Supporting Information

The thin films have been deposited by electron beam deposition technique using the Bühler SYRUSpro 710 technique at a pressure within 8.10^{-6} mbar. Bulk targets made of Sb_2Te_3 and SiO_2 were used as raw materials for the evaporation. Deposition parameters (current and e-beam pattern) were optimized in order to achieve constant deposition rate of 0.5±0.1 nm s^{-1}. The layer thickness was then controlled using a quartz crystal microbalance. A repeatability on the thickness of ±0.2 nm was obtained.

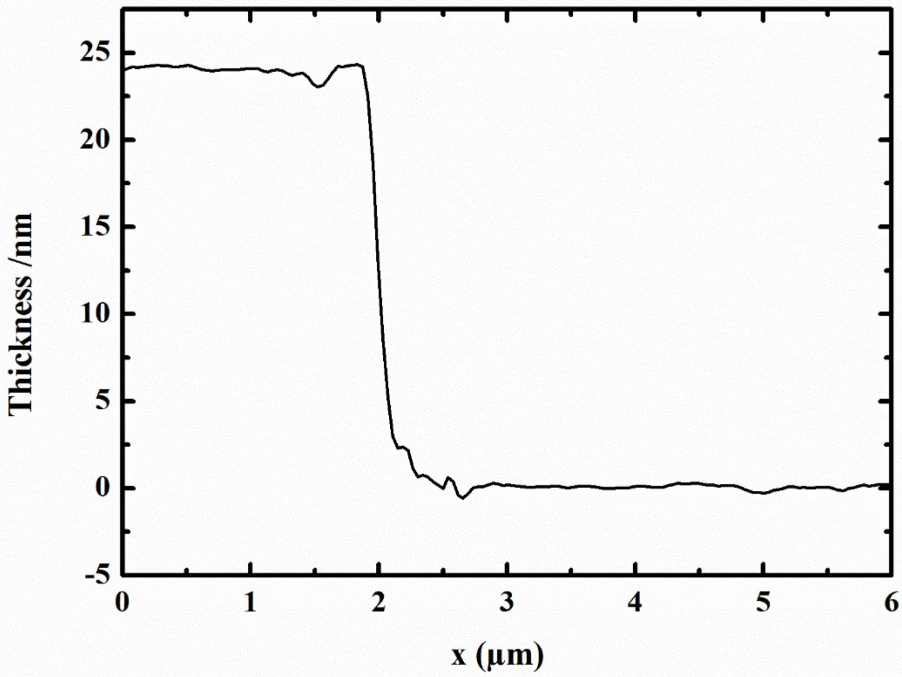

Figure S1 Profilometric study performed by Atomic Force Microscopy, which allowed the determination of the thin film thicknesses.

