

Surface-Enhanced Raman Scattering Substrates: Highly Sensitive Sensors for the Detection of Adsorbate Molecules

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Abstract:

Surface-enhanced Raman spectroscopy (SERS) is one of the most sensitive tools for the detection of adsorbate molecules on roughened metal surfaces. The roughened metal surface produces a large enhancement to the Raman scattering signal. Here, SERS substrates consisting of Au features on SiO_2/Si wafers were manufactured using electron-beam lithography in combination with self-assembled multilayered resists. The initial Au posts (~ 100 nm in diameter with 300 nm spacing) were defined by thermal deposition of a Cr/Au layer onto developed e-beam samples, followed by a lift-off process. Subsequent daughter structures were defined by alternating self-assembled monolayers of an alkanethiol and coordinated metal ions to produce features with ~ 20 nm spacing.

To test the substrates, a monolayer of 4-nanobenzenethiol (4-NBT) molecules were adsorbed on the nanofabricated Au Raman substrates. Then a confocal Raman optical microscope with an incident Ar^+ laser of 514 nm was utilized to collect the spectral data on the 4-NBT adsorbed on the SERS substrates.

Introduction:

The SERS techniques augment Raman signals through both electromagnetic enhancement (EM), associated with

the roughened metal surface and a chemical (CHEM) factor, due to the electronic coupling of molecules adsorbed on the roughened metal surfaces. Here a combination of electron-beam lithography, capable of producing patterns of features at 100 nm or less, and molecular lithography, which allows for precise control of the spacing between the features by selective placement and controlled thickness of self-assembled monolayers (SAMs), are used to nanofabricate Raman substrates. The gap spacing between the features can be estimated by the number of SAMs deposited on the parent structures.

Reported here are the Raman peaks of the 4-NBT adsorbed in the nanoscale hierarchical features.

Procedure:

The initial parent structures were formed using electron-beam lithography: 3" SiO_2/Si wafers were coated with ~ 200 nm of polymethyl methacrylate (PMMA) resist.

Four quadrants of the coated wafer underwent electron-beam exposure with a dose-array of 8 to 9 patterns. Single quadrant-samples were developed one at a time in a 1:3 (MIBK:IPA) PMMA development solution for 1.5 minutes for the lift-off process. The quadrant-sample underwent reactive ion etching with oxygen plasma, for ten seconds, to remove any access exposed PMMA resist. A layer of Cr

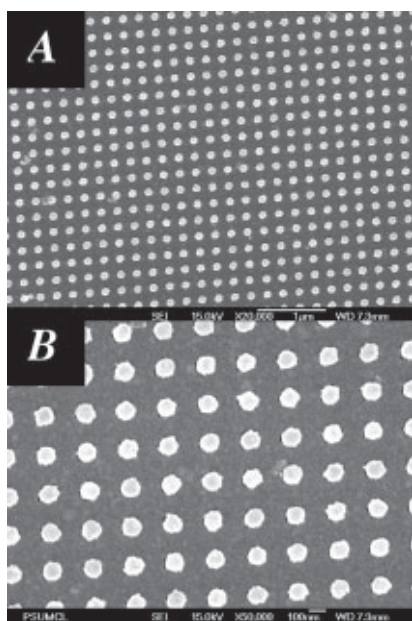


Figure 1: FESEM of nanofabricated SERS-substrate. A) Series of posts fabricated using e-beam lithography. B) The substrate after fabrication. The ~ 20 nm gaps around the posts are apparent.

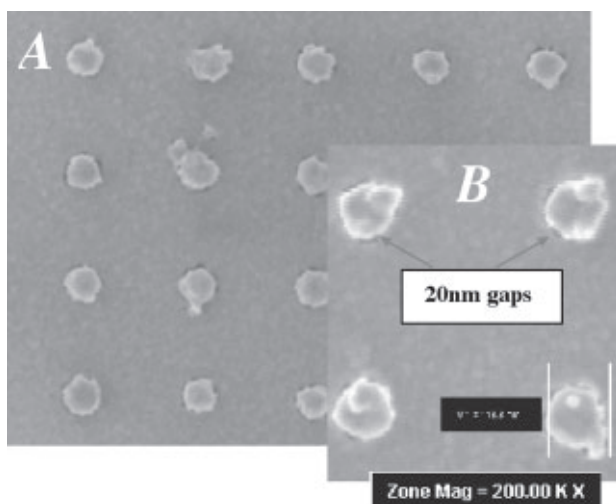


Figure 2: FESEM images of a nanofabricated SERS-substrate. The features seen here are 116 nm in diameter with 250 nm period. A small separation around the posts is apparent.

