Electronic Supplementary Material (ESI) for Analyst.

Supporting Information S1

Single point illumination (SPI) experiment

Results of single point illumination (SPI) experiment on Si wafer and porous PMMA film are given in the figure S1 and S2 respectively. Raman image of the Si wafer thus obtained shows only a single glowing pixel, indicating that the Raman signal is collected only by the fiber corresponding to the illuminated pixel (yellow colored pixel; S1). No cross-talk is observed. However, SPI Raman image of PMMA film shows considerable cross-talk between focal points; not only the center fiber but the neighboring fibers also receive scattering signal (Figure S2). We have also checked the variation of this cross-talk at different depth of the film. In all the images cross-talk reduces to nearly zero at a distance of approximately 5 µm from the center pixel (dashed yellow square). Hence the optimum distance between focal points in the multifocal Raman microscope should be 5 µm for partially transparent (soft) samples. However for studying opaque (hard) solid surfaces like Si wafer one can still retain close-spacing (1 µm) between focal points. Thus the microscope is 441 times faster on opaque surfaces and 36 times faster on transparent samples. We have also tested a 10X10 configuration by using a different DOE that splits laser line into 10X10 beams such that on the focal plane focal points are separated by approximately 5 µm. In this configuration the microscope becomes 100 times faster than the conventional single point mapping.

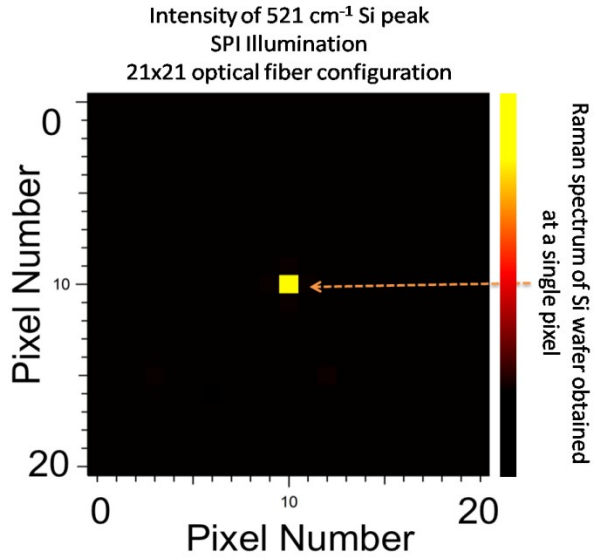

Figure S1. Raman image of Si wafer obtained in SPI imaging. The yellow pixel has the largest intensity of 521 cm^{-1} Si peak.

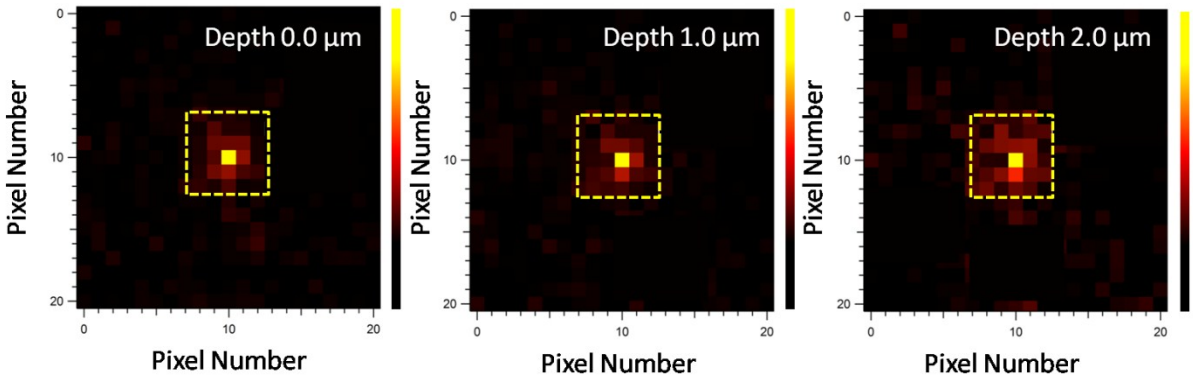

Figure S2. Raman image of porous PMMA film obtained in SPI imaging. The yellow pixel has the largest intensity of 810 cm^{-1} PMMA peak. Considerable intensity is also noticed in the neighboring pixels (cross-talk). The yellow square indicate 5 µm distance from the center pixel. Even at a depth of 2µm from the surface only <5% intensity (relative to the center pixel) is noticed in the pixels at 5 µm distance.

