# Supplementary Information for Reusable Plasmonic Au and Ag Diamond Films for Robust SERS Sensing

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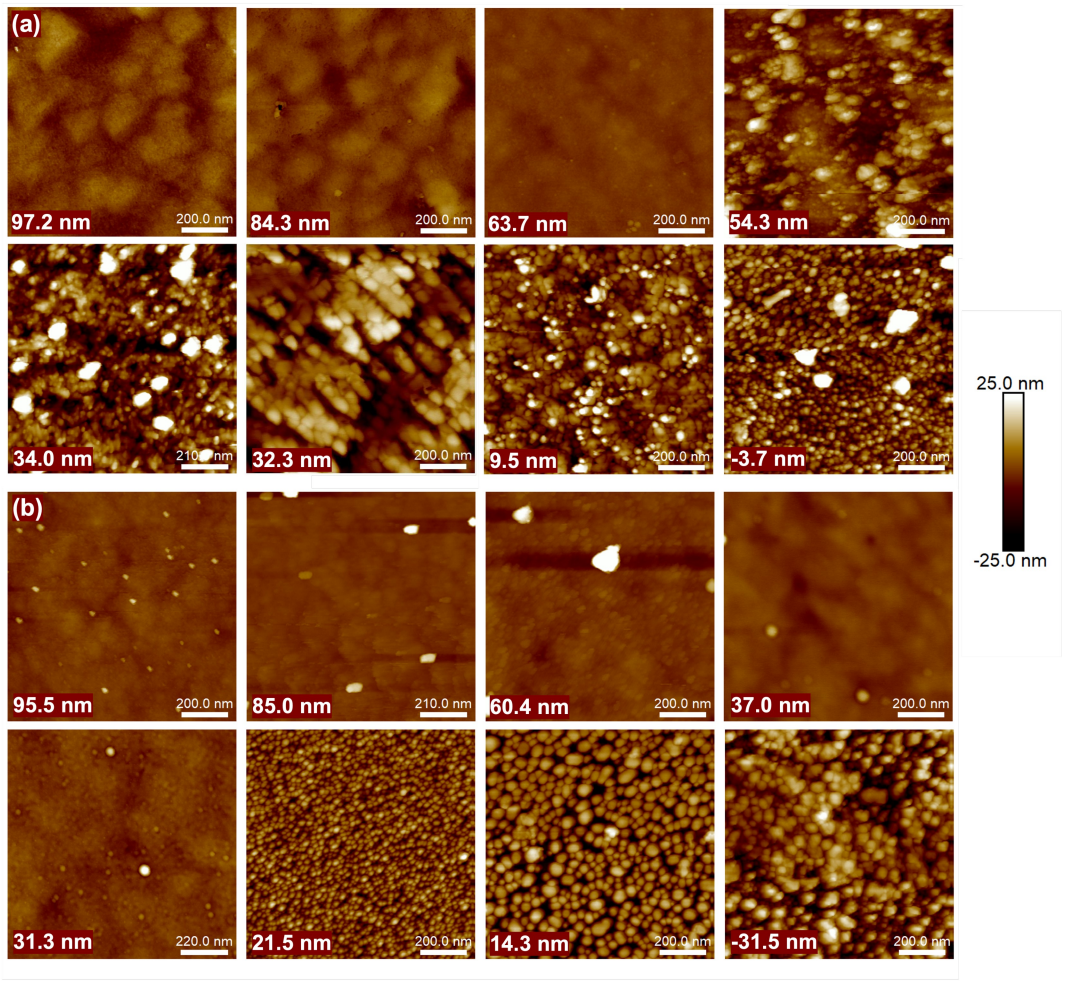



Figure S1: 1 $\mu$m AFM scans of etched diamond films over (a) 29.6 nm Ag-NPs (b) 27.1 nm Au-NPs. Remaining diamond film thicknesses are provided inset to images with etching conducted until diamond film is fully removed.

Table S1: $\sim$ 10 nm substrates diamond film etch depths.

| | Ag | | Au | |
|---|---|---|---|---|
| Etch time (s) | Etch depth (nm) | Remaining film (nm) | Etch depth (nm) | Remaining film (nm) |
| 0 | 0 | 20.4 | 0 | 15.0 |
| 5 | 2.4 | 18.0 | 1.7 | 13.3 |
| 10 | 4.3 | 16.1 | 3.1 | 11.9 |
| 15 | 7.9 | 12.5 | 6.3 | 8.7 |
| 30 | 10.8 | 9.6 | 7.2 | 7.8 |
| 60 | 20.1 | 0.3 | 15.9 | -0.9 |

