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Design and Fabrication of High Enhancement Yet Wafer-Scale Uniform SERS/Plasmonic Structures Based on Nanoimprint Lithography and Self-Assembly

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Surface enhanced Raman spectroscopy (SERS) is of great significance in bio/chemical sensing. However, the two central challenges in SERS application are: low SERS enhancement and “a few random hot-spots” problem (a high enhancement is only at a few random spots). Here we present a new SERS architecture and a new nanofabrication method that have solved both problems and can significantly improve other plasmonic systems design, fabrication and performances.

The new SERS architecture has a 3D cavity nanoantenna array coupled with, through nanometer gaps, dense plasmonic nanodots (rather than just nanoparticle assembles) (Fig 1) [1]; and the new nanofabrication combines nanoimprint, guided self-assembly and self-alignment, and has fabricated the new architecture precisely, simply, cheaply and over large area (4” wafer).

A particular implementation of the new SERS architecture is termed “disk-coupled dots-on-pillar antenna array” (D2PA), (Fig. 1)[1]. The 3-D cavity antenna array consists of a periodic dielectric pillar array on a substrate with a metal disk on top of each pillar and a metal back-plane on the bottom side of the pillars (each disk is exactly aligned with a hole in the backplane, as discussed in fabrication). The disks and the backplane provide a vertical cavity for the light, while the periodic structure forms a lateral cavity. The dense metal nanodots are on each pillar sidewall with a small gap between the edge of the disk and the nanodots as well as between the neighboring nanodots.

In fabrication, the SiO_2 pillars (200 nm pitch and 70 nm) were patterned first on an entire 4” wafer by nanoimprint and RIE. Then a thin gold layer (~40 nm) was evaporated onto the wafer in a normal direction, which simultaneously depositing the gold on the pillar top, the backplane, and the pillar sidewall (Fig. 1 d-f). Guided by the SiO_2 pillars, the gold deposited on the pillar top and the pillar foot formed the disks and the backplane respectively, but on the pillar sidewall the gold self-assembled into nanodots with a small gap (<3 nm) in between and self-aligned precisely next to the metal disk (antenna) (Fig. 1).

High area-average SERS enhancements over 1.7×10^9 have been achieved (tested using BPE molecules) (Fig. 2). Even more importantly, the high SERS enhancements are uniform over the entire sample with a deviation of less than 22.4% (Fig. 3).

The new SERS design principle, architecture, and new fabrication method can be generalized to future design and fabrication of other SERS substrates and plasmonic systems, impacting applications in SERS and others (e.g. solar cells, LEDs, and fluorescence).

[1] Wendi Li and Stephen Chou, unpublished.

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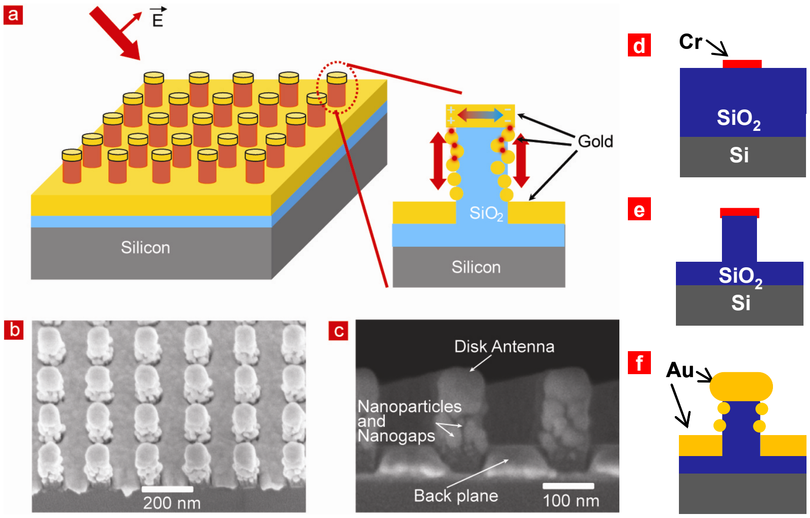

Fig. 1. **Disk-coupled dots-on-pillar antenna (D2PA) structure for surface enhanced Raman scattering**. **a**, Schematic; **b**, top-view scanning electron micrograph (SEM); and **c**, cross-sectional SEM of a D2PA structure, which consists of dense 3D cavity nanoantennas (a metal disk array and a metal backplane on the top and the foot of the SiO2 pillars respectively) coupled to, through nanogaps, dense plasmonic nanodots on the SiO2 pillars' sidewall inside the cavity. **d-f**, Schematic of fabcrication of a D2PA array through: **d**, Cr deposition on SiO2/Si; **e**, RIE etching SiO2 pillar; **f**, Cr etching and Au evaporationi.