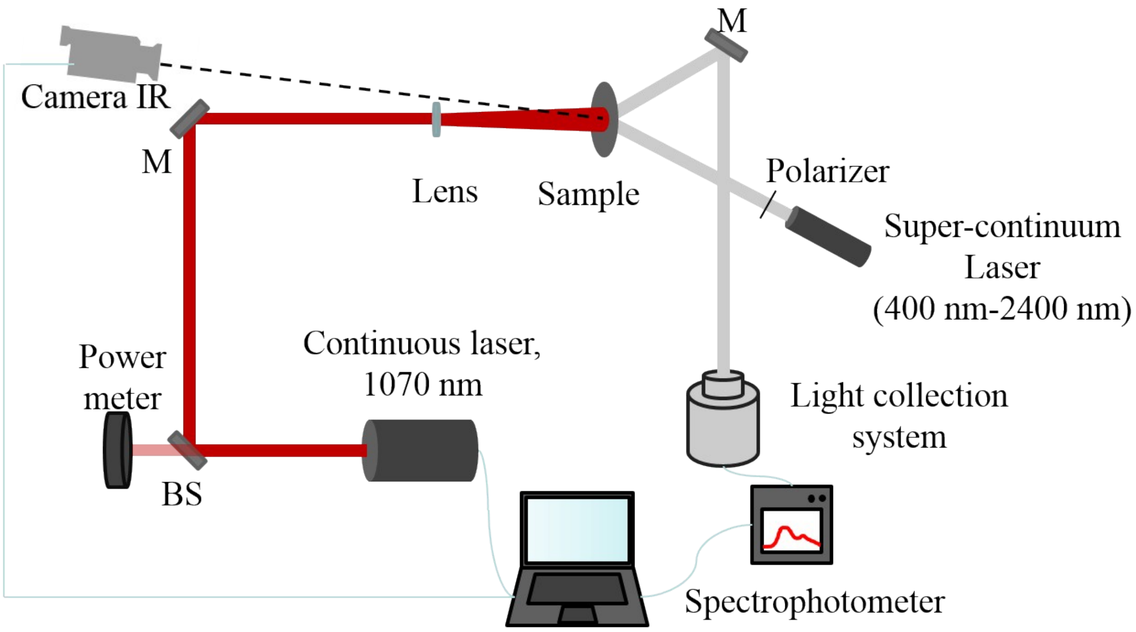

Figure S2: Laser annealing setup (BS: Beam Splitter, M: Mirror).

The laser annealing has been performed by means of a pump-probe setup. Briefly, a continuous ytterbium fiber laser system emitting at 1070 nm has been employed. The laser beam power has been 2.9 W, while the beam diameter has been adjusted to be 1 cm at the sample position, by means of a beam expander. At the same time, a supercontinuum laser, emitting in the 400 nm- 2400 nm range has been irradiating the sample, while the reflected beam has been detected by means of an integrating sphere and a spectrometer. To avoid any interaction between the supercontinuum laser beam and the chalcogenide layers a low power (70 mW) has been used and a mechanical shutter allowed to acquire one spectrum every minute, with a 150 ms integration time. Moreover, in order to precisely monitor the sample temperature, an infrared camera, operating at 7.5–14 μm has been employed, using a 0.4 emissivity.

During the annealing procedure the sample has been firstly heated up to 350°C, with approximately 0.2°C s^{-1} ramp. Then the annealing continued at this maximum temperature for 4 hours. Finally, the thin film layer has been let to cool down to room temperature. During the whole procedure the reflectivity has been recorded between 500 and 1000 nm.