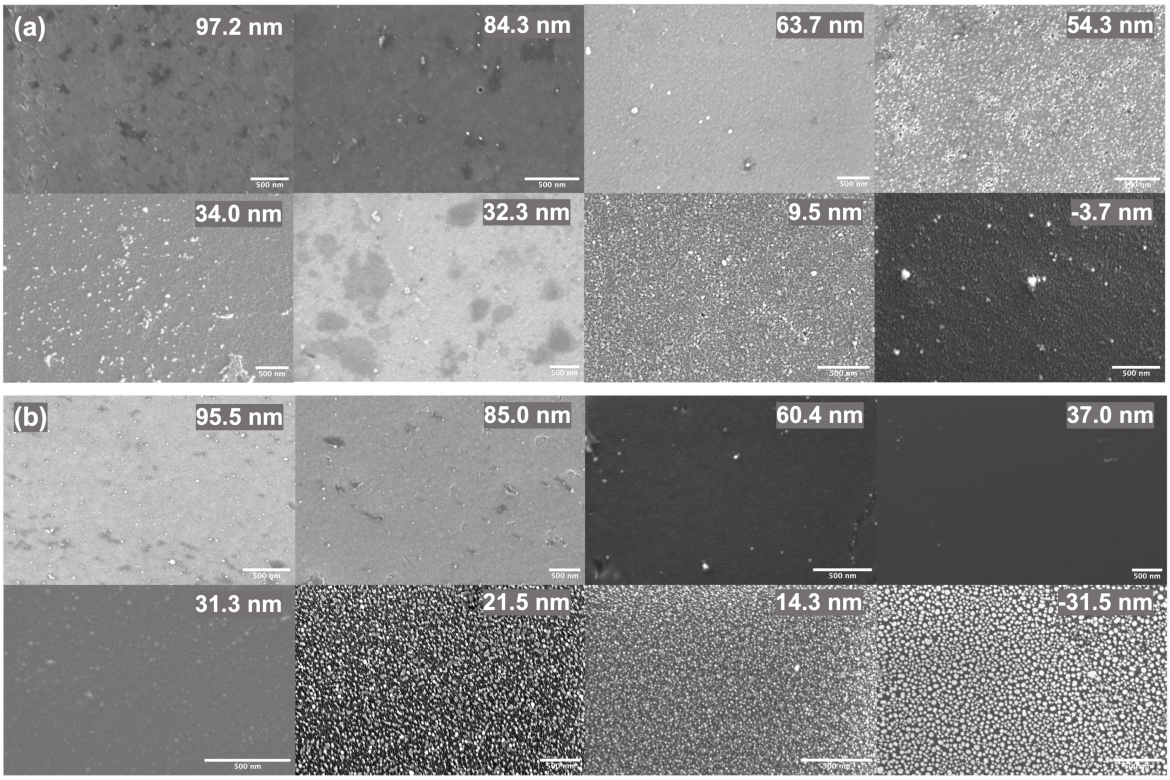



Figure S2: SEM images of etched diamond films over (a) 29.6 nm Ag-NPs (b) 27.1 nm Au-NPs. Remaining diamond film thicknesses are provided inset to images with etching conducted until diamond film is fully removed.

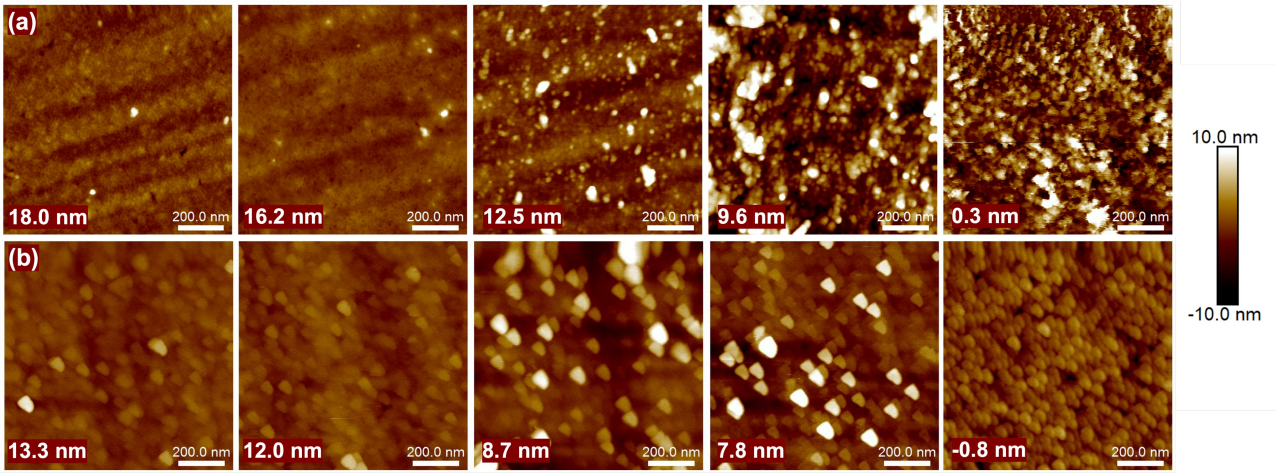



Figure S3: 1 $\mu$m AFM scans of etched diamond films over (a) 10.4 nm Ag-NPs (b) 11.0 Au-NPs. Remaining diamond film thicknesses are provided inset to images with etching conducted until diamond film is fully removed.

