Temporal Airy pulses for controlled high aspect ratio nanomachining of dielectrics: supplementary material

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1. Rate equations

We simulate the temporal laser intensity-dependent $I(t)$ excitation and recombination dynamics in the direction of laser propagation (z -axis) via the following rate equations:

$$\begin{aligned} \frac{\partial N_{CB}(t)}{\partial t} &= \left(\frac{N_{VB}(t)}{N_{tot}} \right) \cdot (\sigma_{VB} \cdot I(t)^6 + \alpha_{VB} \cdot N_{CB}(t_{ret-9}) \cdot I(t)) + \left(\frac{N_{TB}(t)}{N_{tot}} \right) \cdot (\sigma_{TB} \cdot I(t)^4 + \alpha_{TB} \cdot N_{CB}(t_{ret-5}) \cdot I(t)) - \frac{N_{CB}(t)}{t_T} \\ \frac{\partial N_{TB}(t)}{\partial t} &= \left(\frac{N_{TB}(t)}{N_{tot}} \right) \cdot (\sigma_{TB} \cdot I(t)^4 + \alpha_{TB} \cdot N_{CB}(t_{ret-5}) \cdot I(t)) + \frac{N_{CB}(t)}{t_T} \end{aligned} \quad (S1)$$

Where $N_{CB}(t)$, $N_{VB}(t)$, $N_{TB}(t)$, N_{tot} are the time-dependent electron density in the conduction, valence, trapping band and the total (excitable) valence electron density; σ_{VB} , σ_{TB} (α_{VB} , α_{TB}) are the multiphoton (avalanche) coefficients for excitation from the valence band and trapping band into the conduction band, respectively; $t_T = 150$ fs is the trapping time in fused silica [1] and $t_{ret-k} = t - k \cdot \tau_{s,fix}$ is the retarded time [2],[3] for avalanche ionization with $k = 1.5 \times E_{gap}/E_{ph}$ corresponding to the number of required photons with an energy of E_{ph} for impact ionization [4],[5] and $\tau_{s,fix} = 1$ fs is a fixed electron scattering time used to calculate the retarded time [6]. This takes into account that a conduction band electron requires a finite time to reach the critical energy for impact ionization [5],[3] due to several single photon absorption and scattering events. Relaxation processes from the trapping to the valence band take place on a much longer timescale of a few hundreds of picoseconds [7],[8] and are thus neglected.

As we concentrate our studies to an excitation regime, where tunnel ionization has only a minor contribution, it is not included in our simulations. Furthermore the ponderomotive force, which causes an increase in bandgap and photonicity, is also neglected in our model.

2. Intensity evolution of the laser pulse

$I_{in}(t, r, z)$ is the time- and radial-dependent intensity that penetrates into the material and is calculated by

$$\begin{aligned} I_{in}(t, r, z) &= (1 - R(t, r)) \cdot I_0(t, r) \cdot \exp \left[-4 \ln 2 \cdot \left(\frac{t}{\Delta t} \right)^2 \right] \\ &\cdot \left(\frac{w_0}{w(z)} \right)^2 \cdot \exp \left[-2 \cdot \left(\frac{r}{w(z)} \right)^2 \right] \end{aligned} \quad (S2)$$

I_0 is the incident intensity at material's surface, where absorption in air for bandwidth-limited pulses is already subtracted. Absorption in air is calculated in the same way as the absorption inside the sample, however the excitation modelling is based on

results from Liu et al. [9]. $w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_0}\right)^2}$ is the beam radius at a distance z to the beam waist w_0 (measured to be $1 \mu\text{m}$) and $z_0 = \sqrt{\frac{\pi w_0^2}{\lambda}}$ is the Rayleigh length.