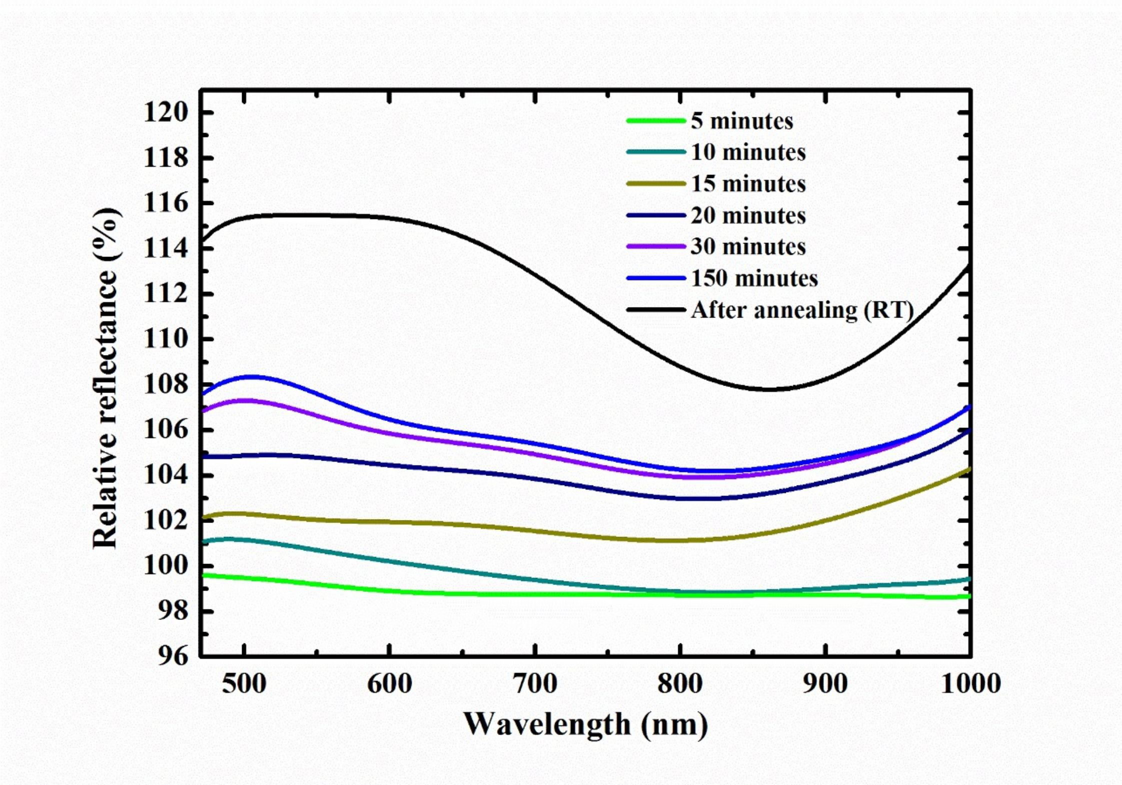

Figure S3: Representative relative reflectance spectra recorded during the laser annealing process. The black curve shows the relative reflectance after the annealing procedure, in room temperature.

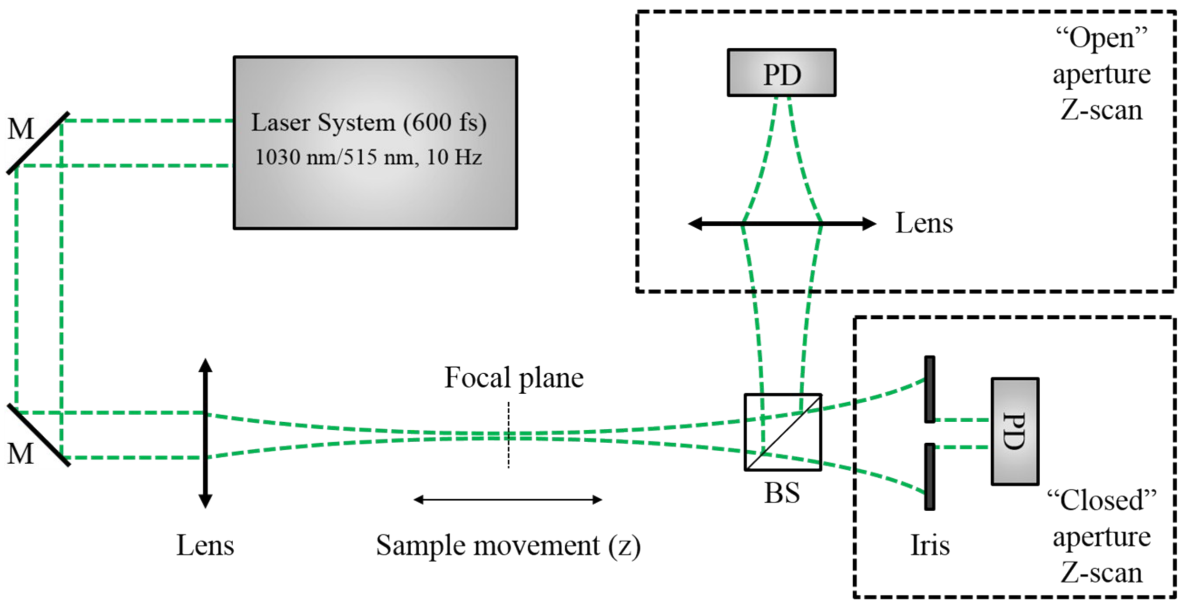

Figure S4: Z-scan experimental setup (M: Mirror, BS: Beam splitter, PD: Photodiodes)

