Supporting Information for

300 mm Wafer-Level, Ultra-Dense Arrays of Au-Capped Nanopillars with sub-10 nm Gaps as Reliable SERS Substrates

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1. Fabrication and characterization of the Au-capped nanopillar arrays

1.1 Fabrication

The 300 mm silicon nanopillar wafer was fabricated according to a previous report.¹ As schematically shown in Figure 1a, in the DUV immersion lithography, vertical and horizontal lines of 193nm light was employed in sequence using a mask with 45 nm width and 45 nm spacing to expose the photoresist on top of a Si wafer coated with amorphous carbon, forming a periodic array of the nanodots with a constant 90nm pitch after positive development. Then, the mask was transferred to the amorphous carbon layer and a Si substrate using a Lam Research 2300® Kiyo® C Series conductor dry etch system. Finally, the carbon mask was removed by O₂ plasma stripping.

A self-assembled monolayer (SAM) of 3-mercaptopropyl-trimethoxysilane (MPTMS, Sigma-Aldrich, 95%) was attached onto the Si pillar surface instead of thin titanium layer as a nondamping molecular linker to enhance the adhesion between the Au and Si without impairing the plasmonic properties.^{2,3} The substrates were immersed in MPTES solution (10%, v/v), in an ethanol and distilled water mixture (95:5 in volume), for 3 hours. After adequate rinsing and N₂ drying, a baking process at 105 °C was taken in a N₂ flowing oven for 10 minutes. Then, various thicknesses of Au ranging from 30 nm to 100 nm were deposited in a commercial Pfeiffer Spider 630 sputtering tool using a low power recipe (40W) for better thickness control.

1.2 Characterization

A Philips XL30 FEG instrument operated at an accelerating voltage of 5 kV was used to take the SEM images. The reflection spectra were measured in water with a Bruker Vertex 80v Fourier transform infrared (FTIR) spectrometer equipped with a Hyperion 2000 microscope. The

unpolarized incident light from a tungsten lamp was focused on the substrates via a $10\times$ magnification water immersion objective with the numerical aperture (NA) of 0.3. The reflected light was collected by the same objective, and detected by a Si diode detector. Reference spectra were taken using a Ag mirror reference. A Horiba Jobin Yvon LabRAM HR 800 system was used for taking the SERS spectra by using 4-aminothiophenol (4-ATP) as the probe molecule. After UV Ozone cleaning for 15 minutes, the Au capped nanopillar substrates were incubated in 1mM 4-ATP ethanol solution overnight, and rinsed adequately using ethanol and deionized water before the SERS measurement. The same $10\times$ water immersion objective was used as in reflection measurements. A 785nm diode laser and a He-Ne laser at 632.8nm (~0.5 mW) were used. Where applicable, the 1078 cm⁻¹ 4-ATP Raman band was integrated from 1045 cm⁻¹ to 1110 cm⁻¹. All the SERS spectra were normalized by the integration time. For the uniformity evaluation, a linear mapping over 200 µm in steps of 1 µm was taken, and the backgrounds were subtracted using a third order polynomial fitting procedure.

2. SEM images of the nanopillar SERS substrates

As the sputtered Au layer thickness increases, the gaps between the Au nanocaps become narrower, until touching between the Au caps start to clearly appear in the T_{Au} =80 nm arrays. For the T_{Au} =100 nm arrays, more Au caps are touching, and fewer sub-10 nm gaps are present. As shown in the cross section images, random Au nanoparticles are also present on the side walls on the H_{pillar} =150 nm nanopillars.



Figure S1. SEM images of the Au capped nanopillar arrays with various Au deposition thicknesses for the nanopillar height of both 70 nm and 150 nm. The scale bars represent 500 nm in the top view images and 200 nm in the cross section images.

3. FDTD model details

The Lumerical FDTD Solution v8.5 (Lumerical Solution Inc., Canada) was used for the numerical simulations. In x- and y- directions, a periodic boundary condition with pitch=90 nm was taken while in the z-direction perfectly matched layer (PML) boundary conditions were used. An x-polarized incidence light was simulated. A mesh size of 0.5 nm was taken for the Au-capped nanopillar volume. A background index of 1.33 was set to fit the measurement conditions. The permittivity data of Si and Au were taken from the Palik and CRC handbooks, respectively. The electric field enhancement was normalized to the incidence field intensity.

In the 3D simulation model, the Au caps, shaped as nanospheroids, were set on top of cylindrical Si nanopillars with a 30 nm diameter and heights of 70 nm and 150 nm, standing on a semiinfinite Si substrate. The geometries of the Au nanospheriods and Si nanopillars are fit to the dimensions measured in the SEM images. Moreover, the shapes of the Au nanocaps growing during the sputtering process are also taken into account. In the manuscript, the SERS signal enhancement is categorized into the *non-touching* effect and the *touching* effect. For the non-touching effect simulations, the sputtered Au caps are shaped as nanospheres for thicknesses smaller than 70 nm. While for thicker Au depositions (80/ 90/ 100 nm), since the growth in the in-plane dimensions is constrained by the small pitch, the gap size is kept as a constant of 5 nm and only the vertical diameter of the spheroids is growing. The detailed radiuses used in the simulations are listed in **Table S1**. The calculated reflection spectra and surface E^4 sum in this method are shown in Figure 2b, f and Figure 3a, b in the manuscript.