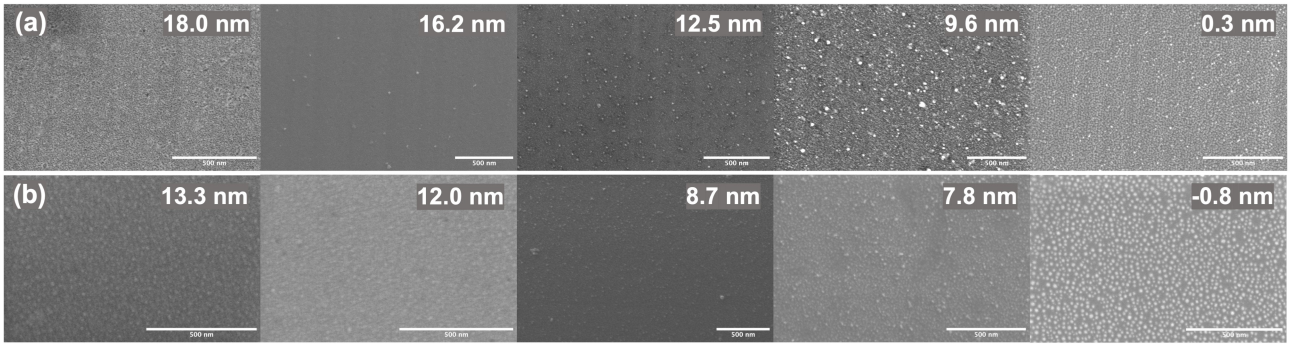



Figure S4: SEM images of etched diamond films over (a) 10.4 nm Ag-NPs (b) 11.0 Au-NPs. Remaining diamond film thicknesses are provided inset to images with etching conducted until diamond film is fully removed.

Table S2: $\sim$ 30 nm substrates diamond film etch depths.

| | Ag | | Au | |
|---|---|---|---|---|
| Etch time (s) | Etch depth (nm) | Remaining film (nm) | Etch depth (nm) | Remaining film (nm) |
| 0 | 0 | 108.3 | 0 | 106.3 |
| 30 | 11.1 | 97.2 | 10.8 | 95.5 |
| 60 | 24.0 | 84.3 | 21.2 | 85.1 |
| 120 | 44.6 | 63.7 | 46.0 | 60.3 |
| 158 | - | - | 69.3 | 37.0 |
| 163 | - | - | 75.0 | 31.3 |
| 180 | 54.1 | 54.3 | 84.8 | 21.5 |
| 195 | 74.3 | 34.0 | - | - |
| 197 | 76.0 | 32.3 | - | - |
| 240 | 98.9 | 9.4 | 92.0 | 14.3 |
| 300 | 112.0 | -3.7 | 137.8 | -31.5 |

Table S3: Diamond film Raman peak analysis.

| **Substrate** | **Peak** | **$\sim$Position ($cm^{-1}$)** | **Normalised Max Intensity (a.u.)** | **FWHM** | **Assignment** |
|---|---|---|---|---|---|
| Ag 10.4 nm | 3 | 1331.2 | 0.893 | 4.26 | Diamond line |
| | 4 | 1345.8 | 0.045 | 222.43 | D-band |
| | 6 | 1582.9 | 0.025 | 129.78 | G-band |
| | 7 | 1607.7 | 0.023 | 47.91 | Microcrystalline graphite |
| Au 11.0 nm | 3 | 1331.2 | 0.981 | 4.63 | Diamond line |
| | 4 | 1345.8 | 0.017 | 130.37 | D-band |
| | 6 | 1582.9 | 0.005 | 54.84 | G-band |
| | 7 | 1607.7 | 0.004 | 2.32 | Microcrystalline graphite |
| Ag 29.6 nm | 1 | 1164.7 | 0.019 | 32.10 | Transpolyacetylene |
| | 2 | 1259.0 | 0.074 | 128.91 | Low-quality diamond |
| | 3 | 1331.2 | 0.508 | 6.69 | Diamond line |
| | 4 | 1345.8 | 0.259 | 109.26 | D-band |
| | 5 | 1509.0 | 0.203 | 597.44 | I-band |
| | 6 | 1582.9 | 0.223 | 52.35 | G-band |
| Au 27.1 nm | 3 | 1331.2 | 0.972 | 4.23 | Diamond line |
| | 4 | 1345.8 | 0.028 | 126.03 | D-band |

