Supporting Information

Micro- and Nano-Patterning of Inorganic and Polymeric Substrates by Indentation Lithography

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Experimental

Preparation of Epoxy Substrates. We first exposed a polished surface of a Si(100) wafer to a vapor of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane in a vacuum desiccator for ~12 h to passivate the surface and to inhibit adhesion. We obtained epoxy (hard and brittle) substrates by puddle-casting a mixed and degassed epoxy prepolymer (Epo-Fix, Electron Microscopy Sciences) against the passivated silicon wafer. We cured the epoxy at 60 ºC for 2 h, and then detached the epoxy from the wafer using a razor blade.

Array of Pyramidal Indentations. We produced arrays of indentations on the 1-μm-thick silica film with a CSM Instruments Ultra Nanoindentation Tester (UNHT) equipped with a diamond Berkovich indenter. The UNHT measurement head was mounted on an Open Platform together with an integrated optical video microscope and an Atomic Force Microscope (AFM) system, thus allowing direct imaging of the indentation array. We patterned the substrates using an automated sample displacement stage to place indentations in a 5 × 5 array with uniform size and a 3 × 3 array with two levels of relief on the silica film. For the 5 × 5 array, the indentations were produced with a maximum applied load of 20 mN. For the 3 × 3 array, the large indentations were produced with a maximum applied load of 10 mN, and the small indentations were produced with a maximum applied load of 0.5 mN. The loading function for the

indentations consisted of a 5-second loading to peak force, followed by a 2-second hold, then by a 5-second unloading.

Fabrication of Channels. We used a CSM Instruments Nanoscratch Tester (NST) mounted on an Open Platform to write channels into the epoxy and silicon surfaces. The sample was mounted on a PI P-733.2 Piezo Nanopositioning Stage. The spherical diamond indenter had a tip radius of 1 μm and cone angle of 90 degrees. We applied a constant feedback-controlled load sufficient to scratch the epoxy surface (250 μN), and the *x* and *y* stages were displaced to replicate the desired pattern. The writing speed was 250 nm/s.

Fabrication of Split Rings. We used the same CSM Instruments NST system to produce an array of split rings. We patterned the substrates by applying a constant feedback-controlled applied load of 800 μN (silicon) and 180 μN (epoxy), while displacing the PI stage in the preprogrammed pattern. Patterns were then immediately imaged using a CSM Instruments AFM integrated on the same platform as the NST.

Generation of PDMS Stamps from Indented Substrates. We transferred patterns produced in SiO_2, silicon, and epoxy substrates by standard soft lithographic procedures. We cleaned the patterned silicon or SiO_2 substrates with a 5-min air plasma and passivated the surface by exposing it to a vapor of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane in a vacuum desiccator for ~12 h. We left the epoxy substrates untreated. To make an elastomeric

stamp, we mixed and degassed a PDMS prepolymer in a ratio of 10:1 of base to hardener (Sylgard 184), poured it over the patterned Si or epoxy template, and cured it at 60 °C for 2 h.

Template Stripping of Patterned Metal Films. The patterned structures on a SiO_2/Si(110) wafer were coated with the desired metal (silver or gold) using electron-beam evaporation with a base pressure of 2×10^{-6} torr and typical rates of deposition of 2-4 Å/second. We placed the substrate directly over the source of metal atoms to obtain uniform filling of the indentations and clean edges of the features. We stripped the metallic film from the substrate by placing a drop of UV-curable epoxy prepolymer (UVO-114) on the film, placing a 1-cm^2 glass slide on the prepolymer as a mechanical support, curing the prepolymer, and stripping off the three-component structure with a razor blade (Figure 1b). This action exposed the ultra-flat surface of the metallic film, as well as metallic features that were inverse replicas of the patterns of indentations.

AFM Images. We obtained AFM images using an Asylum MFP-3D (Asylum Research). The scanning was performed in tapping mode using a silicon tip (Veeco RTESPW). The cantilever spring constant was ~ 30 N/m and its resonant frequency was 260 kHz.

Confocal Raman Microscopy. We prepared the sample for SERS measurements by immersing it in a 1 mM 4-methylbenzenethiol (4-MBT) solution (98%, Sigma Aldrich) in ethanol (ACS grade, 99.98%, Pharmco-Aaper) at ambient conditions. After 2 h, we removed it

from the solution, rinsed it with excess ethanol (removing any 4-MBT not absorbed to the surface), and gently dried it with nitrogen. Confocal Raman scans were then performed on a Witec CRM300 system equipped with a HeNe laser (λ = 632.8 nm, 25 mW). The spectral range of the scan was between 0 and 4000 cm^{-1} with a resolution of 1 cm^{-1}. The spatial resolution of the confocal system was ~450 nm in the scanning plane and ~500 nm in the perpendicular direction.

Calculation of Enhancements Factors. We calculated enhancement factors (EFs) using the intense ring-breathing stretch at 1077 cm^{-1} from both liquid and surface-adsorbed 4-MBT and the equation:

$$EF = \frac{N_{vol} I_{surf}}{N_{surf} I_{vol}} \qquad \textbf{(1)}$$

where N_{vol} is the number of 4-MBT molecules contributing to the normal Raman scattering signal, N_{surf} is the number of 4-MBT molecules contributing to the SERS signal, and I_{surf} and I_{vol} are the intensities of the scattering band at1077 cm^{-1} in the SERS and normal Raman scattering spectra, respectively. Note that the silver film itself is an excellent SERS substrate; the EF of our flat Ag film was calculated to be around 10^5-10^6. The EF at the tip of a pyramid is on an order of 10^7-10^8.