Supporting Information

Ultralarge Area Sub-10 nm Plasmonic Nanogap Array by Block Copolymer Self-Assembly for Reliable High-Sensitivity SERS

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Supporting information text (materials, experimental section) Figures S1 to S6

Materials

All the polymers including BCPs and hydroxyl-terminated PS-*r*-PMMA random copolymers were purchased from Polymer Source Inc. Toluene (99.8 %, anhydrous) and thiophenol (97 %) was purchased from Sigma Aldrich. Tetrahydrofuran (99.5 %) was purchased from J.T. baker.

Experimental Section

Preparation of polymer films.

BCPs and hydroxyl-terminated random copolymers were used as-received without any purification process. Surface energy of all the silicon substrates was neutrally modified with the hydroxyl terminated PS-*r*-PMMA random copolymer brush treatment. Briefly, PS-*r*-PMMA brush thin film was spin coated as 1 wt% toluene solution on an UV ozone treated silicon substrate. The substrates were thermally treated at 160 °C in vacuum for 12 hours and then the substrate was rinsed by toluene to remove unreacted random copolymer brush. PS-*b*-PMMA (M_n : 63 kg mol⁻¹-*b*-142 kg mol⁻¹) thin film was spin coated on the brush treated silicon substrate from 2 wt% toluene solution. The BCP thin films were annealed in the tetrahydrofuran (THF) vapor atmosphere for 1-2 hours at room temperature.

Au nanogap array formation

To obtain Au nanogap array, PMMA matrix of self-assembled BCP thin film were selectively etched by an O₂/Ar plasma reactive ion etching (RIE). The remaining PS post array was cross-

linked by UV irradiation to prevent the pattern collapse. Au thin film was e-beam evaporated onto the entire substrate surface with the deposition thickness of 10 - 80 nm.

Preparation of samples for Raman spectroscopy

Self-assembled BCP nanostructures were characterized by a Hitachi S-4800 Scanning Electron Au nanogap arrays were immersed in a 1 mM thiophenol in ethanol for 12 hours in an atmospheric condition. Then, the samples were washed several times and dried under the gentle blowing of nitrogen gas. For the biomolecular detection, Au nanogap arrays were immersed in an aqueous adenine solution for 15 min. Afterwards, the sample were washed by DI water several times and dried in an atmospheric condition.

FDTD simulation of electric fields

In order to calculate the optical properties of plasmonic nanogap arrays, complex permittivity of Au was modeled. Au permittivity was calculated using a Lorentz model with size effect.^[1] With these material parameters, numerical simulations were conducted using the finite-difference time-domain method. The plasmonic nanogap array was in a hexagonal lattice and the center-to-center distance between nano particles was 130 nm based on experimental results. The simulation volume was meshed into 0.5 nm resolution in the nanogap region. Far removed from the nanogap regions, a larger mesh size was used to reduce computational load. An *x*-polarized plane wave source, propagating in *z*-direction, was used. Anti-symmetric and symmetric boundaries were employed in *x*- and *y*-direction and perfectly matched layers were adopted in the ends of *z*-direction. Three- and two-dimensional monitors were used to collect

electric field data for calculation of the averaged electromagnetic field enhancement and reflection.

SERS Enhancement factor calculation

Raman spectra were collected 5 times for 5 seconds for all the samples using He-Ne laser (λ : 632.8 nm) focused on the samples with a ×50 object lens. The diameter of focused laser beam was 1 µm with the power of 4.25 mW. A thiophenol grafted plain Au thin film was selected as a reference sample. Enhancement factor of SERS was calculated by following equation.

$$\text{EF} \approx \frac{I_{SERS}}{I_{Ref}}$$

where I_{SERS} is the Raman scattering intensity for SERS measurement and I_{Ref} is the Raman scattering intensity from a reference sample (i.e. planar Au thin film). In case of the plasmonic SERS substrate, SERS is mainly occurred at a narrow interparticular gap region, and thus it is difficult to determine an exact number of molecules at the region. So, we assumed that the SERS substrate is a planar surface.

Characterizations

In-plane and cross-sectional morphologies of BCP nanostructures and Au nanogap arrays were characterized using a Scanning Electron Microscopy (SEM, Hitachi S-4800) and Transmission Electron Microscopy (TEM, FEI Talos F200X). All the absorption spectra were collected using

UV/VIS/NIR Spectrophotometer (SolidSpec-3700, Shimadzu) with reflective geometry, and a neat polished silicon was used as a reference mirror to collect spectra only coming from the nanoparticle array (i.e. excluding an absorption effect from bottom silicon substrate). Raman spectra of thiophenol molecules on nanogap arrays were acquired using a high-resolution dispersive Raman spectrometer (LabRAM HR, Horiba Jobin Yvon) and a 633 nm laser with a power of 1 mW focused on the sample surfaces (Beam diameter: 1 μ m). Raman spectra were collect 5 times for 5 seconds for all samples. GISAXS for Au nanogap arrays was performed at the 3C beamline in Pohang Accelerator Laboratory (PAL), Korea. The critical incident angle was 0.22°.



Figure S1. (a) HAADF and (b) EDAX mapping of cross-sectional plasmonic nanogap array.



Figure S2. GISAXS analysis of plasmonic nanogap array. (a) 2D GISAXS image of the plasmonic nanogap structure. (b) in-plane cuts at $q_z = 0.037$ and (c) out-of-plane cut at $q_{xy} = 0.01$ in the GISAXS data.



Figure S3. (a-d) Morphology evolution of nanogap array with deposition thickness. Each of inset figure shows their voronoi mapping. (e) Distribution of number of neighbors as a function of deposition thickness.



Figure S4. (a) Au nanogap arrays in 2 in. wafer with 60 nm deposition thickness, and (b-f) representative SEM images at the 5 points in 2 in. wafer of figure S4a.



Figure S5. (a) All Raman spectra of thiophenol at plasmonic nanogap arrays with different nanogap distances. (b) Normalized SERS signal intensities of thiophenol at 999, 1021, and 1073 cm-1, where the signal is normalized to that with a deposition thickness of 60 nm.



Figure S6. Measured SERS signals of adenine biomolecules at different concentrations by means of a nanogap array with 9.2 nm gap distance.

REFERENCES

 Derkachova, A.; Kolwas, K.; Demcheko, I., Dielectric Function for Gold in Plasmonics Applications: Size Dependence of Plasmon Resonance Frequencies and Damping Rates for Nanospheres. *Plasmonics* 2016, *11*, 941-951.