The nonlinear optical response of the Sb_2Te_3 films has been studied by means of the Z-scan technique, employing 600 fs duration pulses at 1030 nm, with a repetition rate of 10 Hz. Studies have been also performed at 515 nm by frequency doubling of the fundamental laser wavelength. The Z-scan technique is well known for the possibility to provide the nonlinear refraction and nonlinear absorption of materials. This simultaneous measurement is done by the "closed aperture" and the "open aperture" Z-scans experimental arms. Briefly, the nonlinear absorption coefficient (β) has been obtained by means of the following equation:

$$T = \frac{1}{\sqrt{\pi}\left(\frac{\beta I_0 L_{eff}}{1 + z^2/{z_0}^2}\right)} \int_{-\infty}^{\infty} \ln\left[1 + \frac{\beta I_0 L_{eff}}{1 + z^2/z_0^2} \exp(-t^2)\right] dt$$

where I_0 is the on-axis irradiance at the focus, L_{eff} is defined as $L_{eff}=(1-\exp(-\alpha_0 L))/\alpha_0$ and α_0 is the linear absorption coefficient of the sample (at 1030 nm and at 515 nm respectively). With β known, the imaginary part of the third order nonlinear susceptibility is determined by means of the following equation:

$$Im\,\chi^{(3)}(esu) = \frac{10^{-7} c^2 n_0^2}{96\,\pi^2 \omega} \beta(cm\,W^{-1})$$

where c is the speed of light in cm s^{-1}, n_0 is the linear refractive index and ω is the fundamental frequency in cycles per sec.

