Experimental and Simulation Studies on Raman-Enhancing Surface Features from Process-Engineered Substrates

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Since its discovery in the 70s [1], surface-enhanced Raman scattering (SERS) has been extensively studied over 30 years, yet engineered nanostructures (made with design emphasis on electromagnetic enhancement, mainly employing nano-scale gaps) cannot outperform process- or assembly-based SERS substrates for practical purposes [2]. The absence of engineered nanostructures with superior enhancement indicates that it has not yet been sufficiently understood how electromagnetic enhancement functions to enhance Raman signals on process-engineered substrates.

In order to identify the geometrical configurations of surface features responsible for SERS, we have fabricated, tested, and compared four SERS substrates with distinctive topologies. Then we characterized (using AFM) and for the first time simulated the actual geometry of the substrate that showed the strongest enhancement. The tested substrates were (1) a rough substrate, named "H8"; (2) a rough substrate with sparse sharp peaks, named "A7"; (3) a substrate with highly ordered, densely packed nanoclusters, named "H3"; and (4) a substrate similar to (3) but with more closely packed nanoclusters, named "H5" (*Fig. 1*).

The fabrication was done on silicon wafers using thin film & atomic layer depositions and decoupled plasma-source etching in systematic manners, followed by evaporation of gold layers. For optical measurements, substrates were immersed in 25 μM 1, 2-bis (4 pyridyl) ethylene (BPE) methanol solution for 18 hours. The Raman signals were measured using an inverted confocal microscope (with a 100x, 0.95-NA objective lens), a 632.8-nm HeNe and, a liquid N_2-cooled CCD, and a 633 nm long-pass filter. Among all substrates tested, we found that the substrate H3 gave the strongest Raman enhancement - achieving nearly an order of magnitude improvement over the substrates H8 and A7 with good uniformity and consistency (<10% fluctuation) over a large area (*Fig. 2*).

While the confocal measurements demonstrate the overall performance of the substrates, the diffraction-limited spot size used for SERS measurements is much larger than typical feature sizes of our substrates. Hence, to identify the locations of strong near-field enhancement from nanoclusters on H3 at a sub-diffraction-limited resolution, we measured the surface profile of H3 using an AFM with a 2-nm spatial resolution [3] (*Fig. 3(a)*). The measured surface profile was directly imported into COMSOL (finite-element-based multiphysics software) and was meshed using the average Euler-Lagrange method (*Fig. 3(b)*). Then for the first time, we simulated the imported real surface profile as a solid gold structure (*Fig. 3(c)*). Our initial simulation results indicated strong polarization-dependent enhancement from the tips of the nanoclusters, rather than from the nano-scale gaps in the valleys (*Fig. 3(d-g)*).

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1. M. Fleischmann et al, "Raman spectra of pyridine adsorbed at a silver electrode," *Chem. Phys. Lett.,* vol. 26, pp. 163-166, 1974
2. E. C. Le Ru and P. G. Etchegoin, "Principles of Surface-Enhanced Raman Spectroscopy," Elsevier, 2009
3. J. Cejkova, et al, "Characterization of copper SERS-active substrates prepared by electrochemical deposition," *Applied Surface Science*, vol. 255, pp. 7864-7870, 2009

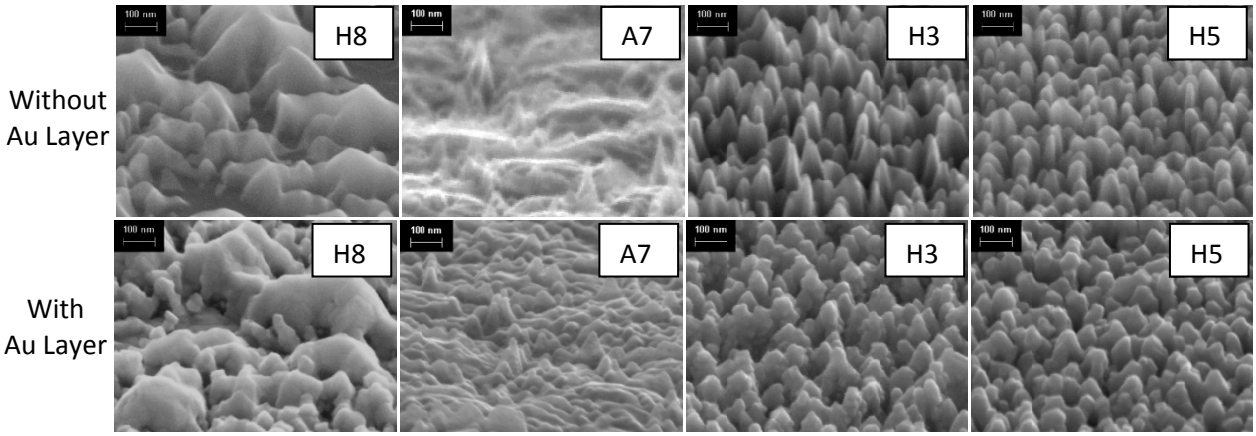

Fig 1: Side view SEM images at 40 degrees: nanofabricated substrates without Au (top) and with Au layer (all scale bars: 100 nm)

