Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Mid-infrared spectroscopy beyond the diffraction limit via direct measurement of photothermal effect

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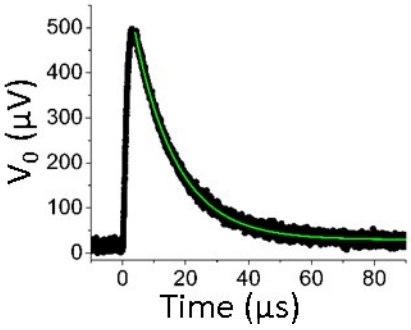

Fig. S1:
STIRM signal (black) obtained on a PMMA domain of *sample-2* (300 nm thick, which is also depicted in Fig. 2 of the main text) illuminated at 1720 cm^{-1}. The exponential fit (green) yields a characteristic relaxation time of ≈ 13 μs, an order of magnitude slower than that calculated for this thin film. The temporal response is thus probe-limited in this case. In general, for samples with relaxation times longer than the probe the temporal evolution of the photothermal signal can be used to obtain the sample thermal diffusivity and potentially its thermal conductivity also (see Fig. 1c and associated discussion).

Thickness (nm)	t_{relax} (μs)	κ ($Wm^{-1}K^{-1}$)
1620	25.5	0.167
1800	32.5	0.162
2780	78.4	0.161
3130	99.2	0.162

Table ST1:
Nominal t_{relax} and κ extracted from measurements on Sample-1. Row 1 corresponds to fig. 1c.

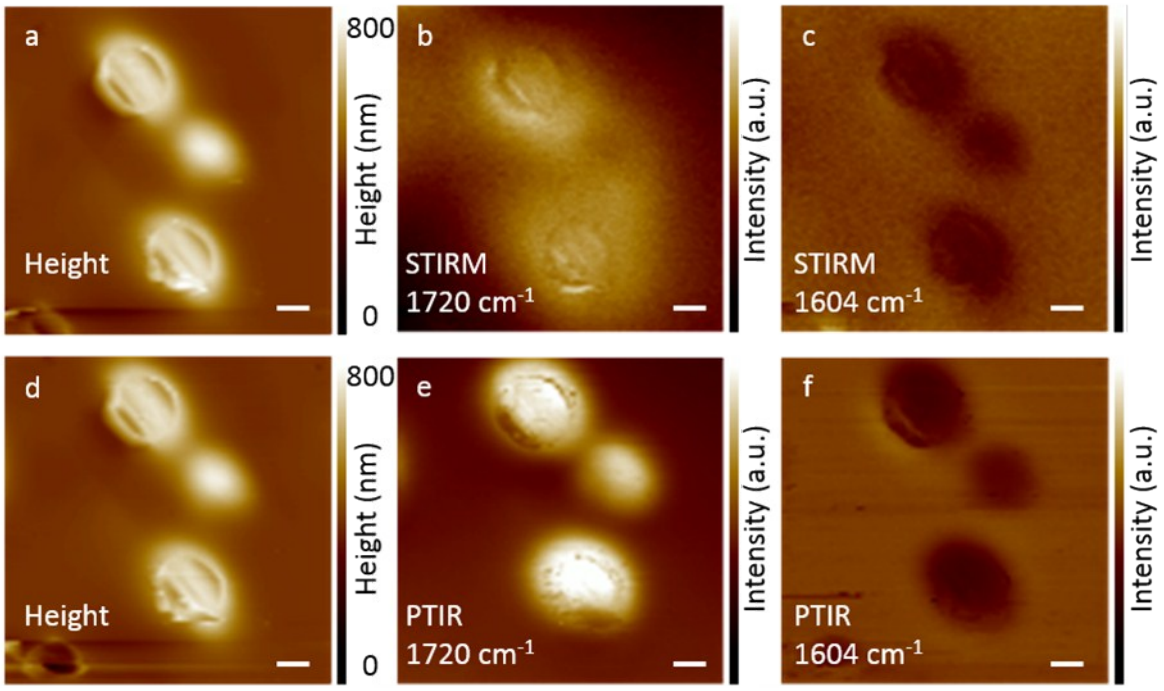

Fig. S2:
Topography (a) and STIRM images corresponding to PMMA (b) and epoxy (c) absorption frequencies for *sample-3* (on a different location with respect to figure 2 of the main text). Topography (d) and PTIR images corresponding to PMMA (e) and epoxy (f) absorption frequencies for *sample-3*. Images were obtained by averaging the signal for 64 laser pulses per pixel. Pixels are 100 nm x 100 nm. Scale bars are 1 μm.

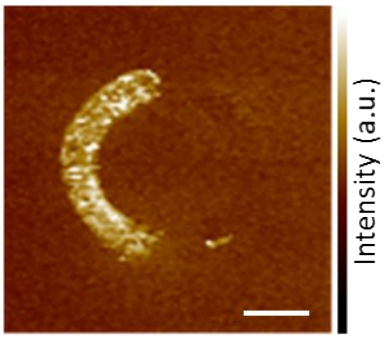

Fig. S3:
PTIR image recorded at 1300 cm^{-1} (7.69 μm) for the ASRR shown in Figure 3 of the main text. The signal distribution is clearly different than that observed by STIRM. Compare with figure 3d of the main text recorded at the same frequency (wavelength). Scale bar is 500 nm. Pixel size is 25 nm x 25 nm. Each pixel corresponds to the average signal generated for 64 laser pulses.