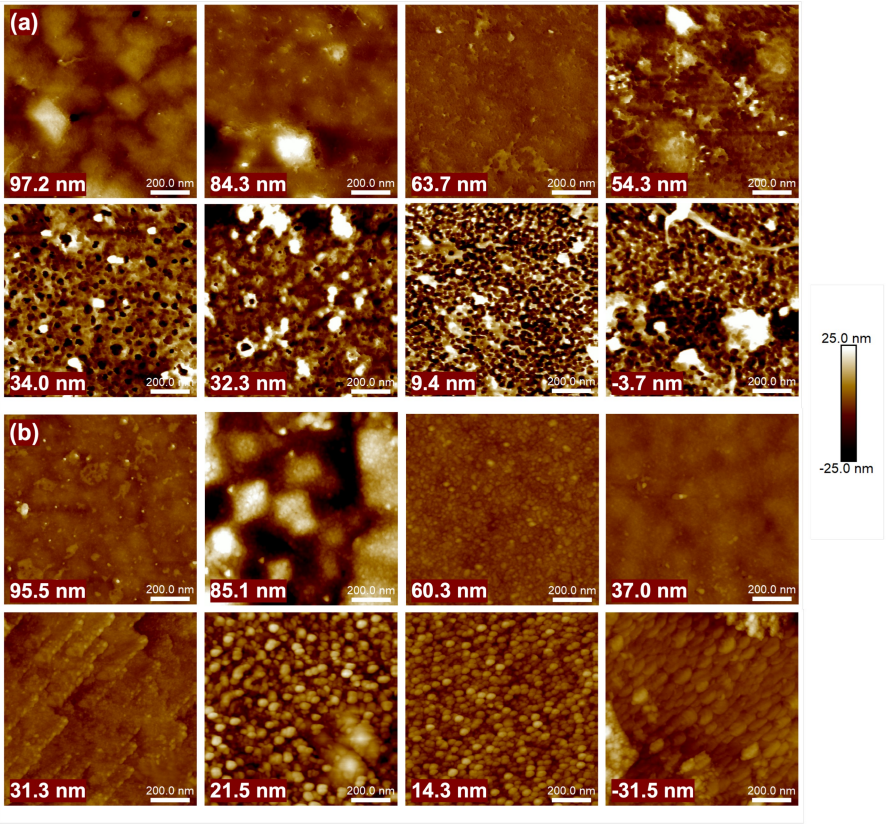



Figure S5: 1 $\mu$m AFM scans of etched diamond films over (a) 29.6 nm Ag-NPs (b) 27.1 nm Au-NPs following exposure to Au etchant removing exposed NPs. Remaining diamond film thicknesses are provided inset to images.

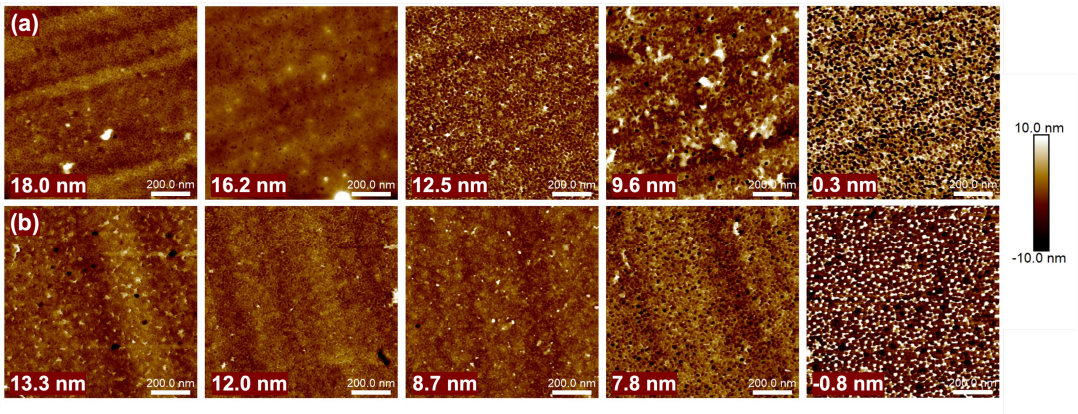



Figure S6: 1 $\mu$m AFM scans of etched diamond films over (a) 10.4 nm Ag-NPs (b) 11.0 Au-NPs following exposure to Au etchant removing exposed NPs. Remaining diamond film thicknesses are provided inset to images.