The reflection coefficient $R(t, r)$

$$R(t, r) = \left| \frac{n_{\text{air}} - \tilde{n}_{\text{exc}}}{n_{\text{air}} + \tilde{n}_{\text{exc}}} \right|^2 = \left| \frac{1 - \tilde{n}_{\text{exc}}}{1 + \tilde{n}_{\text{exc}}} \right|^2 \quad (\text{S3})$$

was calculated using the Fresnel equations at normal incidence in combination with the Drude model. The refractive index of air is $n_{\text{air}} = 1$ and the complex refractive index $\tilde{n}_{\text{exc}}$ of the excited fused silica sample is defined in equation (S5). For bandwidth limited laser pulses, however, the refractive index of air is also affected by the excitation above the sample, leading to an electron density dependent expression, as in the case of fused silica. The depth-dependent laser intensity is calculated by the following differential equation in propagation direction [10]:

$$\frac{\partial I(t, z)}{\partial z} = -6 \cdot \hbar \omega \cdot \sigma_{\text{VB}} I(t, z)^6 - 4 \cdot \hbar \omega \cdot \sigma_{\text{TB}} I(t, z)^4 - \alpha' \cdot I(t, z) \quad (\text{S4})$$

The first two summands (absorption due to multiphoton ionization) are neglected as it is small in comparison to free carrier absorption in the case of the shaped laser pulses. The second term describes the Beer-Lambert absorption where $\alpha' = \frac{2\omega}{c} \cdot \text{Im} \tilde{n}$ is

the absorption coefficient and $\text{Im} \tilde{n}$ the imaginary part of the complex refractive index. The complex refractive index in turn, changes as the material gets excited $\tilde{n} \rightarrow \tilde{n}_{\text{exc}}$ due to the decreasing valence band electrons. This is described by the dielectric function $\mathcal{E}(\omega)$ of the excited material [11] for the laser angular frequency ω based on the Drude-Model:

$$\mathcal{E}(\omega) = 1 + \frac{3(N_{\text{tot}} - N_{\text{CB}})\beta_{\text{CM}}}{3 - (N_{\text{tot}} - N_{\text{CB}})\beta_{\text{CM}}} - \frac{\omega_{\text{pl}}^2}{\omega^2 + i\omega/\tau_s} = \tilde{n}_{\text{exc}}^2 \quad (\text{S5})$$

The first two terms describe the contribution of the valence band electrons to the dielectric function, where β_{CM} is the Clausius-Mossotti parameter [11] chosen such that the refractive index of the unexcited material is $n = \sqrt{\mathcal{E}(\omega)}$ for $N_{\text{VB}} = N_{\text{tot}}$. The third term accounts for the change of the optical properties by the free

electrons via the plasma frequency $\omega_{\text{pl}} = \sqrt{\frac{e^2 N_{\text{CB}}}{m_e \epsilon_0}}$ with e and m_e as the electron charge and its corresponding effective conduction band mass, ϵ_0 is the vacuum permittivity. Scattering time calculation for τ_s were performed similar to Jiang and Tsai [12],[10]. A constant term for electron-phonon ($\tau_{\text{e-p}} = 1 \text{ fs}$) scattering and an electron density-dependent contribution $\tau_{\text{e-CB}}(N_{\text{CB}})$ with $\tau^* = 1 \text{ fs}$ [13] and was employed:

$$\tau_s = \left(\frac{1}{\tau_{\text{e-p}}} + \frac{1}{\tau_{\text{e-CB}}(N_{\text{CB}})} \right)^{-1} = \left(\frac{1}{\tau_{\text{e-p}}} + \frac{1}{\tau^* \cdot \frac{N_{\text{crit}}}{N_{\text{CB}}}} \right)^{-1} \quad (\text{S6})$$

Parameters for beam waist and pulse duration are taken from experimental data.

3. Determination of the parameters for simulation

One set of parameters for excitation coefficients of MPI σ and AI α for excitation from the valence ($\sigma_{\text{VB}} / \alpha_{\text{VB}}$) and trapping band ($\sigma_{\text{TB}} / \alpha_{\text{TB}}$) into the conduction band was extracted from the measured data. To that end, the parameters for all pulse shapes were fitted such that the simulated threshold energies matched the measured ones most closely (Table S1).