Supporting Information S2

Converting 21X21 into 6X6 multifocal configuration: Interpolation and Tiling

A cross-talk between focal points was noticed in the 21X21 multifocus configuration. Hence this configuration was changed to a 6X6 configuration by applying a mask in front of DOE (Figure S3). The distance between foci in this new configuration is ~5 µm. Since there is a gap between focal points, in order to gather full information from the spatial region sample is scanned with 2D multifocal array. The number of sampling points between two adjacent focal points is called interpolation. During 5X5 interpolation this 2D array moves at steps of ~1 µm, 5X5 times in the *x y* directions; each time recording Raman spectra from all the illuminated regions. That is for each *y*-interpolation there are 5 *x*-interpolations.

A large-area scan is performed by splitting the area of interest into smaller regions (called tiles) and by imaging each region (tile) individually in succession by moving the sample under microscope (Figure S5). Desired interpolation could be applied while imaging each tile. These individual tiles are later stitched together with a software program. Using a 6X6 focal point 2D array, with 6X6 interpolation and 20 sec multifocal exposure time a single Raman image (or single tile of ~33x33 μm^2 area) takes approximately 15 minutes. An image acquisition with 3X3 tiling, 6X6 interpolation (~100x100 μm^2 area) using the 6X6 multifocus configuration takes ~

130 minutes (with 20 sec exposure time). A single point mapping experiment with the same exposure time (per point) would typically take ~2 days to finish the same image (under similar experimental conditions).

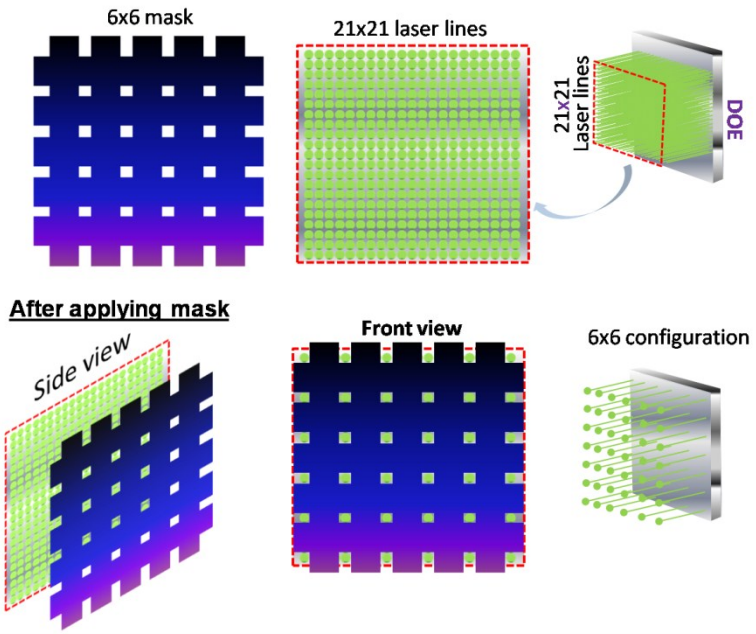

Figure S3. Masking to convert 21X21 configuration into 6X6 configuration.

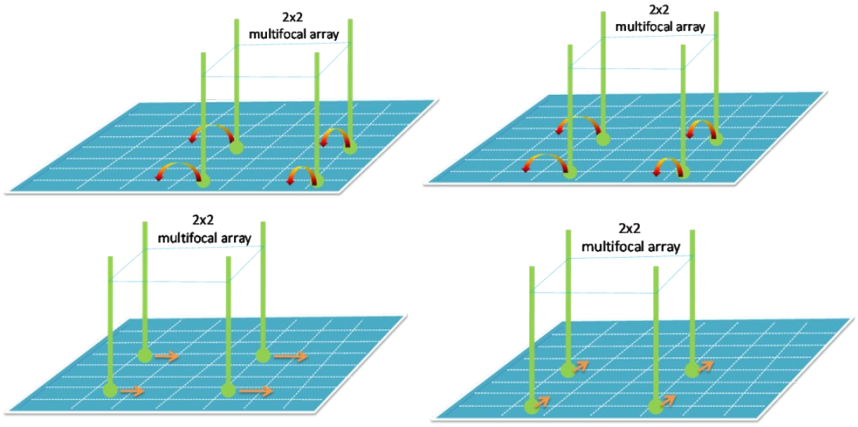

Figure S4. The figure explains interpolation technique used for imaging. The spatial region of interest is scanned stepwise with the focal point array (2X2 multifocal array in the picture). The figure illustrates 2X2 interpolation.

