

Quantum upper limit SERS from sub-1-nm random gaps for quantitative chemical and biological sensing

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Abstract: We report a strategy to fabricate high-density random metallic nanopatterns with accurately controlled nanogaps defined by atomic-layer-deposition and self-assembled-monolayer processes for quantitative chemical and biological sensing with a record-high uniformity over a large area. © 2021 The Author(s)

OCIS codes: (240.6695) Surface-enhanced Raman scattering; (220.4241) Nanostructure fabrication; (160.3918) Metamaterials; (250.5403) Plasmonics; (270.0270) Quantum optics

Metallic nanostructures with nanogap features can confine electromagnetic fields into extremely small volumes [1]. In particular, as the gap size is scaled down to sub-nanometer regime, the quantum effects for localized field enhancement reveal the ultimate capability for light-matter interaction [2]. Although the enhancement factor approaching the quantum upper limit has been reported, the grand challenge for surface enhanced vibrational spectroscopic sensing remains in the inherent randomness, preventing uniformly distributed localized fields over large areas. Here we report a strategy to fabricate high-density random metallic nanopatterns with accurately controlled nanogaps defined by atomic-layer-deposition (ALD) and self-assembled-monolayer (SAM) processes [3]. As the gap size approaches the quantum regime, we demonstrate its potential for quantitative sensing based on a record-high uniformity with the relative standard deviation (RSD) of 4.3% over a large area of 22 mm × 60 mm. This superior feature paves the way towards more affordable and quantitative sensing.

The process flow to fabricate random nanogap structures is illustrated in **Fig. 1a**. First, a silver (Ag) film was deposited onto a pre-cleaned glass substrate using electron-beam evaporation. Following previously reported lithography-free fabrication technique, thermal annealing was used to manipulate the average morphology (e.g., size, spacing) of the first layer of Ag NPs. Then, these NPs were covered by a 1-nm alumina (Al₂O₃) film deposited by ALD. With subsequent evaporation of the second metal layer (e.g., a 10-nm-thick Au film in our experiment), the original gaps will be filled. Therefore, a tiny gap introduced by the ALD layer can be obtained between the first and the second metal patterns. After that, an optical adhesive (NOA 71, Norland Products Inc.) was applied to attach the surface of the film to a glass slide, and cured under a UV lamp. Finally, the entire film was peeled off to obtain the proposed random nanogap structure. Although these directly deposited NPs are random in shape and local spatial distribution, the gaps were independently controlled by the ALD process.

Following this procedure, we fabricated 4 representative samples with different dimensions and densities for the first metal NP layer. As shown in **Figs. 1b-1d**, the initial thicknesses of the first Ag metal layer are 10 nm, 12 nm, and 15 nm, respectively, followed by thermal annealing of 300 °C to form different nanopattern templates. The initial metal can also be Au (or other metals) to obtain different morphologies (e.g., an 8-nm-thick Au film followed by thermal annealing of 400 °C as shown in **Fig. 1e**). One can see that these metallic NPs were clearly surrounded by a dark line, i.e., the 1-nm-thick dielectric film defined by ALD processes as shown in **Figs. 1b-1e**. To reveal the microscopic

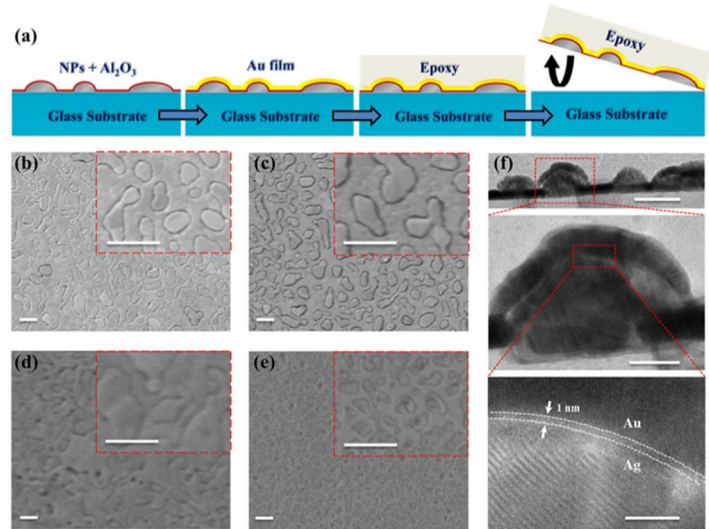


Fig. 1 (a) Schematic of the device fabrication process. (b-e) Top-view scanning electron microscope (SEM) images of different buried random nanopatterns. Red dotted squares: Further zoomed-in images show a 1 nm nanogap surrounding the existing nanopatterns. Scale bar: 300 nm. (f) Cross-sectional TEM of a 10-Å-wide Al₂O₃ layer between Ag and Au layers. Scale bar: 100 nm (Up), 30 nm (Middle), 10 nm (Bottom).

features, we employed the high-resolution transmission electron microscopy (TEM) to verify the 10-Å-thick Al_2O_3 layer on the sidewall of a cross-sectional Ag/ Al_2O_3 /Au nanogap (**Fig. 1f**). Due to this lithography-free process, these random nanogap structures can be fabricated over large areas in foundry facilities to overcome the cost barrier. Importantly, since the gap size is close to the quantum regime, these inexpensive random nanogap structures are attractive to realize boosted field enhancement for vibrational sensing applications.