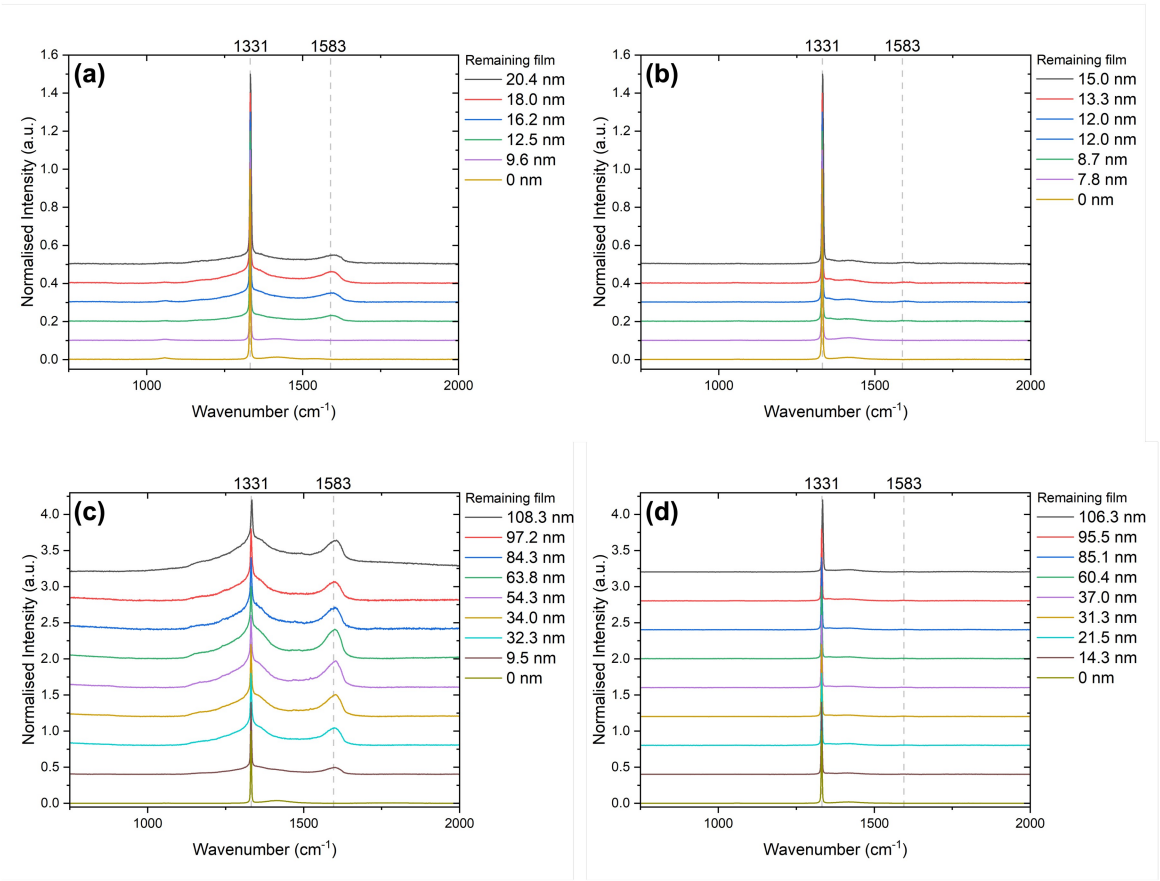
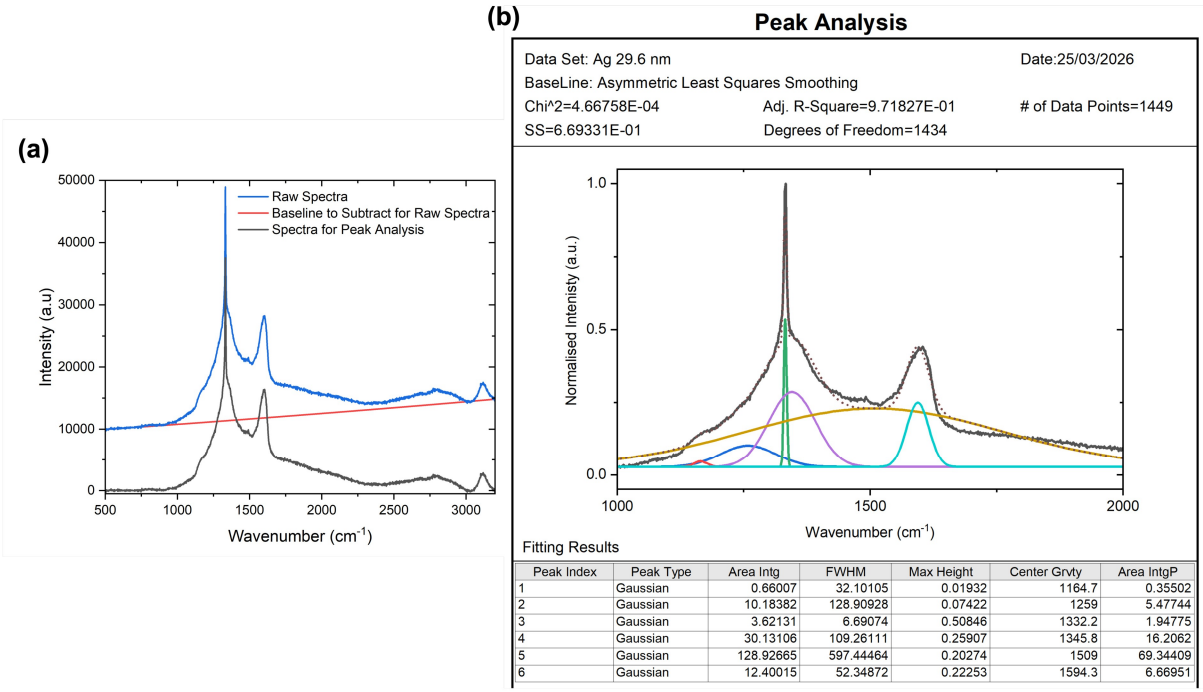



