Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Tuning the Topographical Parameters of Si Pyramids for a Better Surface Enhanced Raman Response

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Method employed for quantification of Si-pyramidal structures

To examine the uniformity of pyramidal textures on Si surfaces with increasing etching time , standard deviation method was used. The standard deviation is a quantity which express the degree of dispersion of group values from the mean value of the group. It is calculated by square root of the arithmetic mean of the deviation squared between individual values and their mean. As the etching time increases the pyramidal base size and height also changes with time. So, if the standard deviation of the pyramidal base length/ height is directly used to evaluate will lead to error in determine the uniformity. Therefore, the base length of the pyramidal surface is normalized first with average base length.

The average base length of the pyramidal surface is calculated by equation(1).

$$B_a = \frac{\sum_{i=1}^{n} B_i}{n} \tag{1}$$

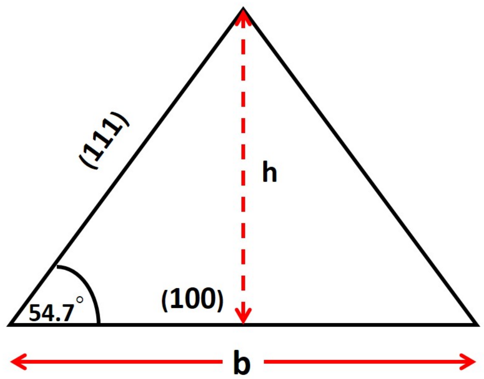
where B_a represents the average base length.

$$b_i = \frac{B_i}{B_a} \tag{2}$$

where b_r represents the relative base length. The relative standard deviation S_{br} is calculated by the equation (3).

$$S_{br} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(b_i - 1)} \tag{3}$$

