

# Configurable 3D Nanoscale High Aspect Ratio Pillars for Surface-Enhanced Raman Spectroscopy

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**Abstract**— Configurable Nanoscale-High-Aspect-Ratio-Pillar (NanoHARP) structures were fabricated by a batch process method. Silver thin films were deposited on the top of NanoHARP to form Raman scattering enhancing substrate. By alternating the NanoHARP fabrication recipe and silver thin film deposition thickness, the density as well as the dimensions of the surface matrix is able to be controlled within a wide range. The results of reflectance spectrum and low-temperature electrical conductivity measurements indicate the non-continuous corrugated Ag surface matrix was formed. The Ag-coated nanopillar structure was utilized as the substrate for Surface Enhanced Raman Spectroscopy (SERS) to detect 1nM Rhodamine 6G sample. The characteristic spectrum of Rhodamine 6G was identified successfully and the Raman signal enhancements were observed to vary within 3 orders of magnitude for different nanopillar structures, which is consistent with theoretical predictions. The controllability of the configurations of nanopillars during fabrication enables us to optimize the nano-structure substrate of SERS for specific biomolecules and thus facilitate the ultra-sensitive biomolecule detections.

**Keywords-component:** Configurable; NanoHARP; SERS

## I. INTRODUCTION

Ultrahigh-sensitivity and high-throughput biomolecule detection has been a research focus in recent years with the demands of dramatically developing genomic and proteomic researches. Among numerous investigation methods, spectral analysis, especially Raman spectroscopy attracts great interests because of its unprecedented specificity since it directly originates from the molecular bond vibration induced by the electromagnetic field excitation though the radiated field is extremely weak. Surface-enhanced Raman spectroscopy [1], born more than two decades ago, has been widely utilized in chemical and biomedical researches as it significantly magnifies Raman scattering intensity with 6 to 7 orders of magnitude for ensemble molecules [2] and even strikingly, 12 to 14 orders of magnitude for single molecules [3, 4]. The usual methods used to fabricate SERS substrates includes metal salt half-cycle oxidation, metal vapor deposition [5], metal colloids

[5], and electron beam or focus ion beam produced metal particle assemblies [7]. All the above fabrication techniques are lack of either geometrical configurability or batch-process compatibility so that they cannot meet the requirements for making efficient and multiplexing devices in today's biomedical research. In this paper, we presented a batch-process fabrication method to create nanoscale pillar-like high-aspect-ratio metal structure array (NanoHARP) as SERS substrate. The diameter of pillar and separation are statistically configurable by changing fabrication recipe. The surface properties of NanoHARP were characterized. SERS spectrum of nano-molar Rhodamine 6G molecules was identified using NanoHARP substrate. Surface-enhanced scattering was observed and the enhancement varies depending on the surface properties of substrate.

## II. MATERIALS AND METHODS

### A. Fabrication

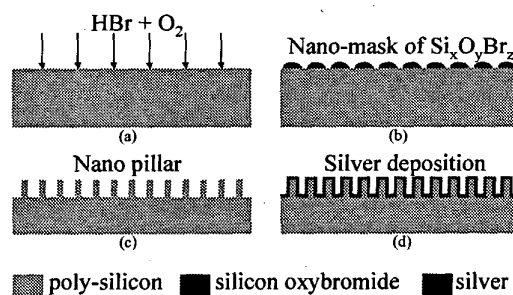


Figure 1. Fabrication process of NanoHARP SERS substrate

In order to make nanoscale high-aspect-ratio structure, the etching-passivation method shown as Fig.1 is used. The substrate, a polysilicon deposited silicon wafer, was etched in Lam Research 9400 TCP etcher with HBr gas at the flux rate of 200 sccm, O<sub>2</sub> at the flux rate of from 3-10sccm, pressure at 35mTorr, top power at 250W and bottom power at 120W. At the beginning few seconds, mixed HBr and O<sub>2</sub> gases are fluxed (a) while HBr etches polysilicon and O<sub>2</sub> oxidizes the etched surface at the same time. Since HBr has very high etching selectivity of polysilicon to oxide (200:1), concurrent selective etching and oxidation lead to nanoscale silicon oxybromide

covering on the polysilicon substrate and naturally form a nano-mask (b) for further pure HBr gas etching to make the nano pillar structure (c). Thereafter, a 50~100nm thin film of silver is thermally deposited to form metallic pillar array (d). The scanning electron microscopy image Fig. 2 shows the pillar-like nanoscale structures in the fabricated device and statically are in order. The statistical pillar diameter and height can be controlled by O<sub>2</sub> passivation time, flux rate and pure HBr etching time.