Table S1: Threshold values for material ablation (experiment, simulation and quotient), calculated Keldysh parameter γ [11],[15] for the peak intensity at $2.5 \times E_{\text{thr, simu}}$ and the fraction of the intensity for which $\gamma > 1$ (MPI is dominant) for each pulse shape. The last two columns indicate the fractional energy contribution for excitation from valence to conduction band (VB $\rightarrow$ CB) and trapping to conduction band (TB $\rightarrow$ CB) with respect to the whole excitation energy, respectively. BWL = bandwidth-limited, TOD = third order dispersion, GDD = second order dispersion.

pulse shape	E_{thr} [nJ]	$E_{\text{thr, simu}}$ [nJ]	$\gamma @$ $2.5 \times E_{\text{thr, simu}}$	fraction MPI regime ($\gamma > 1$) @ $E_{\text{thr, simu}}$	fraction VB $\rightarrow$ CB @ $E_{\text{thr, simu}}$	fraction TB $\rightarrow$ CB @ $E_{\text{thr, simu}}$
BWL	40	46	0.75	75%	>99%	<1%
TOD $\varphi_3 = +1 \times 10^5 \text{ fs}^3$	80	62	0.91	65%	76%	24%
TOD $\varphi_3 = +3 \times 10^5 \text{ fs}^3$	90	81	1.09	100%	58%	42%
TOD $\varphi_3 = +6 \times 10^5 \text{ fs}^3$	100	100	1.21	100%	48%	52%
GDD $\varphi_2 = +1.5 \times 10^4 \text{ fs}^2$	155	178	2.16	100%	64%	36%

Table S2: Listing of simulation parameters, which are used for numerical simulations of SiO₂. VB = valence band, CB = conduction band, TB = trapping band.

description	symbol	value	reference
refractive index in SiO ₂ @ 785 nm	n	1.4536	[16]
refractive index in air @ 785 nm	n_{air}	1	
nonlinear refractive index	n_2	$3.54 \times 10^{-16} \frac{\text{cm}^2}{\text{W}}$	[17]
central laser wavelength	λ	785 nm	
reduced electron mass in material	$0.86 m_e$	$7.83407 \times 10^{-31} \text{ kg}$	[18]
electron scattering time coefficient	τ^*	1 fs	[13]
fixed electron scattering time	$\tau_{s,\text{fix}}$	1 fs	[6]
band gap SiO ₂ (VB → CB)	$E_{\text{gap,VB}}$	9 eV	[19]
band gap SiO ₂ (TB → CB)	$E_{\text{gap,TB}}$	5.2 eV	[19]
band gap air	$E_{\text{gap,air}}$	14.6 eV	[9]
trapping time	t_T	150 fs	[1]
total (excitable) valence band electron density in SiO ₂	N_{tot}	$2.2 \times 10^{22} \frac{1}{\text{cm}^3}$	[20]
coefficient for multiphoton ionization with 6 photons from VB → CB	σ_{VB}	$1 \times 10^{-49} \frac{\text{cm}^9}{\text{W}^6 \text{s}}$	
coefficient for multiphoton ionization with 4 photons from TB → CB	σ_{TB}	$4 \times 10^{-21} \frac{\text{cm}^5}{\text{W}^4 \text{s}}$	
coefficient for AI with $k=9$ photons	α_{VB}	$2.5 \frac{\text{cm}^2}{\text{Ws}}$	best fit for different pulse shapes (this work)
coefficient for AI with $k=5$ photons	α_{TB}	$160 \frac{\text{cm}^2}{\text{Ws}}$	
critical energy deposition for ablation	W_{cr}	$1.4 \frac{\text{kJ}}{\text{cm}^3}$	

We used a critical energy density deposition of ($W_{\text{cr}} = 1.4 \text{ kJ/cm}^3$) into the material as an ablation criterion.

This value takes into account the accumulated energy which is deposited into the material due to the excitation of electrons from the valence and trapping band into the conduction band via the different excitation mechanisms (MPI and AI), respectively [14]. The energy density deposition value in our model is equivalent to the commonly used criterion in which the conduction band electron density $N_{\text{CB}}(t)$ exceeds a value of 10^{21} cm^{-3} . All parameters used are summarized in Table S2.

