Development of optimized nanogap plasmonic substrate for improved SERS enhancement

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SERS enhancement factor (EF) of planar substrates depends on the size and shape of the fine nanostructure forming a defect free, well-arranged matrix. Nano-lithographic process is considered to be the most advanced methods employed for the fabrication SERS substrates. Nanostructured plasmonic substrates with nanogap (NG) pattern often results in stable, efficient and reproducible SERS enhancement. For such substrates, NG and their diagonal length (DL) need to be optimized. Theoretically smaller NGs (∼30-40 nm or smaller) results in higher SERS enhancement. However, fabrication of NG substrates below such limit is a challenge even for the most advanced lithography process. In this context, herein, we report the optimization of fabrication process, where higher SERS enhancement can be realized from larger NGs substrates by optimizing their DL of nanostructures between the NGs. Based on simulation we could demonstrate that, by optimizing the DL, SERS enhancement from larger NG substrate such as 60 and 80 nm could be comparable to that of smaller (40nm) NG substrates. We envision that this concept will open up new regime in the nanofabrication of practically feasible NG based plasmonic substrates with higher SERS enhancement. Initial results of our experiments are in close agreement with our simulated study. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4984769]

I. INTRODUCTION

Surface Enhanced Raman Spectroscopy (SERS) is an optical modality employed for the detection of wide range of analyte from biological to chemical origin.1,2 SERS produces the enhanced vibrational Raman fingerprint of a molecule, which has the potential for being a sensitive analytical tool, even up to the limit of a single molecule. One of the main components of a SERS sensor is the substrate on to which the analyte molecules are physically or chemically adsorbed. Even after more than three decades of research into this field, there is a great demand for simple to fabricate, stable, reproducible and scalable SERS substrate with high density of ‘hot spots’ in a given area. Such stable and reliable plasmonic substrate with high electromagnetic field enhancement (EMF) find tremendous application not only in SERS3 but also in areas such as Metal-Enhanced Fluorescence (MEF)4–9 and metamaterials10–15 etc. The plasmonic nanostructures act like optical nano antennas accumulating and building electromagnetic energy in nanometer-scale, which are called as ‘hot spots’.16–18 This energy results in high local electrical fields, which results in a dramatic enhancement of optical responses. For SERS applications, local electrical field enhancements in the near-field region are the important contributor for the EF/SERS enhancement.19 The local enhancement in the ‘hot spots’ can

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be in the order of $10^6$ to $10^{12}$. These SERS active substrates can exhibit a high sensitivity which results in single-molecule detection.

There are several types of SERS substrates that are available, such as Silicon or metal-based Nanopillars, Random array made of metal nanoparticle, hexagonally packed polymer based Nanosphere lithography, and by growing plasmonic substrate with bottom-up technique such as oblique angle deposition. Compared to them silicon based NG substrate shows a high SERS enhancement. Electrical field enhancement depends on the NG size and it is non-linear, maximum enhancement is achieved when the NG size is $\sim 10$ nm or lower. Though the theoretical limitation of NG is about 1 nm, so far it has been shown only in colloidal nanoparticles. There is a fabrication constraint to make nanostructures with low NG size. Here we expanded our understanding beyond just controlling the NGs to lowest possible value to improve SERS enhancement and also correlate another interesting parameter called DL, which can be altered and tuned for substrate with fixed NG.

In this paper we discussed about the possibility of fabricating plasmonic substrate with high enhancement factor for the fixed NG size by varying the DL between the NG. We have experimentally validated the findings using 2-Naphthalenethiol (2-NT) as Raman active reporter molecules. From our simulation results we found that even for larger (NGs $> 60$ nm) structures, SERS intensity can be enhanced by optimizing the DL of the nanostructures on the substrate.

II. METHODS

A. Materials

All the chemicals are obtained from Sigma-Aldrich and used as received. Field emission scanning electron microscope (FE-SEM) from Joel, was used for imaging the samples. The DL between the NG substrates is measured using “imageJ” programme.