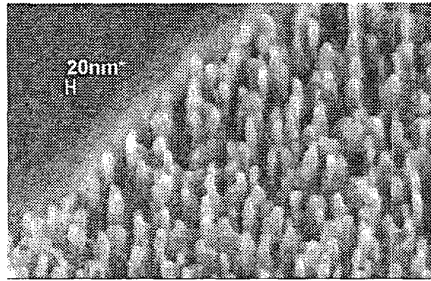


Figure 2. SEM image of NanoHARP

### B. Surface Characterization

The pillar density and height were characterized using an Atom Force Microscope (AFM). Table 1 shows the different pillar density and height with corresponding oxidation flux rate and etching time. As shown, the wide range of nanopillar array configuration can be made by simply modifying fabrication parameters.

Table I. Polysilicon nanopillar feature with different fabrication recipe

Oxidation flux rate (sccm)	3	6	8	10
Pillar density (μm <sup>-2</sup> )	55	518	768	1296
Etching time (min)	1	2	3	4
Pillar height (nm)	300	360	540	720

For the sake of verifying metallic-surface nanopillar array formed, the reflectance spectrum of the surface is measured using a fiber-optics based spectrometer (Ocean Optics, FL). Due to limited spectral range covered by single channel in the spectrometer, two channels were used to acquire reflectance spectrum respectively in UV-visible and NIR range. The fiber terminal (SMA) was positioned by a high-precision 6-axis manipulator to be brought very close and perpendicular to the device surface. The device surface is adjusted to be parallel with the fiber terminal end to accept normal incident illumination. Besides of the fabricated devices, a thin silver film deposited on smooth silicon substrate and the silicon substrate were subject to measurement for comparison. The measurement results are shown in Fig. 3. It can be distinguished that the reflectivity of the fabricated devices are lower than that of the other two kinds of substrates, which indicates a corrugated surface was formed on the NanoHARP devices so that normal angle reflectances decrease. With the deposition of silver thin film on the corrugated polysilicon surface, the normal reflectance increases slightly. It is, however, still much

lower than that of the smooth silver thin film, which indicates silver deposition does not appreciably change the pillar separation distance and the surface undulativity because of the relatively poor silver deposition on the side walls of nanopillars

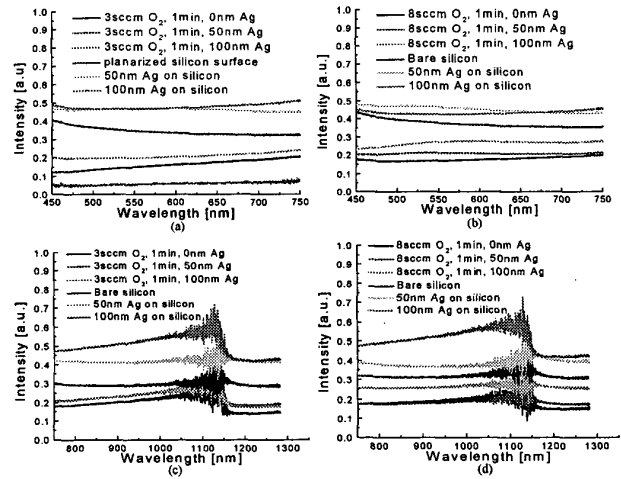


Figure 3. Reflectance spectra of planar silver film, silicon, and NanoHARP devices in UV-visible (a, b) and infrared region (c, d).

The metallic surface characteristics are measured by evaluating its conductivity with respect to the temperature. Four indium electrodes were glued on the NanoHARP device surface and the device was put into a liquid nitrogen tank with temperature sensors. The resistances of the NanoHARP surface at different temperatures in the low-temperature region were measured using four-terminal method to exclude the contact resistance between indium electrodes and device surface. The measurement results are shown in Fig.4. Typical semiconductivity is exhibited especially for more corrugated surface (red curve) since the resistance decreases with the temperature increase, though it is much lower than that of the polysilicon substrate (not shown), which indicates discontinuous silver film was formed that is possibly caused by the poor silver deposition on nanopillar side walls. The smoother surface apparently has higher conductivity indicating on which more continuous metallic surface formed.