Pyramid Height calculation



$$h = \frac{1}{2} b \cdot \tan(54.7)$$

Figure S1: Geometry of a pyramid on a etched Si wafer in two dimensions

Calculated height distribution of pyramidal surfaces

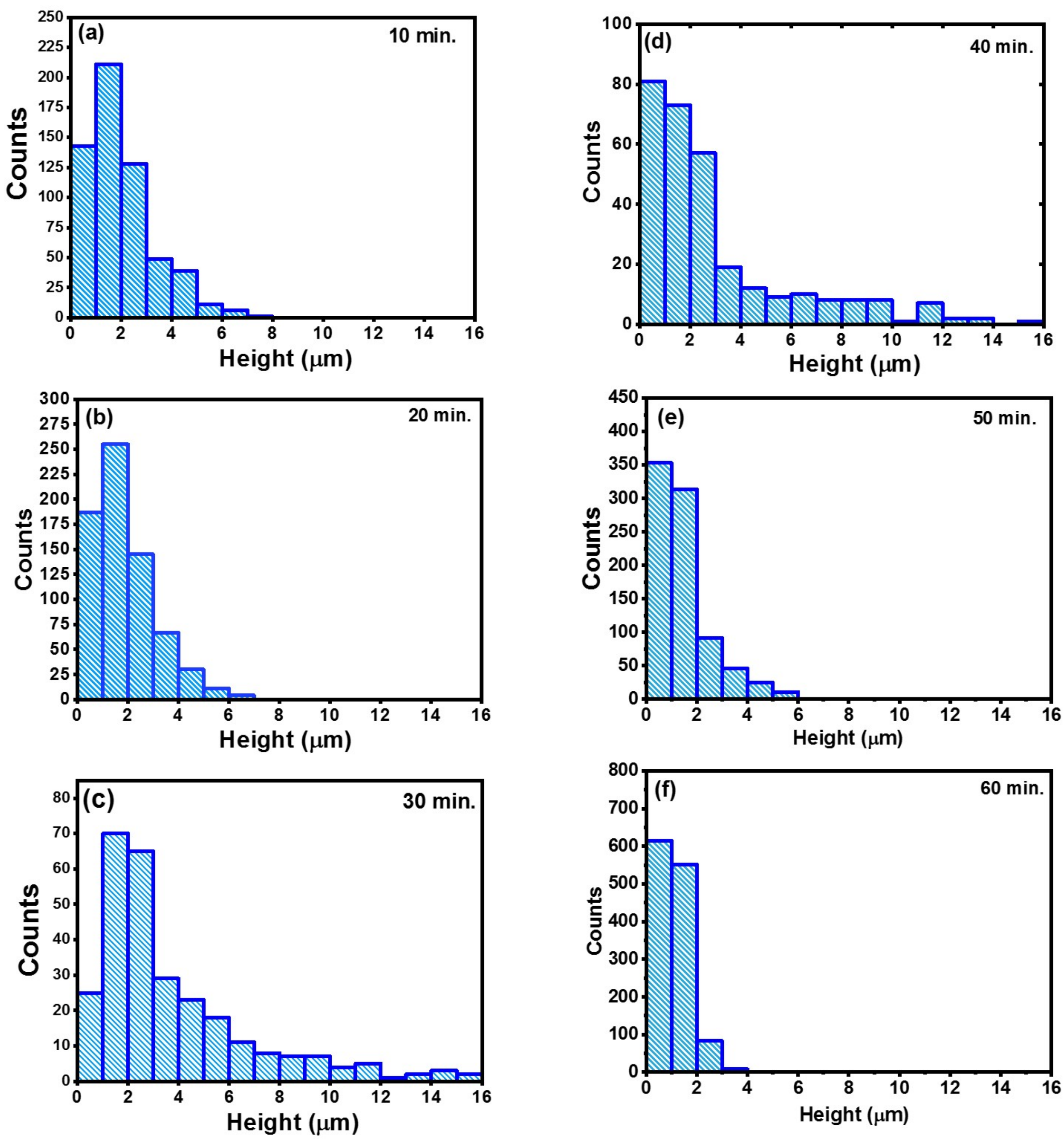
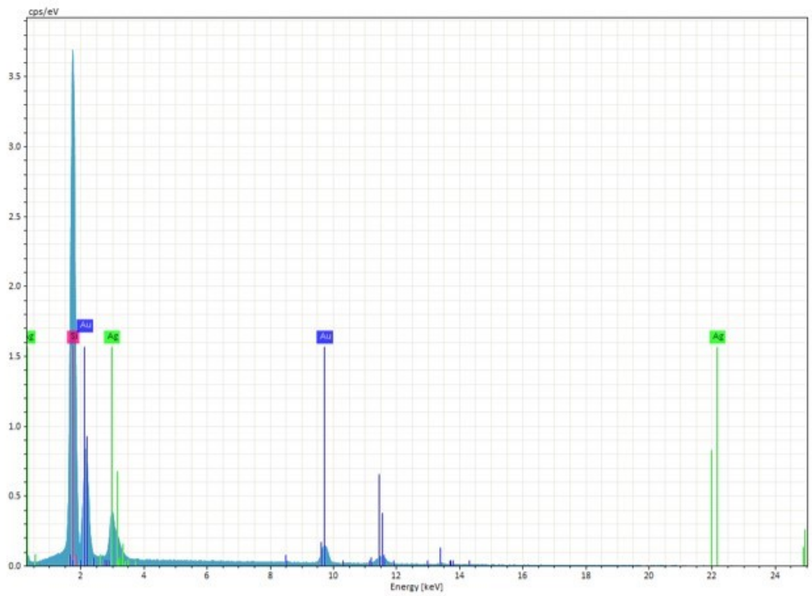


Figure S2: Calculated height distribution from SEM images for (a) 10 min.(b) 20 min. (c) 30 min. (d) 40 min. (e) 50 min. (f) 60 min. etch time respectively.

EDX spectra confirming the 50% - 50% concentration of Au- Ag alloy

Application Note
Company / Department



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Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Silicon	14	103880	45.20	50.23	84.14	2.01	4.45
Silver	47	16529	18.13	20.15	8.79	0.62	3.42
Gold	79	9118	26.65	29.62	7.07	0.76	2.87
		Sum	89.98	100.00	100.00		

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Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Silver	47	16390	24.22	35.71	50.35	0.82	3.39
Gold	79	9129	43.60	64.29	49.65	1.23	2.83
		Sum	67.81	100.00	100.00		

Figure S3: Edx Data Report.

AFM line profile for thickness measurement

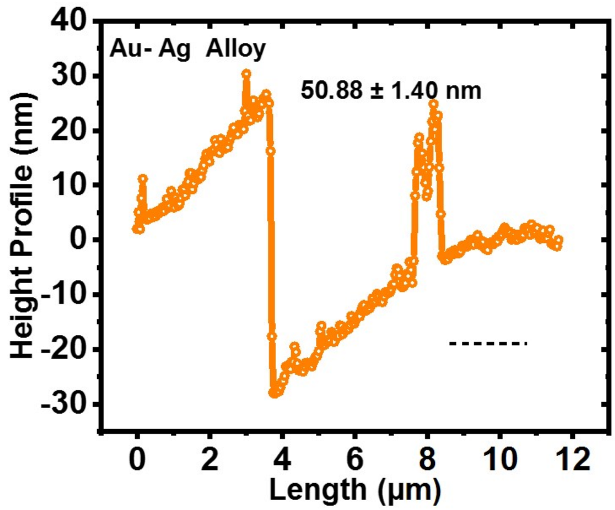

Figure S4: Line profile of AFM images for $Au_{0.5}Ag_{0.5}$ alloy nanolayer thickness measurements.