(5 nm) was electron-gun evaporated onto the developed samples as an adhesion layer prior to the direct-vapor deposition of a Au (55 nm) layer. The unexposed PMMA resist, with the unwanted Au areas, were dissolved in methylene chloride. The lift-off reaction was between 40 minutes to an hour at 200°C with 15 minutes of ultrasonic agitation to quicken the development time and improve the resolution of the features [2]. The nanoscale features were examined under a FESEM to ensure a successful lift-off and take measurements of the Cr/Au posts (~ 100 nm).

Once the parent features were obtained, subsequent daughter structures were defined by molecular lithography. The Si substrates, with the parent structures, were immersed in a 1 mM solution of 16-mercaptohexadecanoic acid in 95% ethanol for 40 minutes to form a self-limiting monolayer exclusively on the Cr/Au features, and not on the SiO₂/Si substrate. The samples were removed from the C16 solution, rinsed with acetone, then ethanol. Next, the substrates were immersed into a 1 mM solution of copper perchlorate in ethanol for 10 minutes to allow the coordination of the Cu⁺ ions with the carboxylate terminal of the alkanethiol.

Ten layers of SAMs of C16 (~ 2 nm long) were deposited onto the initial parent structures. Then a 2nd layer of Cr/Au (5 nm and 15 nm, respectively) was deposited onto the SAMs resist. The ACT935 chemical-striper removed the SAMs resist film to yield SERS-substrates with ~ 20 nm gaps. To evaluate the enhancement factor (EF), the SERS-substrates were incubated in a 1 mM solution of 4-nitrobenzenethiol in 95% ethanol for 24-hours and characterized by a confocal Raman optical microscope with a 514 nm Ar⁺ laser.

Results and Conclusion:

Figure 1 shows two FESEM images of a nanofabricated SERS-substrate. Figure 1A shows a series of posts fabricated using e-beam lithography. The Cr/Au posts are ~ 116 nm in diameter with a 250 nm periods. Figure 1B shows the substrate after fabrication. The ~ 20 nm gaps around the posts are apparent.

Figure 2 shows high resolution FESEM images of a nanofabricated SERS-substrate. The features seen here are 116 nm in diameter with 250 nm period. A small separation around the posts is apparent.

Figure 3 shows a Raman spectrum collected from bare gold with adsorbed 4 NBT and a Raman spectrum collected from a SERS substrate with no chemical modification. The bare gold with our surface-enhancement shows high fluorescence with adsorbed 4-NBT. The second spectrum is the SERS-substrate without 4-NBT.

Figure 4 shows a spectrum collected from the nanofabricated SERS-substrate with adsorbed 4-NBT. A number of peaks are apparent including a silicon peak at

540 cm⁻¹, and peaks at 1140 cm⁻¹, 1330 cm⁻¹, and 1570 cm⁻¹ from the 4-NBT.

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References:

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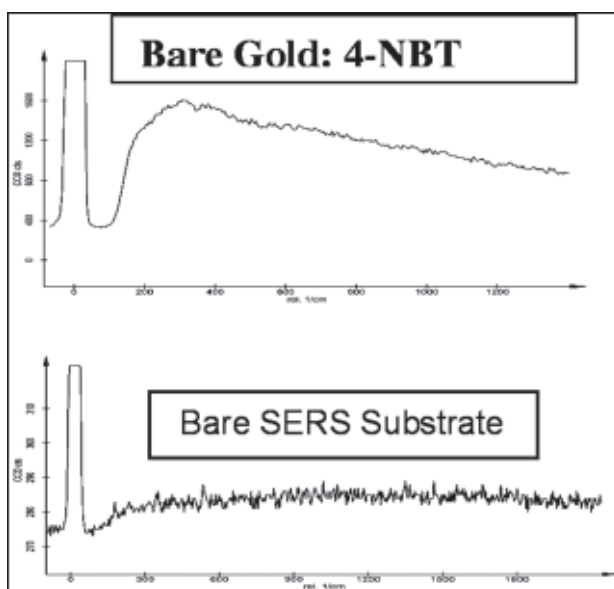


Figure 3, above: A Raman spectrum collected from bare gold with adsorbed 4 NBT and a Raman spectrum collected from a SERS substrate with no chemical modification.

Figure 4, below: A Raman spectrum collected from the nanofabricated SERS-substrate with adsorbed 4-NBT.