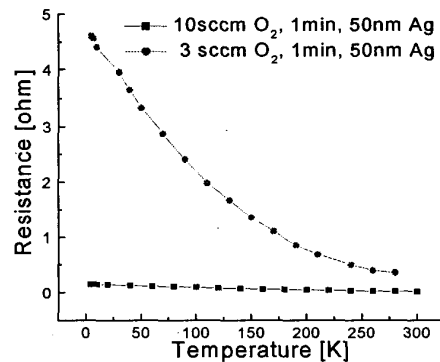


Figure 4. Resistance of NanoHARP devices with respect to temperature

### III. EXPERIMENTS

1 nM Rhodamine 6G solution was prepared and evenly coated on the NanoHARP surface to make better contacts between R6G molecules and silver-coated nanopillars. The same optical detection system setup was configured as that in the previous reflectance spectrum measurement, except that a Raman spectrometer R2001 (Raman System, NY) with a 2048-pixel CCD detector was used. The Raman spectrometer is equipped with a bifurcating fiber optics sampling probe (InPhotonics, CA) that can apply 785nm focused laser excitation on the sample, and collected scattered and reflected light with the same optical path. The focal length and focal spot size are respectively 5mm and 90 $\mu$ m. The NanoHARP device surface is brought to the focal plane of excitation

Different NanoHARP devices were tested in the experiment and the detected Raman scattering intensities were shown in Fig.5. The characteristic peaks of R6G can be clearly identified. Due to the resolution limitation of digitized signal intensity, Raman scattering enhancement factor cannot be assessed in a very accurate manner, however, it is estimated to be more than  $10^4$  times for maximal enhancements. It should be noted the enhancement varies with several orders of magnitude depending on the configuration of NanoHARP devices, that is, the density, diameter and height of nanopillar are, if not determinate, dependent factors to the Raman scattering enhancement.

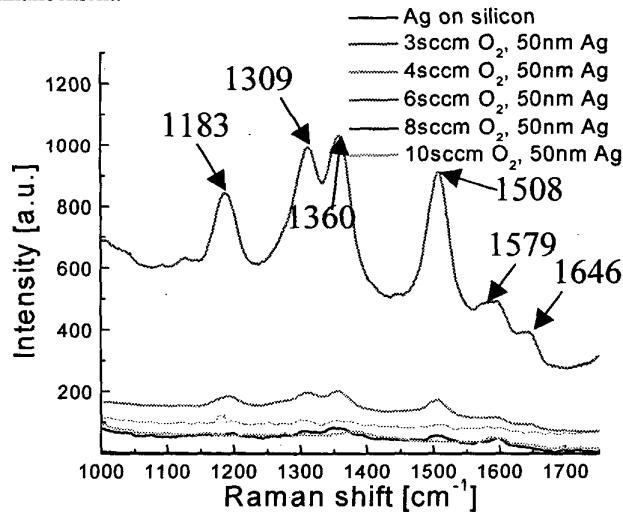


Figure 5. Raman spectra of R6G molecule.

According to the surface characterization results acquired by AFM, 6sccm O<sub>2</sub> passivation makes the average pillar

separation distance about 43.9nm which is very close to the pillar diameter. This result is consistent with the theoretical prediction [8] very well. It should be noted that the in the result shown relative large background signals do exist possibly because of fluorescence emissions of R6G molecule, however, it didn't overwhelm the Raman characteristic peaks. The specific reason is still under investigation.

### IV. CONCLUSION

Batch-process fabrication method is used to make geometry-configurable nano size pillar array. The optimal SERS enhancement can be achieved for specific biological molecules by configuring the substrate to provide an efficient and inexpensive way of making proper substrate for Raman spectroscopy. As well, the device can be monolithically integrated with other micro devices such as microfluidic channel for lab-on-a-chip applications by taking advantages of batch-process nanofabrications.

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