References:

1. Shinki and Subhendu sarkar, $Au_{0.5}Ag_{0.5}$0.5 Alloy Nanolayer Deposited on Pyramidal Si Arrays as Substrates for Surface-Enhanced Raman Spectroscopy **2020**, 2, 7088 .

Real Time normal Raman spectra from reference sample (Plane Si)

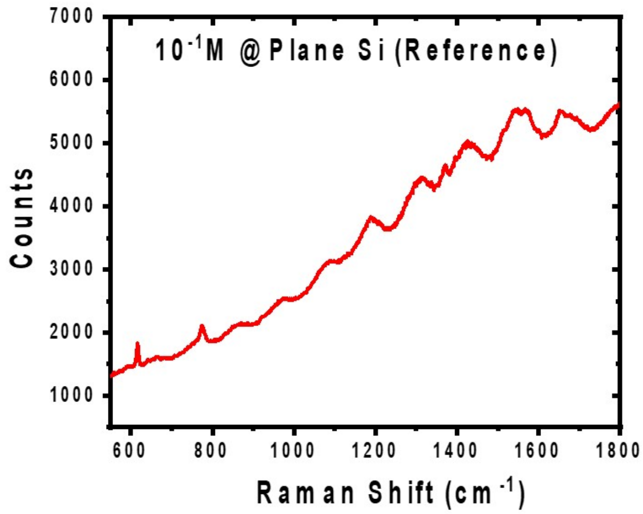

Figure S5: Real time Raman Spectra from reference sample

Vibration modes assigned for Raman peak of Rh6G molecule

Table S1: Vibration modes corresponding to each Raman peak for Rh6G molecule.

Wavenumber (cm^{-1})	612	776	1186	1316	1368, 1513, 1578, 1652
Vibration mode	C-C-C Ring in-plane	C-H out-of plane	C-H in plane bend	N-N in plane bend	aromatic C-C stretching

Calculation of SERS enhancement factor for 612 cm^{-1} Peak

λ = Wavelength of the excitation laser used = 532 nm

NA = Numerical Aperture = 0.5

ρ = Density of analyte molecule (gm/cm^3) = 1.26

A = Area of the sample (cm^2) = 1

Effective surface area of sample after consideration of pyramidal shape with mean base length and height

Etch time (min)	Area coverage by Pyramids (%)	Slant Height (μm)	Effective Surface Area (cm^2)
10	57	2.40	1.42
20	60	2.28	1.43
30	90	4.61	1.65
40	95	3.71	1.69
50	100	1.93	1.72
60	100	1.38	1.73

w = weight of the analyte present in the solution spread on the sample (ng) = 4.79

Laser spot diameter $w_0 = 1.22\ \lambda/$ NA

Laser focal depth $(z_0) = (2\pi/\lambda)\ w_0^2$

Laser focal volume $(\tau) = (\pi/2)^{3/2} w_0^2\ (z_0)$

N_{bulk} =[(confocal volume × Density)/ molecular weight) × Avogadro's number (N_A)]

N_{SERS} =[(Laser spot area / Substrate area) × volume (V) × concentration (C)]

I_{SERS}	I_{bulk}	I_{SERS}/I_{bulk}	$N_{bulk}/N_{SERS}\times 10^6$	$I_{SERS}/I_{bulk}\times N_{bulk}/N_{SERS} \times 10^7$	EF($\times 10^8$)
7145	347	20.59	1.85	3.80	0.38
10699	347	30.83	1.88	5.79	0.58
3889	347	11.20	2.17	2.43	0.24
5165	347	14.88	2.21	3.29	0.33
15781	347	45.47	2.26	10.3	1.03
21745	347	62.66	2.27	14.2	1.42

References:

1. Rao, V. K.; Radhakrishnan, T. P. Tuning the SERS Response with Ag-Au Nanoparticle Embedded Polymer Thin Film Substrates.ACS Appl. Mater. Interfaces **2015**, 7, 12767–12773.

