Fabrication of sub-10-nm-gapped gold structures for plasmonic applications

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Nanoscale gaps between metal structures are of great interest because of the strong electric fields generated in sub-diffraction-limited volumes in the gap region due to excited surface plasmons. The energy focusing effect of these nanogaps is seen to intensify with decreasing gap size. For instance, fields that are orders of magnitude larger than the incident light field are routinely demonstrated. This large field enhancement has applications in spectroscopy, non-linear optics, and optical rectification. [1]

The fabrication of sub-10-nm gaps in metal nanostructures are often cleverly done using edge-lithography,[2] angled-deposition methods, clustering of chemically-synthesized nanoparticles, and breakage of constricted wires due to electromigration. To achieve greater control of pattern design, one would need a direct method for fabricating these nanogaps. Such a method will also enable a dense coverage of the nanogap structures to achieve superior plasmonic activity reliably. Here, we present such an approach which adopts a lift-off process based on high-resolution electron-beam lithography of hydrogen silsesquioxane (HSQ). With this process, sub-10-nm gapped gold nanostructures were readily fabricated.

Figure 1 shows a representative HSQ-based lift-off process. Fig. 1a is the layout for electron-beam lithography. Fig. 1b gives the corresponding HSQ structures after exposure and development, on which a gold layer was subsequently deposited, as shown in Fig. 1c. Finally, the HSQ was removed using hydrogen fluoride (HF), resulting in a nanodisk array, as shown in Fig. 1d and 1e. During this process, the final nanogaps between nanodisks were determined by the initial linewidth of HSQ structures, which could be readily fabricated to be less than 10 nm.

With this process, a set of nanogapped gold structures were fabricated. To investigate their plasmonic properties, microspectrophotometry, surface enhanced Raman scattering (SERS) and its mapping, and numerical simulations will be done. Fig. 2 gives an example of our initial SERS results on nanogapped hexagonal, square, and triangle gold structures, from which we found that triangle structures had the maximum enhancement, presumably attributing to more hot spots in these structures comparing to square and hexagonal structures. Figure 3 gives the Raman spectra of bowtie gold structures with ~10 nm gaps fabricated also by HSQ-based lift-off process. We found that the Raman scattering depended strongly on the size and periodicity of the structures, which could be related to the plasmon resonance at certain structures with optimal size.

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2. H. Im, K. C. Bantz, N. C. Lindquist, C. L. Haynes, S. H. Oh, *Nano Lett.* 10, 2231-2236 (**2010**).
3. H. G. Duan, V. Manfrinato, J. K. W. Yang, D. Winston, B. Cord, K. K. Berggren, J. Vac. Sci. Technol. 28, C6H11 (**2010**).