B. NG substrate fabrication

The complete fabrication protocol is based on our previous work. In brief, the lithographic process used in this method is Deep UV exposure to pattern nanostructures with positive photoresist ($\sim 40 \mu$m). Pre-exposure baking was done at 130 °C for 90 S followed by 60 S of puddle development. The photomask used in this experiment is a single binary mask with circular patterns. The exposure dosage was 74 -78 mJcm$^{-2}$. After developing the wafer, silicon etching has been performed in an ICP (Inductively coupled plasma) system using SF$_6$ and C$_4$F$_8$ chemistry to realize nano-dimensional patterns. After the etching process an additional oxidation step is used in order to control the gap between nanostructures. The depth of the etching is maintained at about 140-160 nm. The resultant NG SERS substrate was obtained by coating 30 nm Ag and 15 nm Au over Ag layer using an e-beam evaporation system. Such a bimetallic coating will provide sufficient plasmonic enhancement from Ag, while the top Au layer provides the protection for Ag from oxidation.

C. Raman probe

2-Naphthalenethiol (2-NT) was used as the Raman active molecule in this study. First, 100$\mu$M of 2-NT (in 100% ethanol) was prepared and sonicated for 10 min to dissolve the analyte. Then, NG substrate with varying gap are incubated with 2-NT solution for 1 hour and subsequently washed with ethanol. This will result in a monolayer of 2-NT on the NG substrate. We have monitored the SERS intensity count for 1066 cm$^{-1}$ peak of 2-NT throughout the experiment to evaluate the performance of various NG substrates. Multiple measurements were made at different locations within the substrate and the final SERS intensity calculated was the average of minimum 5 measurements.

D. SERS measurement

SERS spectra’s were collected using Renishaw InVia Raman microscope (Renishaw InVia, UK) with 785 nm excitation. System was integrated into a microscope (Leica) and laser light was coupled through an objective lens (50X, 0.75 N.A.), which was used to excite the sample and also to collect the return Raman signal Rayleigh scattering was blocked with the help of a notch filter and beam
spot on the sample was $\sim 1 \mu m$. We used an integration time of 10 s for spectral acquisition. For each NG size, several scans were collected at various spots on the SERS substrates. After collecting the SERS spectra, post-processing was done using wire 3.4 software associated with the instrument. The background subtraction was done by a cubic spine interpolation. The instrument was calibrated with signal from standard silicon at 520 cm$^{-1}$.

### III. RESULT AND DISCUSSION

We have fabricated the NG SERS substrates using conventional CMOS process. In order to obtain SERS substrate with varying NG, we increased the silicon etching time after DUV lithography process. All the fabrication protocols are fixed, such as the ratio of the etching gas and the type of silicon wafer etc. By increasing the etching time, the foot prints of the NG structure decreases leading to increased distance between nanostructures, as shown in figure 1. As a result, five different bimetallic NG SERS substrates were fabricated with the NGs ranging from 40 nm up to 140 nm. The DL for SERS substrate with 40 nm NG size was found to be 252 nm. Similarly for 60, 80, 100 & 140 nm NG size, the corresponding average DL was 228, 209, 203 & 155 nm respectively.

The SERS spectra for 2-NT is shown in figure 2A, among the different NG SERS substrate used in our study, we found that the 40 nm NG size with the DL of 252 nm gave the highest SERS intensity. This is attributed to the high SERS enhancement originated from closely packed nanostructure that leads to high EM coupling. This EM coupling results in additional near-field enhancement in the NG, forming the so-called ‘hot spots’ and this improves the Raman reporter molecule enhancement factor by many folds.$^{33-35}$ Upon increasing the NG size, the corresponding signal intensity was reduced drastically. As shown in figure 2B, the signal intensity of 140 nm NG was reduced to less than 2% to that of 40 nm NG substrate.

This can be attributed to the large distance between the nanostructures that couple EM and gives rise to sudden decrease in near field enhancement which results in very low SERS enhancement.

![FIG. 1. FE-SEM image of the silicon based SERS substrate with varying NGs. (A) 40 nm, (B) 60 nm, (C) 80 nm, (D) 100 nm, and (E) 140 nm. The inset shows the magnified images with scale bar 100 nm.](image-url)
We have shown the average 2-NT spectra for NG substrate with different NG’s in figure S1, as supplementary material.