Figure S7: Raman spectra of grown diamond films over (a) 10.4 nm Ag-NPs (b) 11.0 Au-NPs (c) 29.6 nm Ag-NPs (d) 27.1 nm Au-NPs for varied diamond film thicknesses offset in y. Diamond quality can be correlated with $sp^2$ to $sp^3$ ratio comparing the 1582.9 $cm^{-1}$ graphitic carbon peak to the 1331.2 $cm^{-1}$ diamond peak.




| Peak Index | Peak Type | Area Intg | FWHM | Max Height | Center Grvty | Area IntgP |
|---|---|---|---|---|---|---|
| 1 | Gaussian | 0.66007 | 32.10105 | 0.01932 | 1164.7 | 0.35502 |
| 2 | Gaussian | 10.18382 | 128.90928 | 0.07422 | 1259 | 5.47744 |
| 3 | Gaussian | 3.62131 | 6.69074 | 0.50846 | 1332.2 | 1.94775 |
| 4 | Gaussian | 30.13106 | 109.26111 | 0.25907 | 1345.8 | 16.2062 |
| 5 | Gaussian | 128.92665 | 597.44464 | 0.20274 | 1509 | 69.34409 |
| 6 | Gaussian | 12.40015 | 52.34872 | 0.22253 | 1594.3 | 6.66951 |

Figure S8: Example of 29.6 nm Ag-NP grown diamond film Raman analysis. (a) Raw collected spectra, Baseline to subtract and fluorescence subtracted spectra for peak analysis. Following baseline subtraction spectra were normalised to 1 and analysed with origin fit peaks function using Gaussian peak shapes and auto fit control. (b) Provides the resulting peak analysis.

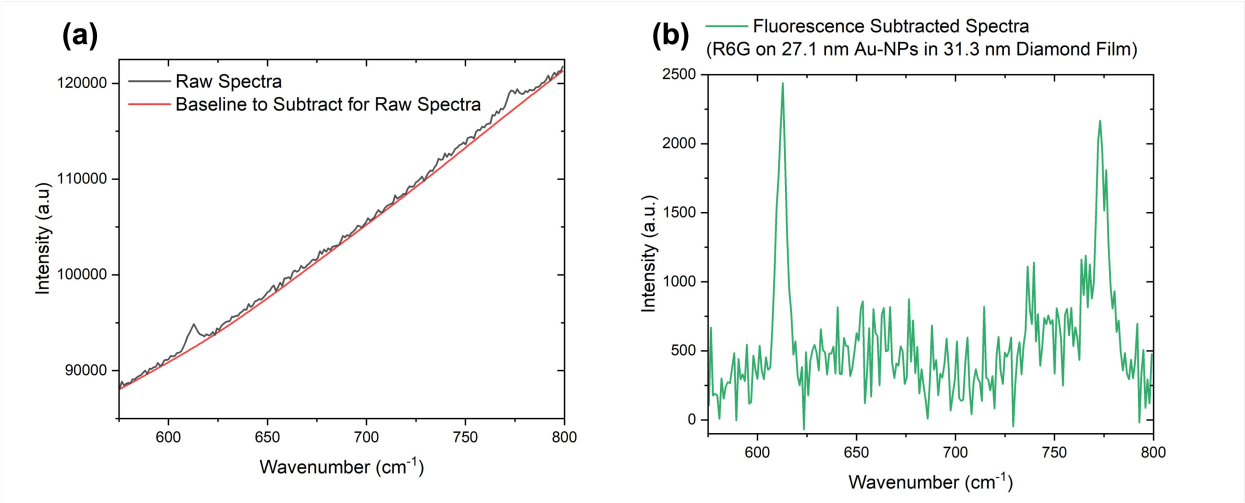



Figure S9: Example of fluorescence subtraction for R6G $1 \times 10^{-4}$ M on 27.1 nm Au-NPs in 31.3 nm diamond film. The raw collected spectra and baseline to subtract is provided in (a) and the fluorescence subtracted spectra in (b). Fluorescence was subtracted by asymmetric least squares baseline subtraction (Asymmetric Factor = 0.001, Threshold = 0.01, Smoothing Factor = 3, Number of Iterations = 10) in OriginPro software. No additional smoothing or cosmic ray removal was performed.