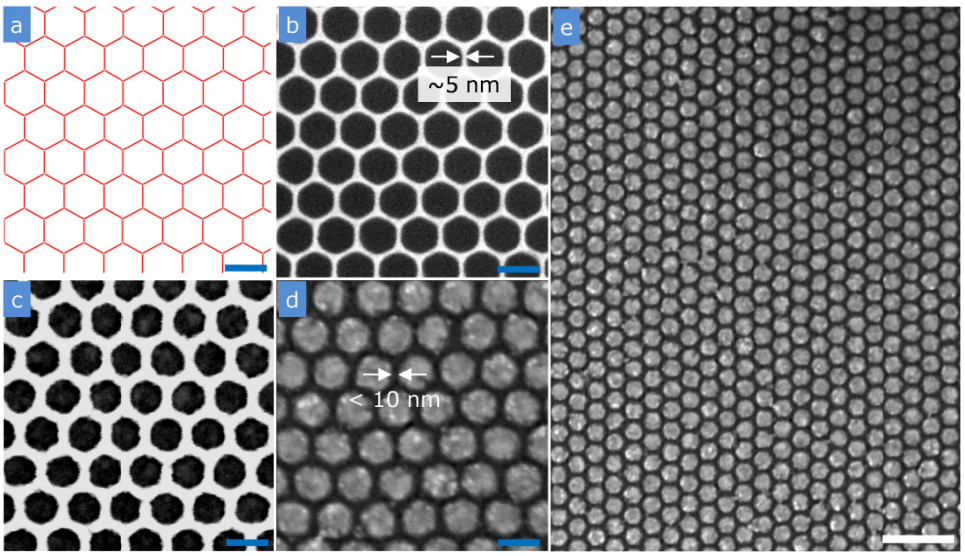

Figure 1. A presentative process to fabricate sub-10-nm gapped gold structures using HSQ-based lift-off process: (a) the layout consisting of single pixel lines for electron-beam lithography, and the edge length in a hexagon was 30 nm; (b) SEM image of HSQ high-aspect-ratio networking structures after exposure and development; (c) HSQ structures after electron-beam evaporation of 15 nm gold; (d) gold nanodisk array after removing the HSQ by HF; (e) low magnification SEM image showing a large array of gold nanodisks. The initial HSQ thickness was 150 nm. Electron-beam lithography was done on an Elionix ELS-7000 system operating at 100 kV with a beam current of 50 pA . HSQ was developed by a salty developer (1% NaOH + 4% NaCl) for 4 min at 24°C and the resultant HSQ structures in (b) was estimated to be ~ 5 nm. The gold evaporation was done in a Denton Explorer system. Before gold deposition, 1 nm Cr layer was deposited as the adhesion layer. The lift-off was done in 1% buffered HF for 4 min with agitation. SEM was done by an Elionix ESM-9000 system operating at 1 0 kV with a working distance of 5 mm. Scale bars: (a-d) 50 nm; (e) 200 nm.

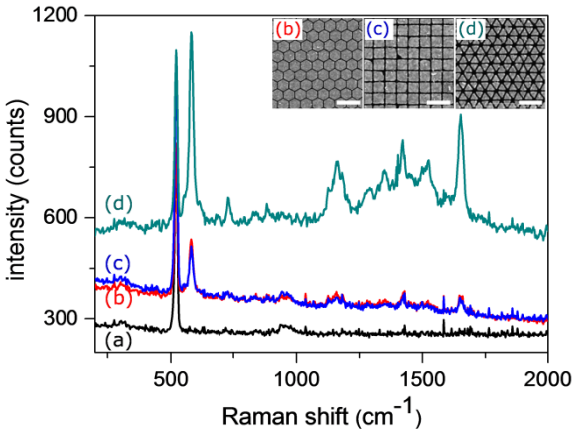

Figure 2. Surface enhanced Raman scattering (SERS) of sub-10-nm gapped gold structures fabricated by HSQ-based lift-off process: (a) gold film without gaps; (b) hexagonal structures; (c) square structures; (d) triangle structures. The edge length and the thickness of these structures were ~90 nm, and 15 nm, respectively. The SERS was done on a WITec system with an excitation wavelength at 633 nm using brilliant cresyl blue as the analyte.

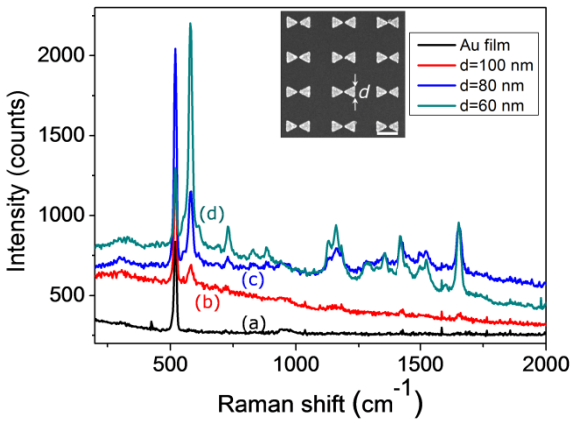

Figure 3. Surface enhanced Raman scattering (SERS) of bowtie gold nanostructures with ~15 nm gaps fabricated by HSQ-based lift-off process: (a) gold film; (b) bowties with 100 nm edge length; (c) 80 nm edge length; (d) 60 nm edge length. The thickness of gold was 15 nm. All fabrication and SER measurement parameters were same as described in Fig. 1 and Fig. 2.