Remarkably, it is feasible to introduce other materials (e.g., molecules, quantum dots, fluorophores, etc.) into these nanogaps to boost light-matter interaction for optical sensing. As illustrated in **Fig. 2a**, we fabricated a nanogap sample on a glass slide ($22\text{ mm} \times 60\text{ mm}$) using a SAM of 4-methylbenzenethiol (4-MBT) molecules as the isolation

layer and cut it into 12 pieces ($11\text{ mm} \times 10\text{ mm}$). In this experiment, a 12-nm-thick Ag film was first deposited onto a pre-cleaned glass substrate using electron-beam evaporation followed by 300°C thermal annealing process for 1 hour. Next we placed $10\text{ }\mu\text{L}$ 4-MBT methanol solutions with the concentrations ranging from 100 mM to 1 pM onto each piece to control the effective thickness of the molecule layer thickness. Then, these chips were air-dried for the second 10-nm-thick Au layer deposition to form the ultimate nanogap chips for SERS sensing. As shown in **Fig. 2a**, the signature Raman peaks of 4-MBT at ~ 1078 and $\sim 1592\text{ cm}^{-1}$ were observed clearly through a $20\times$ objective lens. Remarkably, low concentration down to 1 pM is still observable as shown by the inset of **Fig. 2a**, representing the record high performance of SERS sensing of this particular molecule, 3 orders of magnitude better than previous literature based on ordered nanopillar SERS chips [4]. The most intriguing phenomenon is that the signal amplitude maximized at the concentration of $\sim 1\text{ mM}$. The signal amplitude decreases for both higher (i.e., region I) and lower molecule concentrations (i.e., region II), indicating that quantum enhancement limit regime was approached at this concentration. In particular, in the low concentration region II, those measured data points can be fitted using the Langmuir model. In our experiment, the concentration-dependent SERS signal intensity profile can be fitted by the Langmuir adsorption isotherm very well with the fitting degree, R^2 , of 0.9978, as shown by the solid curve in **Fig. 2b**. Importantly, this ideal fitting degree indicates the potential for quantitative sensing of 4-MBT at a low concentration range (i.e., region II).

To validate the quantitative sensing capability, small and large area uniformity over the fabricated sample is essential (i.e., the $22\text{ mm} \times 60\text{ mm}$ glass slide). As shown in **Fig. 2c**, we still cut the sample into 12 pieces. On each small piece, a two-dimensional Raman mapping at the peak of $\sim 1078\text{ cm}^{-1}$ was performed using the $20\times$ objective lens, resulting in 900 data points collected on each small sample. The RSD of these 12 pieces ranges from 1.80% (**Fig. 2d**) to 2.60%. To our best knowledge, this uniformity is much better than previously reported SERS substrates. By analyzing all 10800 points from all 12 pieces, the RSD of Raman intensities on this $22\text{ mm} \times 60\text{ mm}$ slide is 4.3%. This slightly larger RSD can be attributed to the surface molecule distribution difference and the fabrication variation of random NPs over large areas on the entire slide. However, this value is much better than most previously reported results on different SERS nanostructures fabricated by various advanced nanomanufacturing methods.

In conclusion, we developed a high-density random metallic nanogap structure based on lithography-free ALD and SAM procedures to approach the quantum plasmonic enhancement limit.

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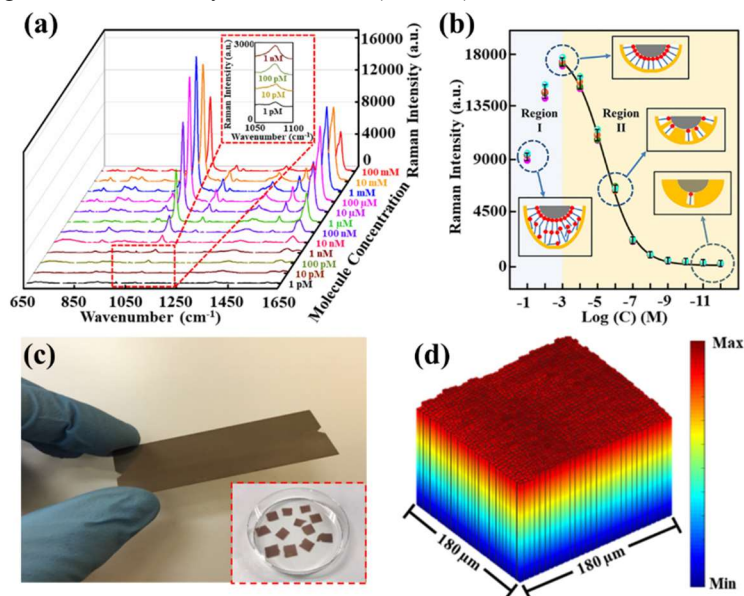


Fig. 2 (a) SERS spectra of 4-MBT solutions with different concentrations on the nanogap structure. (b) Relationship between the Raman intensities at the peak of $\sim 1078\text{ cm}^{-1}$ and different concentrations of 4-MBT methanol solutions. Inset: Illustrated molecule distributions at different concentration levels. (c) Photograph of the fabricated random nanogap structures on a glass slide ($22\text{ mm} \times 60\text{ mm}$). Inset: 12 pieces cut from the whole sample on a glass slide. (d) Raman mapping of random nanogap structure over a $180\text{ }\mu\text{m} \times 180\text{ }\mu\text{m}$ area.