

Ultra-dense gold nanostructures fabricated using hydrogen silsesquioxane (HSQ) resist and applications for surface-enhanced Raman spectroscopy (SERS)

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Although polymethyl-methacrylate (PMMA) resists have been commonly used to produce ultra-dense nanometer-scale structures, however, the fabrication of highly uniform and smooth ultra-dense metal structures using PMMA and lift-off still remains a very challenging task. The metal thicknesses are usually restricted to being very thin with the quality of the gratings being rather poor.¹ As an alternative approach, we report a process using hydrogen silsesquioxane (HSQ), which is a high-resolution, negative-tone resist, to fabricate ultra-dense gold (Au) structures. Due to its high resolution and excellent etch durability, HSQ has previously proven to be very useful in fabricating ultra-dense silicon nanostructures.²

Figure 1 shows the schematic of the sample structures used in our experiment with dense HSQ lines on the Au surface. Electron beam lithography was performed using a JEOL JBX-6000FS system (beam voltage = 50 kV and current = 20 pA). The HSQ patterns were transferred into Au layer using inductively-coupled-plasma reactive ion etching (ICP-RIE). Instead of Ar ion bombardment that has been commonly used for Au patterning, a gas mixture of Cl₂/O₂/Ar was applied to achieve good etch selectivity between the HSQ layer and Au films (25 nm) as well as the thin Cr adhesion layer (5 nm). Gratings with excellent quality were fabricated as demonstrated with the 50-nm-period Au gratings shown in Fig. 2. No defect or discontinuity was found along each line.

For a promising optical application, we utilized the ultra-dense Au gratings for surface-enhanced Raman spectroscopy (SERS) as illustrated in Fig. 3 inset. Recently, SERS substrates with a variety of metal nanostructures have been actively studied for the sensitive detection of chemical agents and biological molecules.³ In this work, 1,1'-diethyl-2,2'-cyanine iodide was used as probe molecules and characterized using a JY LabRam HR 800 micro-Raman set-up (wavelength = 633 nm, beam size = ~1 μm). As revealed in Fig. 3, the ultra-dense Au nanostructures acted as an effective SERS-active substrate. Using the Au gratings, the intensity of Raman spectra noticeably increased compared with the same thickness of Au films or oxide substrates without any metal structures. Detailed processing steps and the paths to better SERS-active substrates will be presented and discussed.

¹ S. Thoms, D. S. Macintyre, and M. McCarthy, *Microelectron. Eng.* **41/42**, 207 (1998).

² S. Choi, N. Jin, V. Kumar, M. Shannon, and I. Adesida, *J. Vac. Sci. Technol. B* **25**(6), 2085 (2007).

³ P. L. Stiles, J. A. Dieringer, N. C. Shah, and R. P. Van Duyne, *Annu. Rev. Anal. Chem.* **1**, 601 (2008).

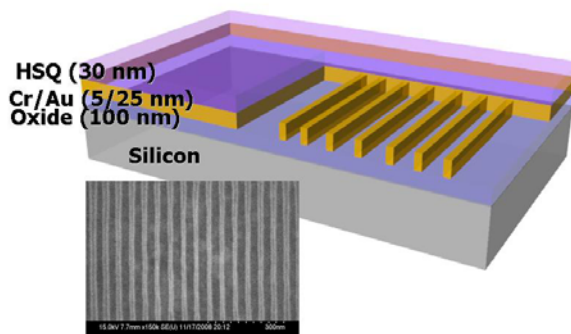


FIG. 1: Schematic of the sample structure for Au gratings using HSQ resists and scanning electron micrograph of HSQ lines (pitch = 50 nm) on Au surface.

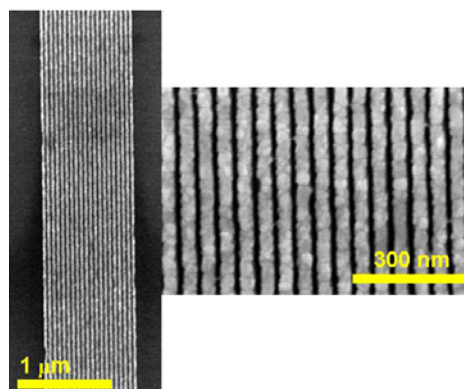


FIG. 2: Scanning electron micrographs of 50-nm-period Au gratings (after ICP-RIE and HSQ removal).

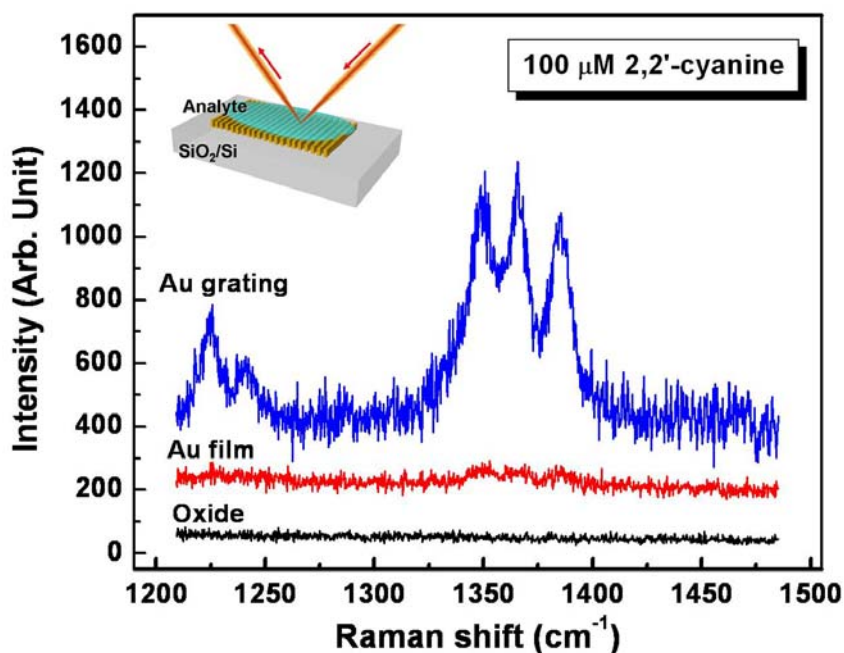


FIG. 3: SERS spectra obtained from 2,2'-cyanine absorbed on Au gratings, Au films, and oxide surface, respectively. Inset figure: Illustration of SERS experiment with Au gratings.