Multiple 2-NT SERS spectra were collected from different locations on the 40 nm NG substrate (few tens of micro meters apart) and found that the SERS intensity is varying at few points; at the same time we observed negligible variation in NG within the substrate. We observed SERS intensity variation of ~10% on an average, as shown in figure 2C; To confirm our findings, we have also performed SERS intensity mapping using the streamline setting of the Renishaw Raman microscopic system using characteristic peak at 1066 cm⁻¹ of 2-NT Raman reporter molecule, as shown in Figure S2 of the supplementary material. Mapping was done on the NG substrate at an approximate area 500 µm × 400 µm and could able to clearly observe SERS enhancement distribution all over
the substrate. We could able to spot regions with relatively less enhancement in-between the high enhancement regions. The high enhancement region is shown in bright red color and relatively less enhancement regions were shown in shades of black (dark patches). We could attribute this change in signal intensity due to possible variation in their DL. Since it is highly difficult to locate the exact point at which the strong SERS signal is obtained, we could not produce their corresponding FE-SEM image to elucidate the change in the nanostructure pattern. In order to investigate the reason behind varying SERS enhancement within the same NG substrate, we have done the theoretical study using parameters similar to that of the experimental condition, such as NG size, DL and the height of the nanostructures to understand their inter-dependency resulting in higher SERS enhancement.

IV. SIMULATION ON PLASMONIC SUBSTRATE

For our simulation study, we have used finite element method (FEM) to calculate the normalized electrical field (|E|) which corresponds to SERS enhancement arising from the nanostructured substrate with different NG sizes and DLs. As the SERS substrate is identical on two directions, the cross section of the NG SERS substrate (2D) is built for simulation with 785 nm laser light source.

FIG. 3. (A) Scheme of simulation, the NG structure was excited with 785nm light from top. (B) Calculated normalized electrical field intensities versus DL’s, the colored curves represent different NG and the red circles represent the DL experimental obtained from data for different NG’s.
excited from top of the boundary. According to the SERS substrate design, the nanostructures were on the top of the silicon layer with 30 nm and 15 nm of silver and gold coating on the top of the structures, respectively. The DL of nanostructures and the NG between them are the two variables in the simulation, which were clearly shown in figure 3A. Plasmonic ‘hot spot’ is created between the nanostructures and concentrated within the NG.

During simulation, the NG size of the model is changed from 35 nm to 140 nm and DL varied from 270 nm to 155 nm for each gap size. It can be observed that the nanostructure create strong ‘hot spot’ between the NG, which explains the strong SERS enhancement originated from the substrate. The calculated SERS enhancement at the center of the ‘hot spot’ is recorded for each gap size and DL.

The simulation results are plotted in Figure 3B. The curves in different colors correspond to different NG (gap sizes) between 40 nm to 140 nm and the experimental data (in red circles) represents the DL from 155 nm to 270 nm corresponding to each NG. Each curve represents the SERS enhancement of the substrate with a fixed NG size and a changing DL. According to the results, at a fixed DL, smaller gap size results in stronger SERS enhancement. However, for a fixed gap size, there is an optimized DL which results in maximum SERS enhancement and this optimal length is increasing with the gap size (black arrow line). For example, the optimized DL for 35 nm NG is 110 nm, while it is increased to 120 nm for 100 nm NG substrate. The result is interesting, as it points that though it is difficult to decrease the NG size during fabrication, we were still able to achieve higher SERS enhancement by choosing the optimized DL for larger NG substrates. According to experiment results (red circles), NGs around 40 nm with DL around 252 nm gives higher SERS intensity, which coincident with the simulation result. Further, it is clear that SERS enhancement from 60 nm NG substrate can be comparable to that of 40 nm NG substrate if former’s DL is varied from its current value of 228 nm to 210 nm. Similarly, in theory, it is possible to achieve better SERS enhancements from larger NGs (80, 100 and 140 nm) as compared to 40 nm NG substrates by tuning their DL to smaller value by 13.9%, 18.7% & 22.6% respectively from their existing DL.

At current stage, even though there is a theoretical possibility, we still lag the fabrication capability to achieve the tailored narrow range of DL over fixed NG size. Thus, in future with improved nanofabrication technology, we could realize the tailored high enhancement even with sub-40 nm NG SERS substrates.

V. CONCLUSION

In this study we were successful in demonstrating the feasibility of fabricating plasmonic substrates with very high SERS enhancement even with large NG between nanostructures. We have shown simulation results, which clearly supports our findings. Due to current limitations in the fabrication process, we were not able to realize the nanostructure pattern with very high EMF for a fixed NG in a SERS substrate. Despite this we were able to show the varying enhancement factor for 2-NT confirming the presence of different DL within the same NG plasmonic substrate.

SUPPLEMENTARY MATERIAL

See supplementary material for detailed evaluation of substrate by SERS mapping method.

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