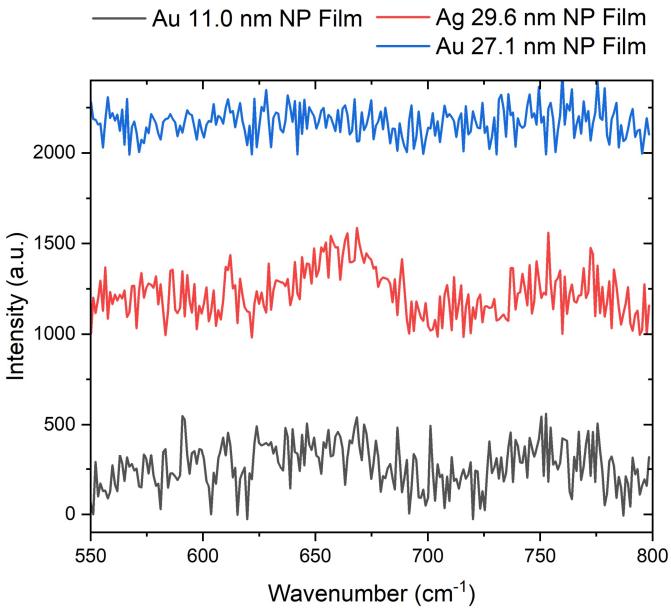



Figure S10: Spectra of $1 \times 10^{-6}$ M R6G measurement where no R6G peaks are present. Measurements were taken on substrate optimised film thicknesses (12.0 nm on 11.0 nm Au-NPs, 54.3 nm on 29.6 nm Ag-NPs, 31.3 nm on 27.1 nm Au-NPs). Spectra are offset in y to aid comparison.

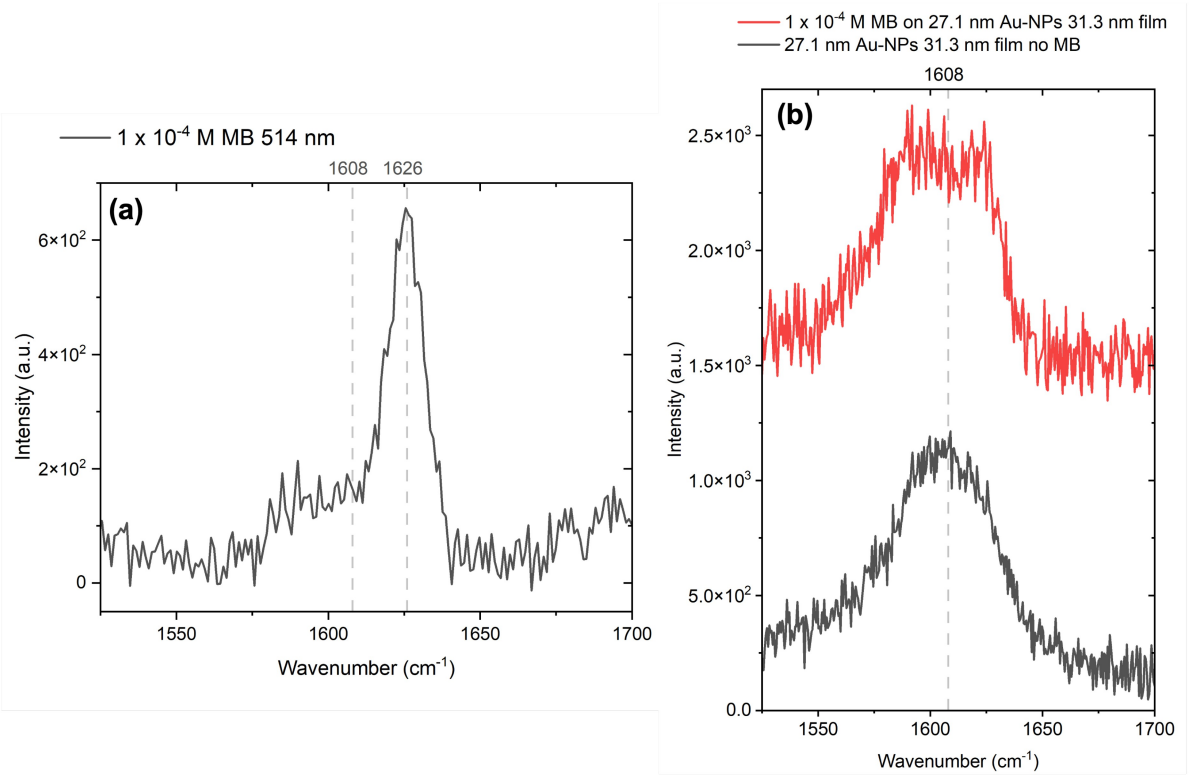



Figure S11: Spectra of $1 \times 10^{-4}$ M MB measurement on 27.1 nm Au-NPs with 31.3 nm diamond film. With (a) 514 nm excitation and (b) 633 nm excitation. For 633 spectra are offset in y to aid comparison.

