

# Tunable Silver Nano-pillar Arrays as a Surface-enhanced Raman Scattering Sensor by a Self-aligned Nanofabrication Process

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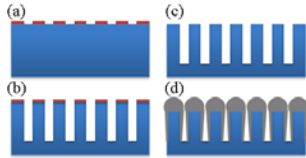
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The Surface-enhanced Raman Scattering (SERS) effect is dominated by the localized plasmon modes created by strong electromagnetic coupling between adjacent metallic objects in a nano-scaled array. Hence, preparation of ordered nanostructures with evenly plasmonic field distribution and ideal enhancement factors is a key issue. We have recently developed a nanofabrication technique to prepare a tunable silver nanopillar array as a SERS sensor. A high resolution electron beam lithography (EBL) process using ZEP520A resist was first carried out by a state-of-art beamwriter, VB6HR supplied by Vistec Lithography Ltd, to replicate a pillar array in resist on a silicon surface. The pillar array has the diameter of 50 nm with a gap between two adjacent ones of 30 nm. This pattern in resist was then transferred to the silicon substrate by an anisotropic reactive dry etch in fluorine based plasma. A silicon pillar array with the height of ~150 nm was formed, shown in Figure 2 a. Then silver film was deposited on the top of the Si pillars by DC magnetron sputtering. The deposited Ag film naturally forms an array of metallic dots by a self-aligned process, as illustrated in Figure 1. One of the advantages with such a technique is that the ultimate gap between two silver pillars can be tuned by the control of the deposition time, that is, using the same structure, different gap sizes can be obtained, which can not realize in the conventional lift-off process. Fig.2 b, c, d show the SEM images of the nanostructures film with different gap sizes by deposition of Ag films in 180, 360 and 720 seconds.

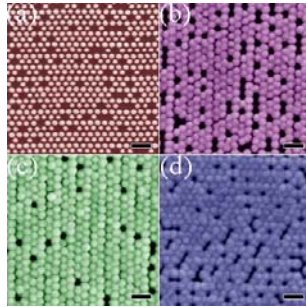
Such small metallic gaps are essential to observe enhanced Raman scatter effect. The tunable capability of this process offers us a good opportunity to study the effect of gap size on enhancement factor. Rhodamine 6G (R6G) is used as the molecular probe to testify the enhancement factor of the as-prepared substrates. Three Raman spectral lines of R6G with a concentration of  $10^{-5}$  mol/L are shown in Figure 3. The enhancement factors for the three structures are similar, around  $10^7$ . The sub-10 nm gaps of the engineered silver nano-pillar arrays contribute primarily to the strong local electric field enhancement thereby leading to a high density of hot-spots for excellent SERS performance. Nevertheless, the experimental results are not quite consistent with the prediction of FDTD

simulations. At least there is no exponential order fold enhancement distinction observed. This is probably due to the fact that the molecular probe concentration is too high and the scattering light has reached certain level. But it should be addressed that the baseline for the sample with longer deposition time, i.e., narrower gap is much more progressed. The improved baseline of the obtained spectra definitely will increase the molecule identifying capability of the substrates. Meanwhile, the fluorescence interference decreases as the continuous silver film thickness increases which can also increase the Raman resolution and is favorable to interpret the fingerprint information of the spectra, especially for the biological samples. Further work for the clarification is underway.

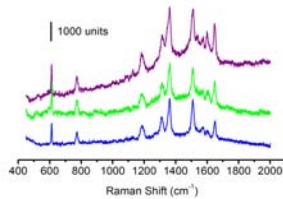
In brief, tunable silver nano-pillar arrays were fabricated by using EBL and DC magnetron sputtering technique successfully. The as-prepared substrates retain an excellent Raman-enhancement characteristic. It provides a reproducible and reliable method to fabricate the SERS sensor particularly in the high sensitivity biological detections.



*Figure 1: The Schematic of the Si Pillar Fabrication Process: (a) E-beam lithography of the ZEP520 resist on the Si substrate; (b) RIE in the F-based atmosphere; (c) the formed Silicon pillar array; (d) deposition of Ag by DC Magnetron sputtering.*



*Figure 2: SEM Images of the As-prepared Template and SERS Substrates: (a) the silicon pillar array of 50 nm diameter with a periodicity of 30 nm; (b), (c), and (d) the silver arrays prepared by DC magnetron sputtering in 180 s, 360 s and 720 s, respectively. The scale bar is 200 nm.*



*Figure 3: The SERS Spectral Lines of  $10^{-5}$  M R6G: From top to bottom, 180 s, 360 s and 720 s silver deposited samples. All the spectra and data are obtained at 633 nm laser excitation for an integration time of 30 s and a laser power of 0.2 mW.*