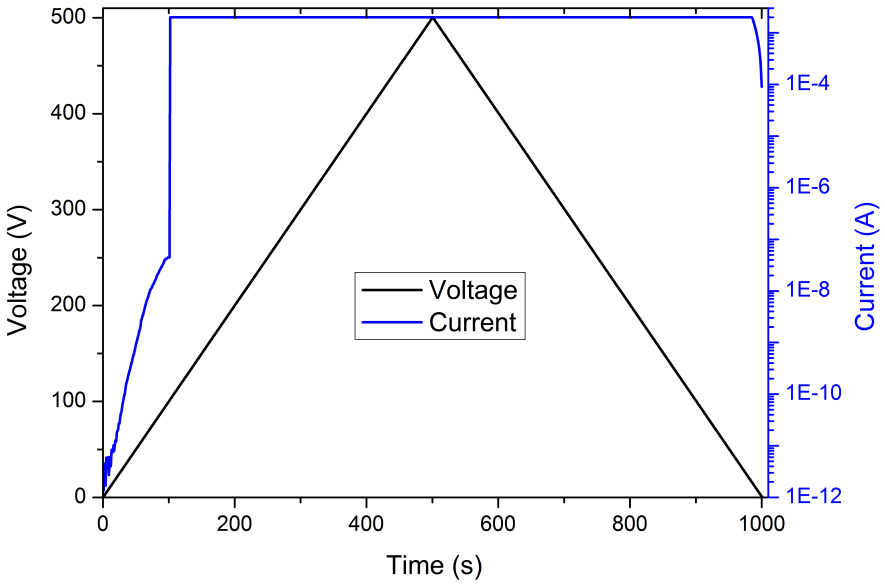

Fig. S6: The turn on of a single DLW via written at 10000 pulses/μm using a 0–500–0 V sweep. A compliance value of 2 mA is used.

S8 Electrical stability measurements

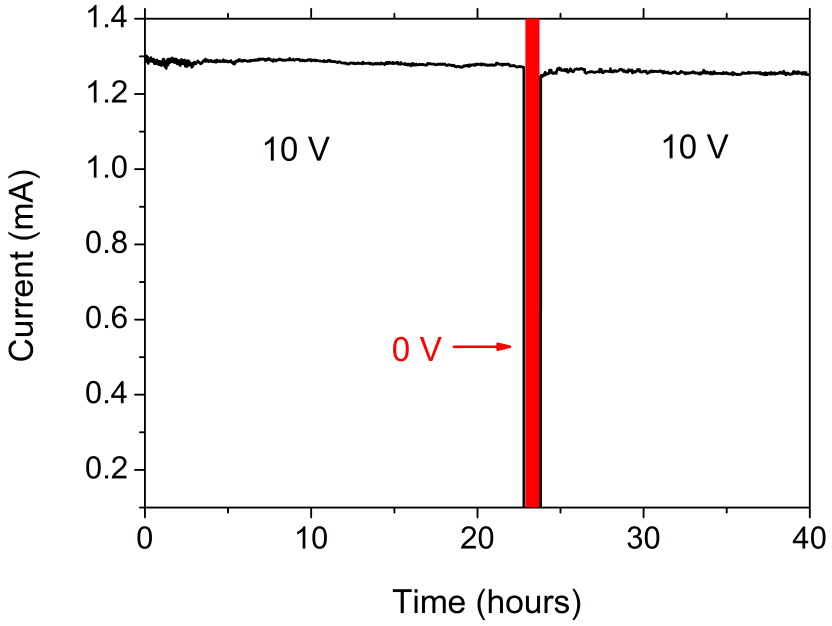

Fig. S7: The current stability of a single DLW via over time and without applied bias. The average current loss was 0.06%/hour.

References

[1] Liu, M. J. (1982) *Opt. Lett.* **7(5)**, 196–198.

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