Nanoparticles-Decorated Nanocone Array of Gold for Anti-Reflective Enhancement of SERS Sensing

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Metallic nanostructures have gained great interest in recent years due to their ability to create electromagnetic hotspots which can be exploited in sensing applications such as surface enhanced Raman scattering (SERS). To create these hotspots and effective SERS substrates, it is necessary to have nanogap arrays in the order of 10's of nm. To this end, current fabrication methodologies have mostly focused on serial lithographic techniques that can directly write features for such dimensions (e.g., e-beam or focused ion beam lithography). It should be noted that there has been limited work done to use larger-scale features capable of exploiting additional optical properties of the larger-scale nanofeatures in SERS. Since SERS sensing is typically conducted with an excitation wavelength in a visible range, we hypothesize that larger-scale nanofeatures with greater anti-reflective properties at the excitation wavelength as well as the increase of an optical path scattering between interactions would improve the SERS signal. Furthermore, using larger-scale nanostructures would also allow for the design of large-area (e.g., wafer-scale) SERS substrates using parallel lithographic techniques such as holographic lithography (HL)[1, 2]. To verify the hypothesis, nanocone array (500 nm in periodicity) of gold was created uniformly over 4-in wafer by using HL, followed by lift-off process (Fig. 1). The high-aspect-ratio nanoporous photoresist (PR) layer patterned by the HL led to grow high-aspect-ratio conical nanostructures of gold in e-beam evaporation[3]. The conical shape of gold nanostructures with sharpened tips is effective to trap light due to the 3D graded refractive index[4], providing the surface with great anti-reflectivity. In order to add smaller nanogap arrays needed for a SERS active substrate, 50-nm gold nanoparticles were self-assembled on the nanopillared surface via evaporation of colloidal solution (Fig. 2a). To measure the SERS enhancement of the anti-reflective nanocone array incorporating the finer nanoparticles' gap array, two additional surfaces were prepared as controls, including the bare nanocone array with no nanoparticles added (Fig. 2b) and the planar silicon substrate featured with nanoparticles only (Fig. 2c). The SERS analysis of Rhodamine 6G (R6G) revealed that the nanocone array decorated with nanoparticles enhanced the SERS signal by more than ten times, compared to the controls (Fig. 2d). The result verifies that the larger-scale nanocone array with the anti-reflective optical properties enables the significant enhancement of the SERS sensing of the finer nanogap array of nanoparticles.

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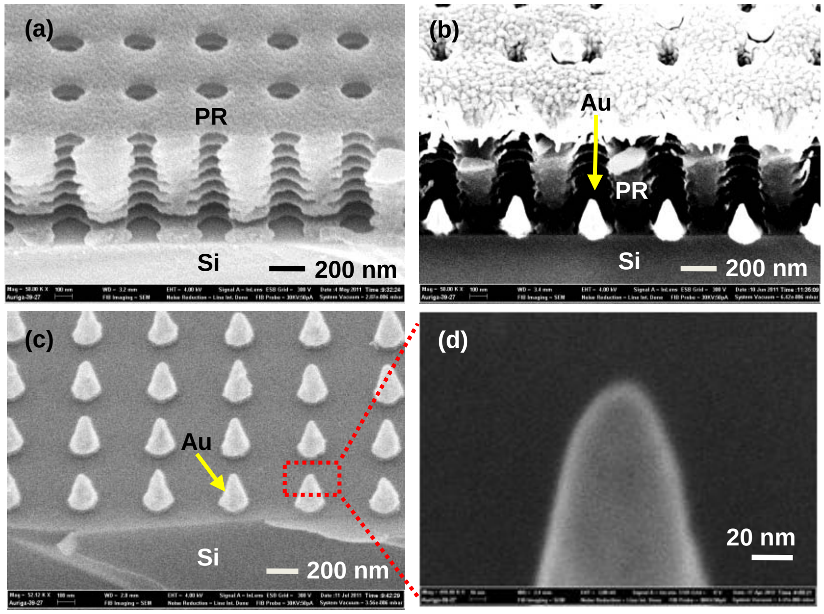

Figure 1: Scanning electron microscope (SEM) images of fabrication results. (a) High-aspect-ratio pore patterns (~200 nm in diameter) produced using HL. (b) Deposition (e-beam evaporation) of gold through the nanoporous PR layer. The closing of the pores during deposition results in the sharpened tips of the gold nanostructures. (c) Conical gold nanostructures left on a silicon substrate after lift-off process. (d) A sharpened tip.

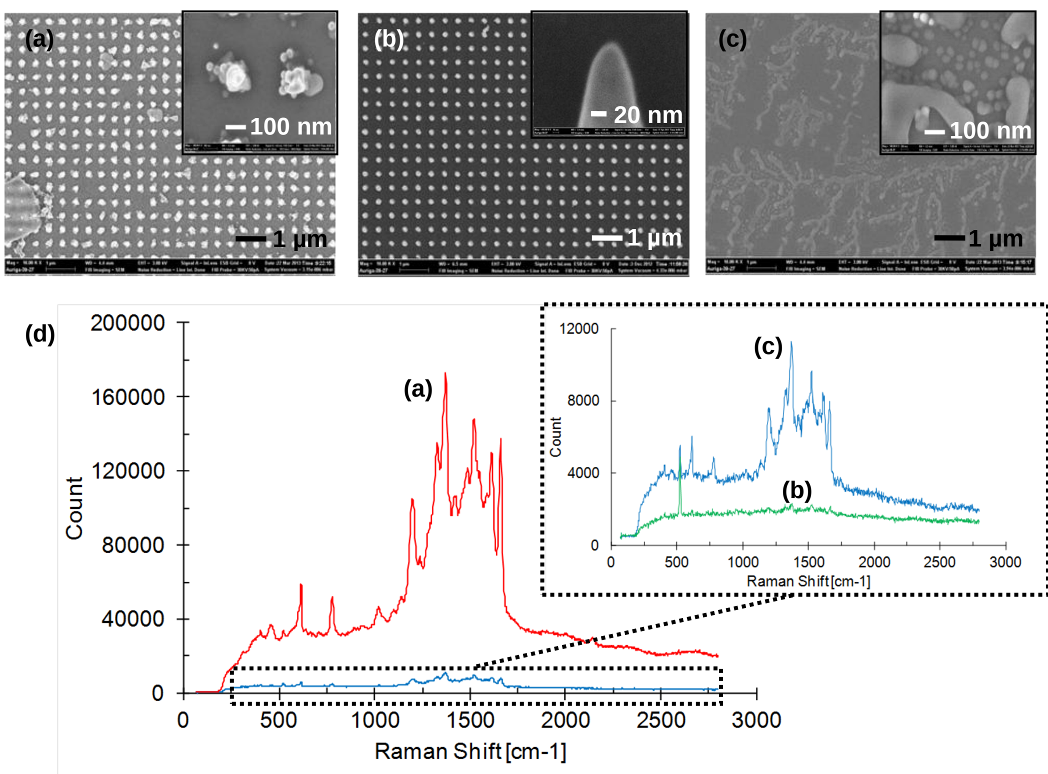

Figure 2: (a) Nanocone array of gold decorated with 50-nm gold nanoparticles. (b) Nanocone array of gold with no decoration with nanoparticles. (c) Gold nanoparticles assembled on a non-patterned planar silicon substrate. (d) Measured SERS signal of R6G resident on the samples of (a)-(c).