Table S1. The vertical and in-plane radiuses (R_z/R_{xy}) of the Au nanospheroids for the substrates with various nanopillar heights H_{pillar} and Au deposition thickness T_{Au} used in the FDTD simulations. All the values are in nanometers.

R_z/R_x T H_{pillar}	^{Au} 30	40	50	60	70	80	90	100
70	25/25	27.5/27.5	30/30	35/35	40/40	45/42.5	50/42.5	52.5/42.5
150	25/25	27.5/27.5	30/30	35/35	37.5/37.5	42.5/42.5	47.5/42.5	52.5/42.5

For the touching effect, the vertical diameter of the nanospheroid is kept as a constant while the in-plane diameter increases to simulate various touching degrees. The touching degree is defined by the touching size as if the Au nanocaps are shaped as whole spheroids as shown in the schematic of Figure 3 in the manuscript. It equals the diameter of the imaginary nanospheriod in the in-plane dimension minus the distance between adjacent nanospheroid centers. A negative touching size actually means the gap size instead. Calculated surface E^4 enhancement sum in this way is summarized in Figure 3c in the manuscript.

In Lumerical FDTD Solution v8.5, the electric field enhancement on the Au nanospheroid surface is extracted from a 3D field profile monitor with an index monitor of the same dimension to ensure that only the E^2 data where the probe molecules have access to were extracted.

4. Electric field enhancement maximum on the Au nanospheroid surface

The electric intensity enhancement maximum spectra were simulated using the same geometry parameters as listed in Table S1. Typically the enhancement maximum is on the Au nanospheroid equator along the polarization direction. As demonstrated in **Figure S2**, similar to the reflection spectra results (Figure 2a, b, e, f), no sharp resonances are present due to the fact that the high density of the Au nanospheroids spectrally smears out the global optical responses. Nevertheless, large enhancements are still present in arrays with narrow gaps and give rise to the amplified SERS signals.



Figure S2. FDTD calculated electric field intensity E^2 enhancement maximum for (a) H_{pillar} =70 nm and (b) H_{pillar} =150 nm substrates with various Au deposition thicknesses. The black dashed lines indicates the excitation wavelengths used in SERS measurements (633 nm and 785 nm),

and the red ones are the corresponding stokes shifted wavelengths for the 4-ATP 1078 cm⁻¹ vibrational mode (679 nm and 857 nm).

5. SERS substrate enhancement factor

We also calculated the experimental SERS substrate enhancement factor (EF) for the substrates with 80 nm Au deposition under the full surface coverage assumption according to I_{sers}/N_{abs}

 $EF = \frac{I_{sers}/N_{abs}}{I_{bulk}/N_{bulk}}$,⁴ where I_{SERS} and I_{bulk} are the SERS intensity for our pillar substrates and Raman intensity for a pure bulk sample, and N_{abs} and N_{bulk} are the amount of molecules adsorbed on the Au nanospheroid surface and in the detected volume of the bulk sample, respectively. The peak corresponding to the 4-ATP C-S bond stretching vibrational mode around ~1078 cm⁻¹, which is indicated with the green dashed box in Figure 2c, d and g, h, is used for the calculation.

For the SERS signal calculations, I_{SERS} is taken from the results shown in Figure 2c, d and h, g.

The number of the adsorbed 4-ATP molecules N_{ads} , which equals $\frac{N_{pillar} \times S_{Au-cap}}{S_{4-ATP}}$, is obtained by assuming full coverage of a 4-ATP monolayer on the Au cap surface. The number of nanopillars excited by the laser N_{pillar} is calculated as the laser focal spot area (~ 5 µm in diameter) multiplied by the density of the square nanopillar array (lattice constant is 90 nm). The Au cap is approximately shaped as a sphere with a diameter of 85 nm. Due to the fact that the Au cap is standing on top of the Si nanopillar with a diameter of 30 nm, it is estimated that ~96% of the whole sphere surface is accessible to 4-ATP molecules (Au sphere surface area minus Si

nanopillar top area). Therefore, the surface area covered by the 4-ATP monolayer per Au cap $S_{\text{Au-cap}}$ is ~ 2.2×10⁴ nm². The surface area occupied per adsorbed 4-ATP molecule is ~0.2 nm².