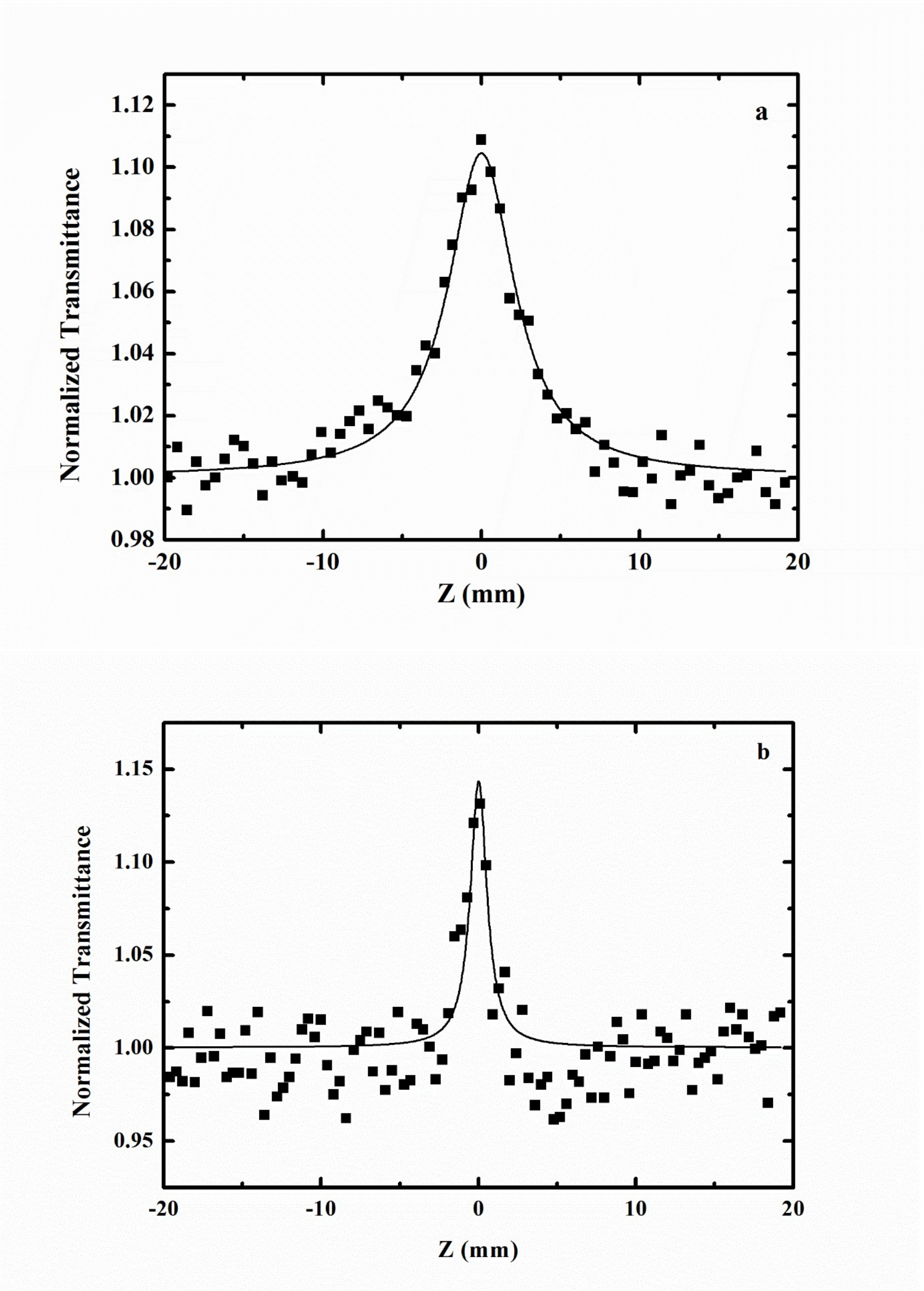

Figure S5: Representative "Open-aperture" Z-scan curves obtained for the laser annealed samples using 600 fs laser pulses at a) 1030 nm, I=2.4 GW cm^{-2} b) 515 nm, I=2.2 GW cm^{-2}