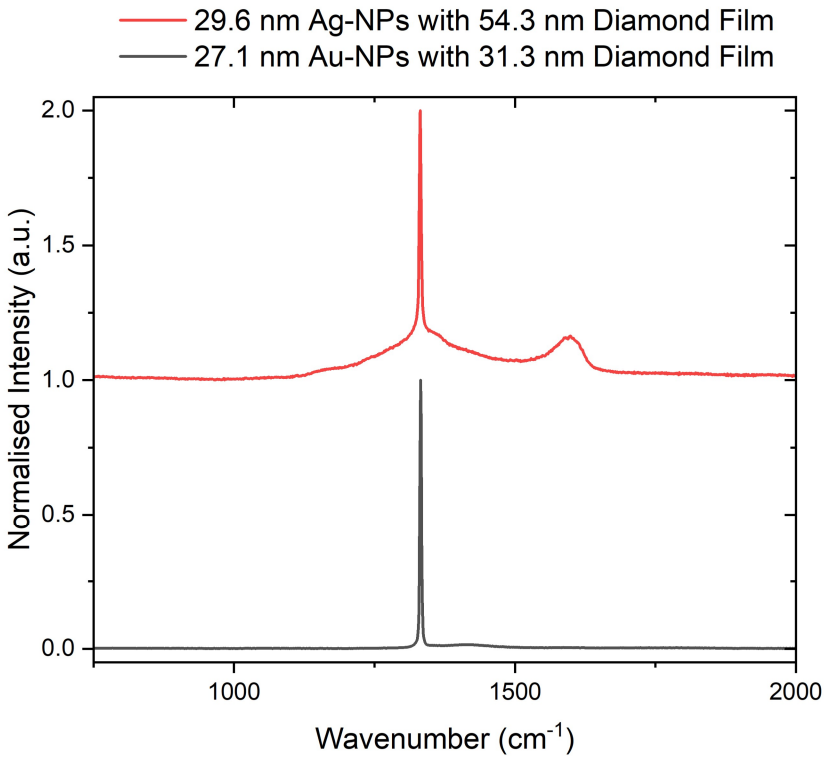



Figure S12: Substrate Raman spectra following 1 hour 400 ℃ anneal in atmosphere. No additional peaks or noticeable increase in intensity can be seen in the spectrum indicating resistance to combustion at this temperature. Spectra are offset in y to aid comparison.

## Example enhancement factor calculation

Using values from a SERS measurement of the optimised fabricated film (27.1 nm Au-NP: 31.3 nm diamond film):

$$EF = \frac{I_{SERS}/N_{SERS}}{(I_{Raman}/N_{Raman}) \times \frac{Re_{SERS}}{Re_{Raman}}}$$

To calculate $N_{RAMAN}$:

$$D = \frac{1.22\lambda}{NA} = \frac{1.22 \times 532}{0.75} = 865\ nm$$

(SERS active beam area)

$$A_{eff} = \pi(\frac{D}{2})^2 = \pi(\frac{865}{2})^2 = 588180\ nm^2$$

largest R6G molecule could be 4 $nm^2$,
assuming R6G molecules have formed a monolayer on surface given analyte sampling method (pipette, rinse, dry)

$$N_{RAMAN} = \frac{A_{eff}}{R6Garea} = \frac{5488180}{4} = 147045 \text{ molecules}$$

To calculate $N_{SERS}$: Average % coverage of 27.1 nm Au-NPs (from SEM and ImageJ) = 28.19%

$$A_{eff} \text{ with NPs} = A_{eff} \times 0.2819 = 588180 \times 0.2819 = 165808\ nm^2$$

$$N_{SERS} = \frac{165808}{4} = 41452$$

Enhancement Factor:

$$EF = \frac{I_{SERS}/I_{0,SERS} \times t_{SERS} \times N_{SERS}}{(I_{RAMAN}/(I_{0,RAMAN}) \times t_{RAMAN} \times N_{RAMAN}) \times \frac{Re_{SERS}}{Re_{RAMAN}}}$$

$$EF = \frac{I_{SERS}/7.65 \times 10^{14} \times 20 \times 41452}{(605/(7.65 \times 10^{18}) \times 20 \times 147045) \times \frac{Re_{SERS}}{4275}}$$

$$EF = \frac{I_{SERS}/7.65 \times 10^{14} \times 829040}{(2.326 \times 10^{-10}) \times \frac{Re_{SERS}}{4275}}$$

$$EF = \frac{2611/7.65 \times 10^{14} \times 829040}{(2.326 \times 10^{-10}) \times \frac{6788}{4275}} = 7661 = 7.7 \times 10^3$$

EF values are averaged from the calculations of three SERS measurements. Using this calculated value (and the two others) the average EF for this area (27.1 nm Au-NP: 31.3 nm diamond film) = 6.9 $\times 10^3$