Supporting information

Bottom-up growth of Ag/a-Si@Ag Arrays on Silicon as a Surface-Enhanced Raman Scatting Substrate with High Sensitivity and Large-area Uniformity

Liwei Liu,^a Mingliang Jin,^b Qingwei Zhou,^a Runze Zhan,^c Huanjun Chen,^c Xubing Lu,^a Xingsen Gao,^a Stephan Senz,^d Zhang Zhang,^{a*} and Junming Liu,^{e*}

^{*a*} Institute for Advanced Materials and Laboratory of Quantum Engineering and Quantum Materials, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, People's Republic of China.

^b Electronic Paper Display Institute, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, People's Republic of China.

^c State Key Laboratory of Optoelectronic Materials and Technologies, Guangdong Province Key Laboratory of Display Material

and Technology, School of Physics and Engineering, Sun Yat-sen University, Guangzhou 510275, People's Republic of China.

^d Max Plank Institute of Microstructure Physics, Weinberg2, Halle06120, Germany.

e Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China

International Center for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, China

*email: zzhang@scnu,edu.cn



Fig. S1 Low magnification SEM images of Ag NPs arrays on Si substrate to illustrate the solid-state dewetting behavior. The samples were annealed at 540 $^{\circ}$ C with different annealing time: (a) 20 min, (b) 60 min. The Ag NPs were obtained through the dewetting of continuous Ag films with a 15 nm thickness. The substrates were heated up to 540 $^{\circ}$ C in 30 min in the CVD chamber and annealed with a pressure of 10 Torr and an H₂ mass flow of 40 sccm.



Fig. S2 Top-view and 75⁰ tilted-view SEM images of Ag/a-Si nanosphere arrays grown on Si substrate by a CVD with growth times: (a), (b) 30 min, (c), (d) 60 min.



Fig. S3 TEM images of individual Ag/a-Si nanosphereS with different growth times of Si: (a), (b) 30 min, (c), (d) 60 min. The thickness of a-Si shell increased with the growth time.



Fig. S4 (a) TEM image of Ag/a-Si NSs after CVD process with a growth time of 30 min, which were separated from the substrate. The average diameter of Ag NPs is 73 nm, and the a-Si layer was uniformly grown onto the Ag cores. (b) Selected-area electron diffraction (SAED) pattern from Ag/a-Si NSs showed a polycrystalline structure of Ag cores, with, $\{2 \ 0 \ 0\}$, $\{2 \ 2 \ 0\}$, $\{3 \ 1 \ 1\}$ planes according to the JCPDS file number 04-0783. ^{1,2}



Fig. S5 Top-view SEM images of the Ag/a-Si@Ag nanosphere arrays with different Ag out-layer coating thickness: (a) 5nm, (b) 10nm, (c) 15nm, (d) 20nm, (e) 25 nm, (f) 30 nm. With the increase of coating thickness, the Ag out-layer was from a serious of discrete NPs to a continuous film.



Fig. S6 (a) SERS spectra of p-Tc molecules chemisorbed on the Ag/a-Si@ Ag nanosphere arrays with different Ag coating thickness (5nm, 10nm, 15nm, 20nm, 25nm, 30nm). (b) Plots of the Raman peak intensities of 1076 cm-1 with different Ag coating thicknesses, on SERS substrate (red line) and plain Si substrate (black line). The Raman intensity obtained on plane Si substrate is small compared with the ones on SERS substrate.



Fig. S7 (a)SERS spectra of p-Tc (chemisorbed at a concentration of 10^{-13} M) on different positions of the sameAg/a-Si@Ag nanosphere arrays as SERS substrate. (b) Raman spectra of p-Tc (chemisorbed at concentrations from 10^{-5} M to 10^{-9} M) on a plane Si substrate with a 15 nm thick Ag film coating. The detection limit of the plane Si substrate is 10^{-6} M. The laser wavelength is 633 nm and the acquisition time is 10 s.



Fig. S8 Schemes of 2-D FDTD simulations illustrate the electric field distribution in a model of two adjacent Ag/a-Si@Ag NSs with different inter-sphere gaps: (a) 5 nm, (c) 10 nm, (d) 20 nm. (b) Electric field intensity distribution curve along the X axis corresponding to (a), calculated at an excitation wavelength of 633 nm.



Fig. S9 (a) A schematic drawing of our approach to estimate the number of analyte molecules trapped in the hot spots between two NSs. The hot spot region is assumed to comprised a cap (red area) on the surface of each sphere.³ The number of trapped molecules (N_{trap}) was obtained by calculating the total surface area of the two caps. In our FDTD simulation, bottom radius of the cap is about 25 nm, thus h = 4 nm (where h is the height of the cap and r is the mean radius of the NSs). (b) Raman spectra obtained from the SERS substrate (red curve) and pure powder of p-Tc on a plane glass substrate (black curve). For clarity, the signal of pure powder of p-Tc has been multiplied by 10 marked in the curve.



Fig. S10 Intensities of Raman peaks p-Tc molecules at 1076 cm⁻¹ (a) and 1593 cm⁻¹ (b) of the at 100 locations. The calculated relative standard deviation (RSD) of the Raman intensity is 8 % and 9 %, respectively.