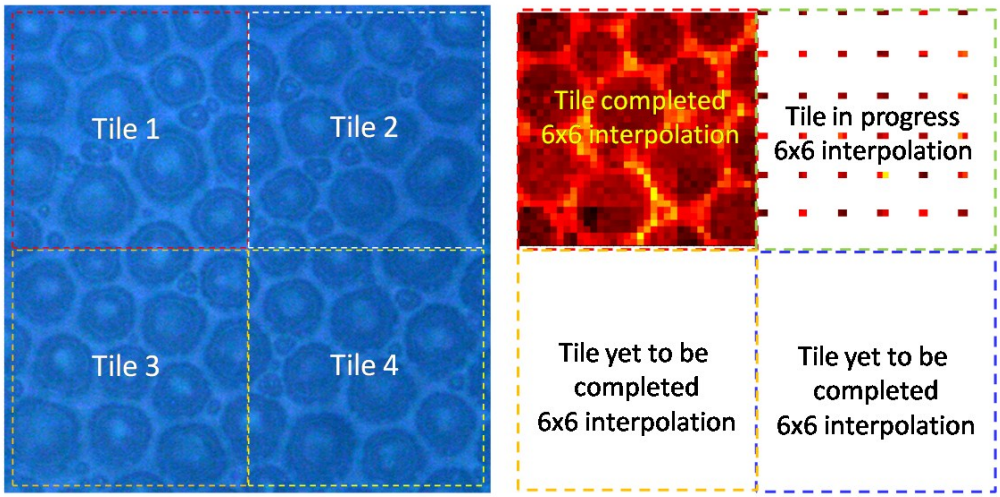

Figure S5. The figure explains *interpolation+tiling* technique used for imaging. The area of interest is split into tiles. Each tile is scanned separately with desired interpolation. The white light image on the left hand side shows a region of porous polymer film. This was split into 4 tiles. On the right hand side corresponding Raman image is shown, where the first tile is completed and the second tile imaging is in progress. The imaging finishes when all the tiles are completed.

Supporting Information S3

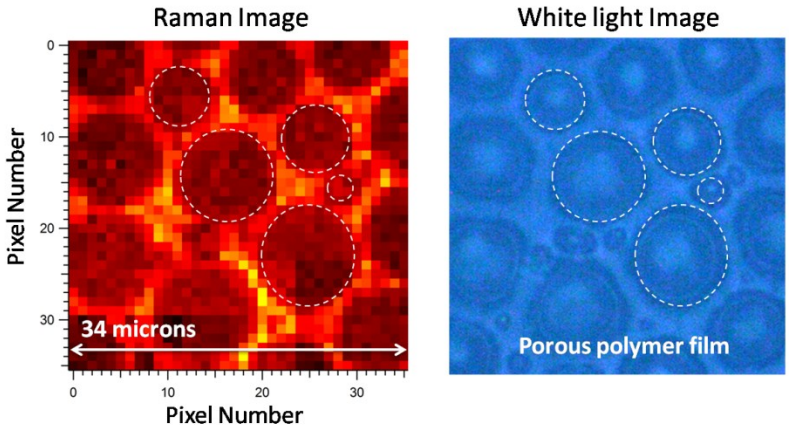

Figure S6. Comparison of the Raman image (with 6X6 configuration) and the corresponding white light image of the porous PMMA film. The porous regions are highlighted using white circles. The Raman image shows smaller intensity for 810 cm^{-1} PMMA peak in the pores (contrast). It is clear from the comparison that the spatial specificity is maintained during the imaging.

Supporting Information S4

Variation of morphology with depth

Raman imaging studies show that these smaller pores are not connected to the larger pores on the surface. The shape of the larger pores on the surface differs from the usual cup-shaped morphology (curved inner surface) of pores commonly observed in porous polymer films. This conclusion is based on the pore sizes observed at different depths. If the pores were cup-shaped, the pore size should reduce at different depths. But instead no change in pore size is seen at different depths. Hence, these pores are like holes punched on thin film and disappear abruptly at a distance (Figure S7 & S8). The immediate layer has smaller pores with diameter close to 2 µm. Highly porous interconnected morphology is observed in the deeper regions of the thin film.