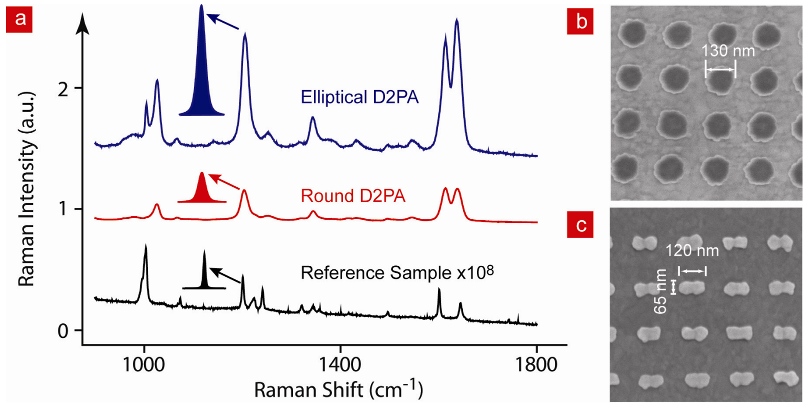

Fig. 2. **Experimental high area-average SERS enhancement factor for BPE.** **a**, Typical experimental Raman spectra on a D2PA substrate with round pillars (red) and elliptical pillars (blue), and on a reference flat substrate (black and its signal scaled up by 10^8), showing enhancement factors of 3.1×10^8 and 1.2×10^9 for D2PA substrates with the round and elliptical pillars respectively; **b** and **c**, top-view SEMs of the two different D2PA substrates.

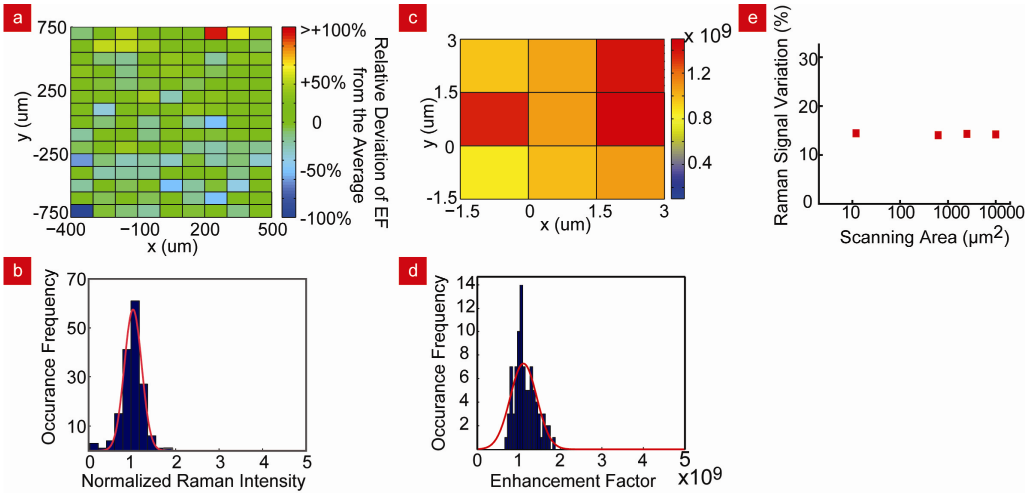

Fig. 3. **Experimental uniformity of high SERS over large area.** The mapping and the histogram of the SERS enhancements of: **a-b**, an optimized D2PA substrate of 1.6 mm by 1.0 mm area, showing an average SERS enhancement of 3.1×10^8 and a variation of 25%; and **c-d**, a special D2PA substrate (elliptical pillars) of multiple 4.5 μm by 4.5 μm pattern areas using a step size of 1.5 μm (hence 9 sampling points for a given area (**c**.)), but the histogram and enhancement variation calculation are based on the measurements of the 10 identical pattern areas (total 90 points) on the same sample (d.)), showing an average SERS enhancement of 1.2×10^9 and a variation of 22.4%. **e**. The variation of SERS enhancement versus excitation laser spot size on a D2PA substrate.