2. Roy, A.; Maiti, A.; Chini, T. K.; Satpati, B. Annealing Induced Morphology of Silver Nanoparticles on Pyramidal Silicon Surface and Their Application to Surface-Enhanced Raman Scattering.ACS Appl. Mater. Interfaces **2017**, 9, 34405–34415.

Raman mapping analysis on comparing with map area for 10 min. etch surface

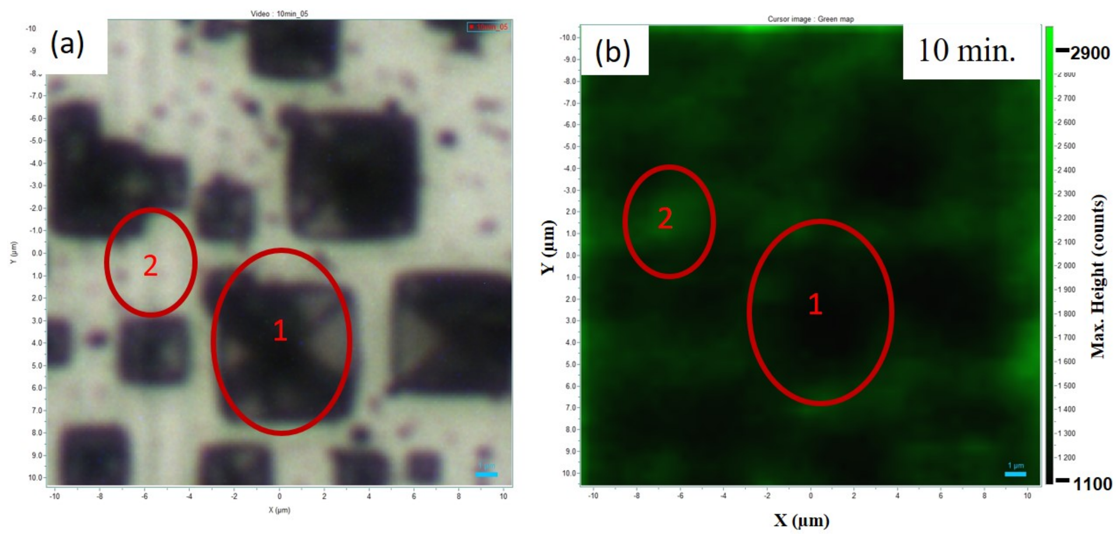

Figure S6: Raman mapping analysis on comparing with map area for 10 min. etch surface

Normal Raman spectra of MB and MP from reference sample (plane Si) with 1 mM bulk concentration of both analytes

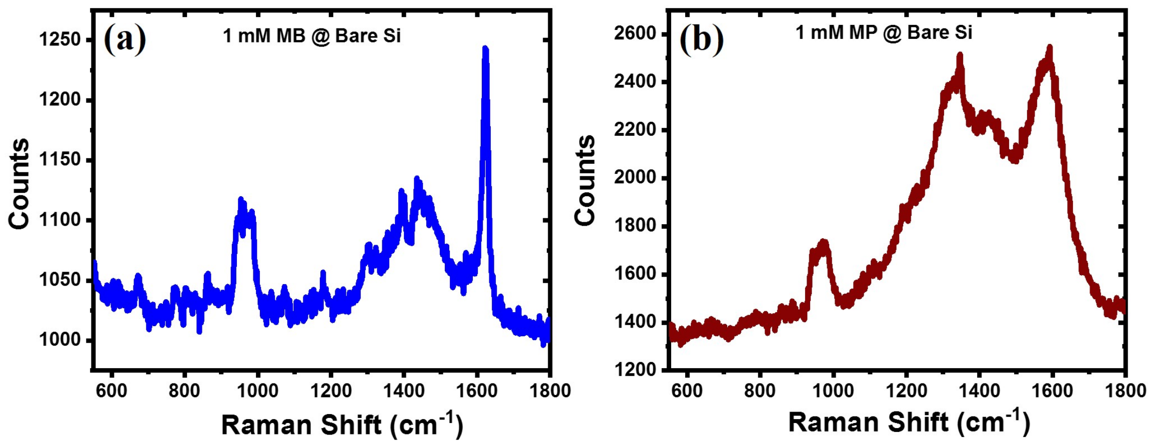

Figure S7: Real time Raman Spectra of MB and MP from reference sample