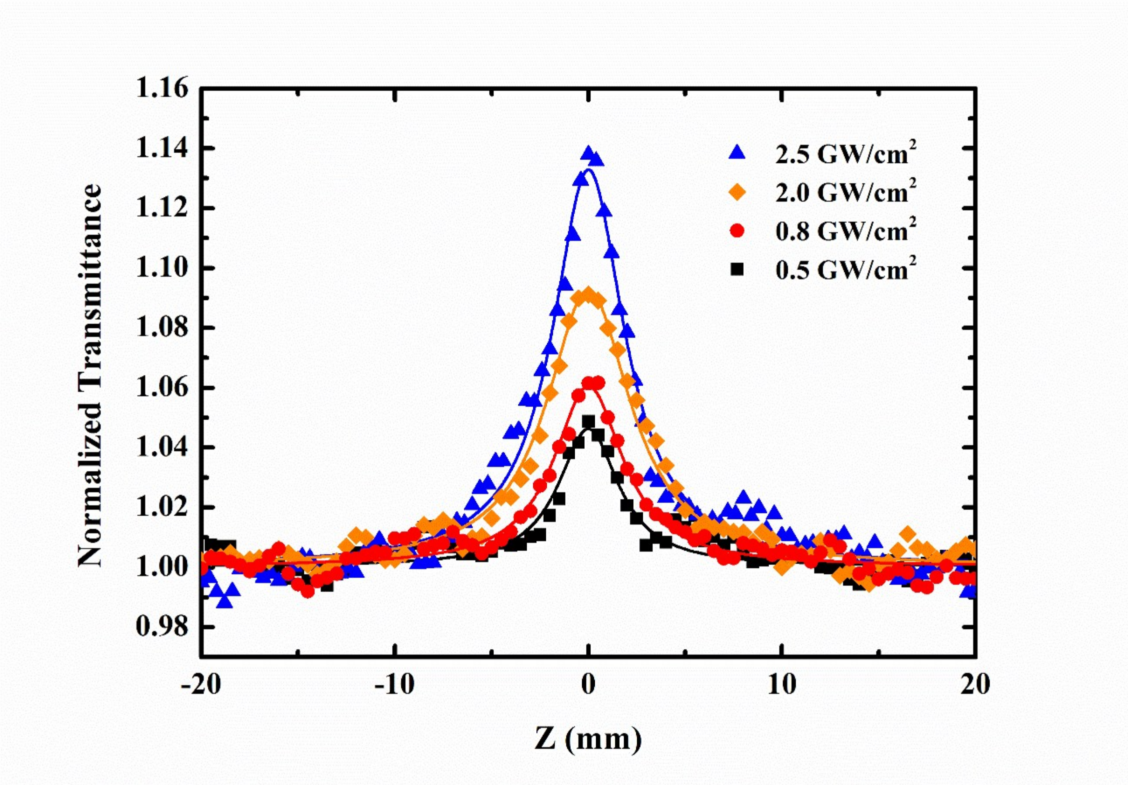

Figure S6: Representative "Open-aperture" Z-scan curves obtained with different laser intensities at 1030 nm, 600 fs for an oven annealed sample.

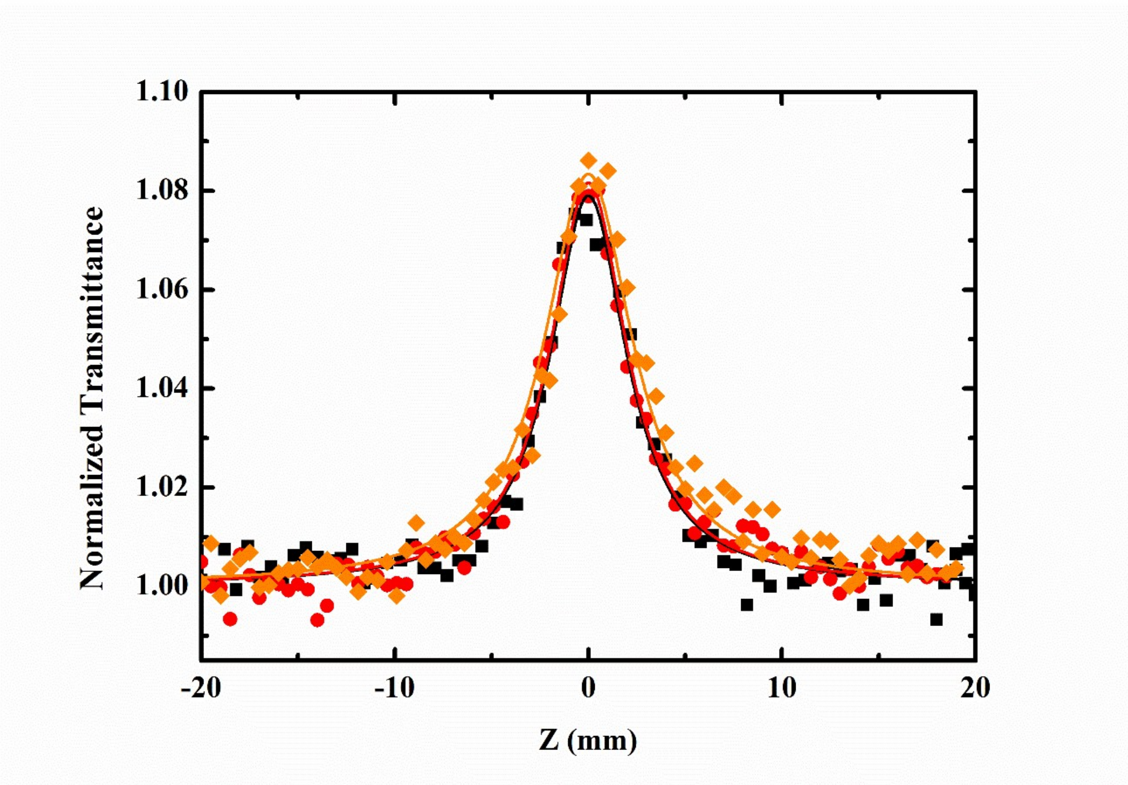

Figure S7: Representative "Open-aperture" Z-scan curves obtained with the same laser intensity (I=2 GW/cm^2, 1030 nm, 600 fs) at different areas of an oven annealed thin film.