For the normal Raman signal calculations, we measured the normal Raman spectra of 4-ATP molecules in high concentration methanol solutions, as suggested by E.C.Le Ru *et al.*.⁵ These results are shown in **Figure S3**. The number of 4-ATP molecules illuminated by the excitation laser N_{bulk} is calculated as $c_{4-\text{ATP}} \times V_{\text{laser}} \times N_A$. $c_{4-\text{ATP}}$ is the concentration of the 4-ATP methanol solution (1M), and N_A is the Avogadro constant. The volume V_{laser} excited by the laser is defined as the focal spot area multiplied by the confocal depth, which is measured using the method described by W. B. Cai *et al.*,⁶ and is ~645 µm and ~620 µm for the 785 nm and 633 nm excitation wavelengths, respectively.



Figure S3. Normal Raman spectra of 1M 4-ATP methanol solution and pure methanol solvent excited at (A) 785 nm and (B) 633 nm. The measurements were carried out using the same setup as in Figure 2c, d, g, h for the 4-ATP SERS detections. The peak at 1086 cm⁻¹ indicated with the green box is assigned to the C-S bond stretching vibrational mode and used for the enhancement factor calculations. The other peak at 1032 cm⁻¹ corresponds to the C-O stretching of the methanol solvent.

The experimentally calculated EFs are on the order of $10^4 \sim 10^5$ for the nanopillar substrates with 80nm Au as shown in **Table S2**. We also calculated the substrate EF for the KlariteTM substrate under the same full coverage assumption as follows. The 4-ATP molecule number on the

KlariteTM could be calculated as
$$N_{4-ATP \text{ on Klarite}} = \frac{N_{Klarite} \times S_{Klarite}}{S_{4-ATP}}$$
. The number of the inverted pyramid in the KlariteTM excited by the laser $N_{Klarite}$ is obtained by considering the laser focal spot area (~ 5 µm in diameter) and the density of the pyramid (lattice constant is 2 µm). The width of the inverted pyramid is 1.6 µm and the pit depth is 1 µm. Thus, the surface area per

$$\frac{N_{4-ATP \text{ on pillar}}}{N_{4-ATP \text{ on pillar}}} = 1.12$$

unit structure is ~9.64 μ m². (^N₄-ATP on Klarite , therefore similar number of 4-ATP molecules is adsorbed on the Au cap and the KlariteTM surfaces.) The final EF results are also listed in Table S2, which shows that the KlariteTM EFs are on the order of ~10⁴.

Table S2. Experimental and simulated SERS substrate enhancement factors for T_{Au} =80 nmsubstrates and KlariteTM

Pillar Height [nm]	Excitation@785 nm				Excitation@633 nm			
	Exp ^a	Exp ^b	۶ FDTD	FDTD ^d	Exp ^a	Exp ^b	۶ FDTD	FDTD ^d
70	2.3×10 ⁵	2.5×10 ⁹	4.8×10 ⁴	3.5×10 ⁷	6.2×10 ⁴	6.8×10 ⁸	2.3×10 ⁵	1.6×10 ⁸
150	2.1×10^{5}	2.3×10 ⁹	2.5×10 ⁴	2.5×10 ⁷	2.1×10^{4}	2.3×10 ⁸	4.4×10 ⁴	1.2×10 ⁸
Klarite TM	8.4×10 ⁴	-	-	-	1.5×10 ⁴	-	-	-

^a Experimental results obtained under the full monolayer coverage assumption.

^b Experimental results obtained under the few molecule coverage assumption.

^c FDTD results simulated using the geometrical parameters listed in Table S1 with a gap size of 5 nm.

^d FDTD results simulated with a zero gap size (or zero touching size) and the same vertical radius.

In addition, under the assumption of few molecule coverage (In Ref ^{7,8} it is assumed that 5 molecules in each nanogap contribute the most to the SERS signal enhancement. In our calculation, ten 4-ATP molecules in each nanogap is used assuming five molecules on each of the adjacent non-touching Au nanocaps), the obtained EFs are much larger ($\sim 10^9$) as listed in Table S2.

Moreover, in Table S2 the simulated $E^4 = E^2_{\text{incidence}} \times E^2_{\text{stokes}}$ at the maximum field enhancement positions on the surface using two different sets of the Au cap geometrical parameters are also summarized. The second set of the simulated results with the zero gap size (set b) features the EF peak as shown in Figure 3c in the manuscript, and demonstrates ~3 orders of magnitude larger EFs than the results obtained with a 5 nm gap size.

6. Batch-to-batch reproducibility

Batch-to-batch reproducibility is another important factor for industrial applications. We independently produced three substrates with the nanopillar height of 70 nm and the Au layer thickness of 80 nm. The SERS intensities measured at both 785 nm and 633 nm excitation are shown in **Figure S4**. The good signal reproducibility is first derived from the inherent uniformity of the Si nanopillar arrays. Furthermore, since the SERS signals largely depend on the electric field enhancement in the regions between the Au nanocaps as thoroughly discussed in the manuscript, fine-tuned Au sputtering deposition is critical in order to produce arrays with uniform and reproducible gaps between the Au caps.



Figure S4. 4-ATP SERS spectra of three independently produced substrates with nanopillar height of 70 nm and Au deposition thickness of 80 nm excited at 785 nm and 633 nm, respectively. The spectra are off-set for clarity.

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