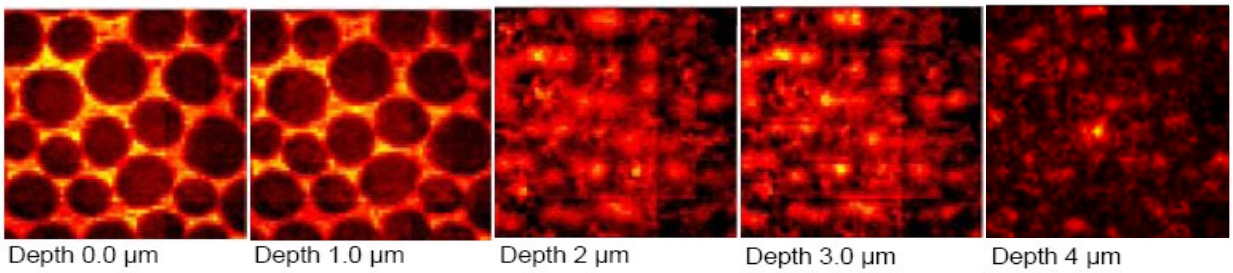

Figure S7. The Raman images obtained at different depths from the top surface. The larger pores abruptly end at a distance of 3 microns. This indicates absence of curved inner surface morphology (cup-shaped) of the porous features. Morphology abruptly changes to smaller pores at about 3 µm and then to highly porous inner bulk features at the deeper regions.

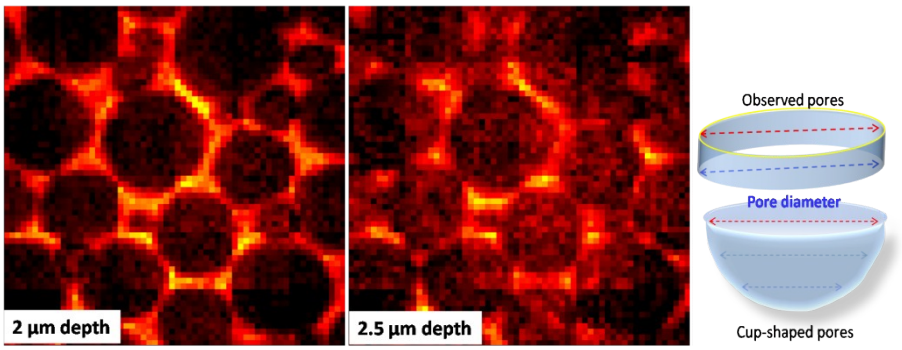

Figure S8. Raman images of porous PMMA film at different depths. The abrupt disappearance of larger pores is clear here. The pore size is not different at different depths, even prior to disappearance. A cartoon depiction of cup shaped and observed porous morphology is shown on the right hand side.

Supporting Information S5

The images obtained were processed using Matlab (Gaussian filtering). Images obtained before and after Gaussian filtering is shown in Figure S9.

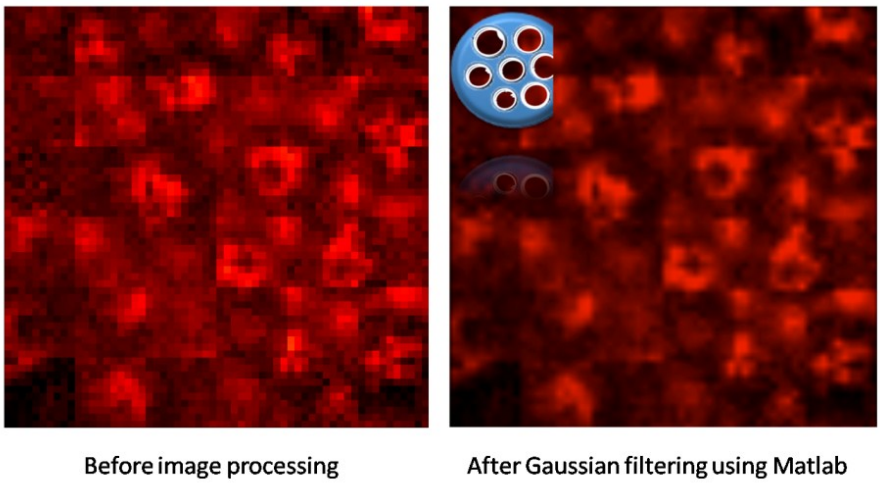

Figure S9. The Raman Images before and after image processing.