4. Discussion of nonlinear propagation effects

Nonlinear propagation effects like plasma defocusing are neglected as well as self-focusing and filamentation, as the longest temporal Airy pulses with third order dispersion of $\phi_3 = +6 \times 10^5 \text{ fs}^3$ used have a power of only $P = 0.131 \text{ MW}$ for the main pulse at $2.5 \times E_{\text{thr}}$, which is one order of magnitude below the critical power for self-focusing (see Table S3).

The critical power P_{cr} for self-focusing of Gaussian beams is given by [22]:

$$P_{\text{cr}} \equiv 3.77 \frac{\lambda^2}{8\pi n n_2} \quad (\text{S7})$$

Where n is the linear and n_2 is the nonlinear index of refraction for fused silica. Values for n_2 are reported to be in the range from 2×10^{-16} to $3.54 \times 10^{-16} \text{ cm}^2/\text{W}$ [23],[20],[17],[24].

For a wavelength λ of 785 nm and the largest value for n_2 of $3.54 \times 10^{-16} \text{ cm}^2/\text{W}$ we obtain a critical power for self-focusing of

about $P_{\text{cr}} = 1.8 \text{ MW}$ and $P_{\text{nl}} = \frac{\pi^2}{4} P_{\text{cr}} = 4.4 \text{ MW}$ (according to

Couairon and Bergé [21]) as the lower limit. The power for the bandwidth-limited pulse at $2.5 \times E_{\text{thr}}$ is about $P = 3.2 \text{ MW}$ (for experimental value) and $P = 3.7 \text{ MW}$ (for simulation), respectively.

Table S3: Calculated ratio of pulse power to critical power for self-focusing and filamentation, respectively of different pulse shapes and intensities. The critical P_{fil} power for filamentation is calculated by $P_{\text{fil}} = \frac{\pi^2}{4} P_{\text{cr}} = 4.4 \text{ MW}$ according to Couairon and Bergé [21]. For temporal Airy pulses, only the contributions of the main pulse (energy E_{main} and power P_{main}) to P_{cr} and P_{fil} are considered and listed below. I_{main} corresponds to the peak intensity of the main pulse. BWL = bandwidth-limited, TOD = third order dispersion, GDD = second order dispersion.

pulse shape	threshold factor	pulse duration [fs]	pulse duration [fs] (main pulse)	energy E_{main} [nJ] (simulated)	P_{main} [MW] (main pulse)	I_{main} [TW/m ²] (main pulse)	$\frac{P_{\text{main}}}{P_{\text{cr}}}$ (main pulse)	$\frac{P_{\text{main}}}{P_{\text{fil}}}$ (main pulse)
BWL	1	30	30	46	1.472	98	0.82	0.33
	2.5	30	30	115	3.680	244	2.05	0.83
	5.4	30	30	250	8.000	531	4.45	1.80
TOD $\varphi_3 = +6 \times 10^5 \text{ fs}^3$	1	1539	221	12	0.053	26	0.03	0.01
	2.5	1539	221	30	0.131	64	0.07	0.03
TOD $\varphi_3 = +3 \times 10^5 \text{ fs}^3$	1	770	88	15	0.163	32	0.09	0.04
	2.5	770	88	37	0.409	79	0.23	0.09
TOD $\varphi_3 = +1 \times 10^5 \text{ fs}^3$	1	260	63	21	0.319	44	0.18	0.07
	2.5	260	63	52	0.797	111	0.44	0.18
GDD $\varphi_2 = +1.5 \times 10^4 \text{ fs}^2$	1	1387	1387	178	0.123	8	0.07	0.03
	2.5	1387	1387	445	0.308	20	0.17	0.07

Even at an applied pulse energy of 250 nJ, where the incoming power of $P = 8 \text{ MW}$ exceeds the critical power for filamentation by a factor of approx. 2 (see Table S3), no filament-like structures

could be observed by applying bandwidth-limited pulses (compare Figure 2).

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