Calculation of SERS EF

To estimate the Enhancement Factor (EF) of the SERS substrate, p-Tc solid films of known volume and weight was placed on a clean glass slide for the measurement of normal Raman spectrum. The SERS peaks of 1076 cm⁻¹ and 1593 cm⁻¹ correspond to the p-Tc Raman peaks of 1093 cm⁻¹ and 1595 cm⁻¹, respectively. EF of p-Tc on Ag/a-Si@Ag nanosphere arrays was calculated for the SERS peaks at 1076 cm⁻¹ and 1593 cm⁻¹.

The experimental Raman EF of the SERS substrate was estimated using the equation:

$$EF = \frac{I_{SERS}}{I_{bulk}} \frac{N_{bulk}}{N_{SERS}}$$
(Eq. S1)

Where I_{SERS} denotes the Raman intensity of the p-Tc molecules under the condition of Ag/a-Si@Ag nanosphere arrays and I_{bulk} represents the Raman intensity of the p-Tc molecules under non-SERS conditions. N_{SERS} is the number of the p-Tc molecules contributing to the SERS signals, N_{bulk} is the number of the p-Tc molecules used for the non-SERS measurement. For the calculation of N_{bulk}, different methodologies have been reported to estimate it.^{4, 5} Here, we used pure p-Tc powder to get values of N_{bulk}. The number of molecules excited in the non-SERS substrate was determined by assuming the excitation volume, which had the shape of cylinder with circle diameter equal to the focused laser beam spot diameter and height equal to the effective probe depth (H_{obj}).The objective lens (50×, 0.6) was used, and the focus laser beam diameter is 1.54 µm.⁶ The H_{obj} was determined by changing the substrate sample stage out of the laser focus plane at 1µm increments and recording the Raman peak value at 1076 cm⁻¹ at each position.⁷ While integrating the maximum Raman intensities over all positions, the 1/2 power points were recorded, yielding H_{obj} =16.5 µm. The number of molecules N_{bulk} in the bulk sample inside the interaction volume (30.88 µm³) was calculated to be 1.50×10^{11} molecules. While focusing on the centre of the non SERS substrate, I_{bulk} was measured at the excitation wavelength of 633 nm. The average background intensity was subtracted from the Raman spectrum to obtain the real peak value. The Raman intensity (I_{bulk}) at 1076 cm⁻¹ and 1595 cm⁻¹ was calculated to 224 counts and 70 counts, respectively.

To measure the number of N_{SERS}, p-Tc molecules chemisorbed on the surface of Ag/a-Si@Ag nanosphere arrays (after 1 hour incubation), the density of p-Tc molecules can be estimated to be sub-monolayer. Here the coverage of p-Tc molecule for a dense monolayer was estimated to be about 4 molecules/nm^{2,8} Taking the topography of the Ag/a-Si@Ag NSs surface into consideration, as shown in SEM image, approximately 30 spheres were seen in the laser focus area. It is assumed that all the spheres in the laser spot have contributed to the SERS signals and the probe molecules are distributed evenly across the surface of spheres. The effective surface area underneath the laser was $1.36 \,\mu\text{m}^2$. This gives an estimate of N_{SERS} calculated to be 5.44×10^6 . Using identical conditions as for I_{SERS} , a Raman intensity of 6834 counts at 1076 cm⁻¹ and 4641 counts at 1593 cm⁻¹ were measured. Hence, the mean EF came to 8.4×10^6 and 1.83×10^6 , respectively.

If we assumed that it was only molecules located on the gaps between the Ag/a-Si@Ag NSs, i.e. the "hot spots" were the main factors that contributed to the Raman enhancement signals a higher enhancement factor is estimated. Finite difference time domain (FDTD) calculations had been used for further insight into the possible geometries of highly active sites. 2-D FDTD simulations of the electromagnetic fields distribution showed that the hot spot region was a cap on the surface of each nanosphere in the inter-particle region (red color), as illustrate in Figure S9. That is, just the probe molecules trapped in the hot spot regions contributed to the detected SERS signals. In our estimation, N_{trap} is obtained by calculating the total surface area of the cap among average 30 NSs. Here we assume h = 5 nm (where h is the height of the cap and r = 85 nm is the radius of the spheres), and yield $N_{trap} = 3.20 \times 10^5$. This number represents a theoretical maximum number of molecules. For the gap distance between two spheres exceeding 15 nm, no distinct Raman enhancement signals were observed. However, we neglected this. According to such an approach, the EFs of the hot spot were calculated to be: EF (1076 cm⁻¹) = 1.43×10^7 ; EF (1593 cm⁻¹) = 3.11×10^7 .

- 1 Z. Zoya, Rafiuddin, Colloids Surf. A: Physicochem. Eng. Aspects 2011, 384, 427.
- 2 N. Ahmad, S. Sharma, M. K. Alam, V. N. Singh, S. F. Shamsi, B. R. Mehta, A. Fatma, Colloids Surf. B: Biointerfaces 2010, 81, 81.
- 3 W. Li, P. H. Camargo, X. Lu, Y. Xia, Nano lett. 2009, 9, 485.
- 4 M. S. Schmidt, J. Hübner, A. Boisen, Adv. Mater. 2012, 24, 8.
- 5 H. Mao, W. Wu, D. She, G. Sun, P. Lv, J. Xu, Small 2014, 10, 127.
- 6 A.-P. Ramón, Phys. Chemi. Lett. 2012, 3, 857.
- 7 M. A. Khan, T. P. Hogan, B. Shanker, *JNST* 2009, 1,1.
- 8 C. Jianing, Y. Weisheng, D. Kimberly, D. Knut, H. Q. Xu, S. Lars, X. Hongxing, Appl. Phys. Lett. 2008, 92, 93.