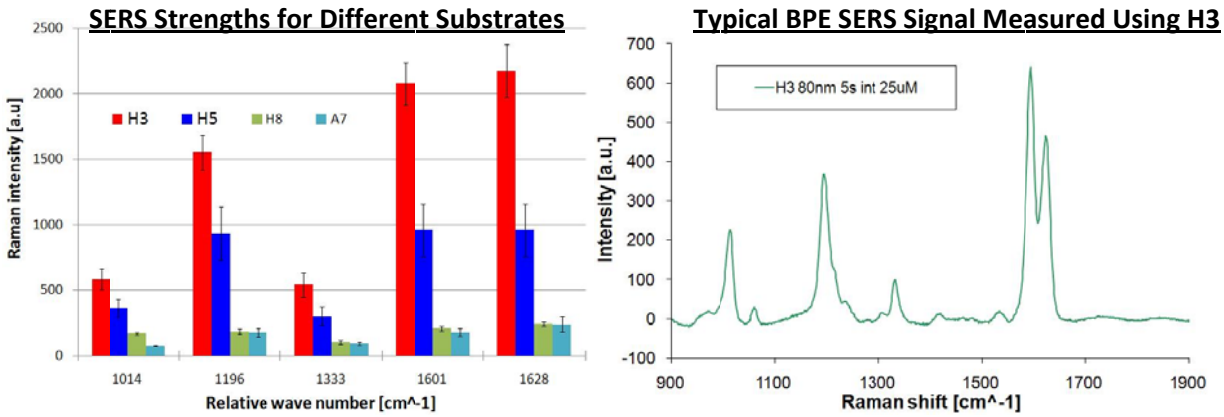

Fig 2: BPE-SERS signals measured using the substrates

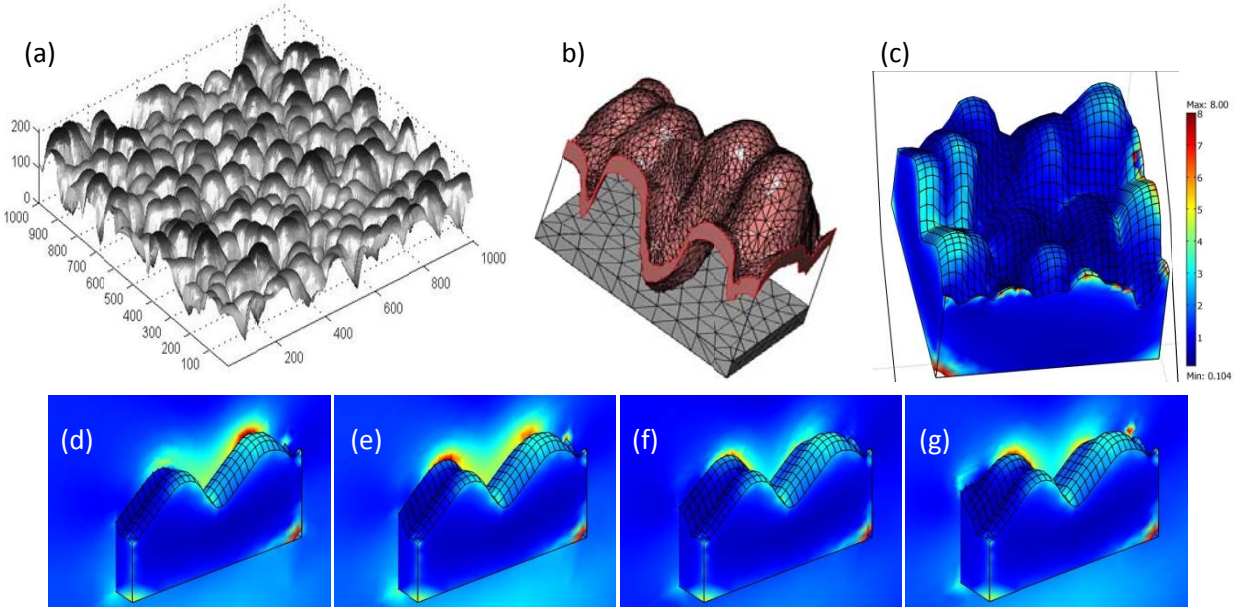

Fig 3: (a) Reconstructed topologies of H3 from the AFM characterization; (b) Meshed surface profile; (c) Simulation result based on the measured geometry of H3; and (d-g) Sliced view of simulation result - clearly enhancement present at the tips, rather than at the gaps in the valley