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Assessment of SERS activity and enhancement factors for highly sensitive gold coated substrates probed with explosive molecules

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ABSTRACT

The surface enhanced Raman spectroscopy (SERS) is one of the most sensitive tools for trace analysis and the fabrication of effective and robust SERS substrates is the subject of intensive research in view of their possible applications. In this Letter, the SERS activity of an ordered structure of inverted pyramids (Klarite, Ltd) was examined by using nitro-based explosives, as Raman probe molecules. Enhancement factors up to 10^6 and detection limits of tens of pg were measured with an excellent run to run reproducibility. These findings provide new opportunities for the utilization of SERS for analytical detection at trace level.

Introduction

Since the discovery of the large Raman signal enhancement, occurring when a molecule is on or near a metallic nano-scale roughened substrate, the surface enhanced Raman spectroscopy (SERS) attracted a great interest in view of its possible applications and now is one of the most powerful tools for both chemical and biochemical sensing with trace level sensitivity [1–3]. It is widely recognised that the surface enhancement effect is based on the generation of an electromagnetic field at the surface of noble metals induced by the laser excitation. As an example, areas with particularly large electromagnetic fields can be found in between adjacent metal nanostructures if these are located at a distance of few nanometers, sharp tips and surfaces, interstitial crevices and gaps between nanoparticles. Therefore, when the analyte molecule is subjected to this intensified field, a comparably larger Raman signal is measured. The electromagnetic mechanism is believed to be responsible of the main part of the enhancement, however an additional enhancement is provided by the increase of polarisability of the adsorbed molecule, when a resonant charge transfer occurs between the metal and the adsorbate.

The potential of SERS for trace analysis was explored actively in recent years [4–7], but although single molecule SERS detection was reported, its application to real-world situations has remained challenging mainly due to the difficulties in mass producing large areas of highly sensitive and spectrally/physically reproducible SERS substrates.

To be used in a sensor system, a SERS substrate should enhance the Raman effect sufficiently to enable consistent and uniform chemical detection sensitivity across the surface, maintaining its properties as long as possible in the time. Several methods have been developed to produce substrates with ordered and uniform nanostructure including chemical etching, mechanical deformation, electroplating and oblique angle deposition, electron beam lithography, or co-block polymer patterned chemical seeding [8–20], however, despite these recent advancements, the reproducibility is yet to be resolved.

For the SERS measurements reported in this Letter we used substrates (Klarite, D3 Technologies Ltd) fabricated by vapour deposition technique in which a thin gold layer is deposited on a silicon surface with an ordered structure of inverted pyramids. The pyramidal pits were produced by chemical etching of Si surface, after definition of a mask by optical lithography. The inverted pyramids have a fixed apex angle (70.5° along the (1 1 1) direction of Si) and a scalable depth. The Raman signal enhancing properties of Klarite substrates were already experimentally demonstrated [21–23] and detailed calculations on plasmon resonance behaviour as a function of exciting wavelength and incidence angle have been provided [16–18]. Up to now, to compare the theoretical expectations with experimental behaviour, the SERS signal of aminothiophenol and benzenethiol dropped on Klarite surface as a function of pit depth was measured [16,17]. To push this comparison to a higher degree of sophistication, we measured the enhancement factors (EFs) of Klarite surfaces with a different pit depth ranging from 400 to 1200 nm.

As Raman probe molecules, we analysed some of the most commonly used explosives for military and industrial applications as pentaerythritol tetranitrate (PETN), trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX) and potassium nitrate to compare the Klarite substrates SERS response to two different nitrogen containing group (NO_2 and NO_3, respectively). In addition, we

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examined the changes in Raman signal from spot to spot on the same substrate, as well as the EF reproducibility from substrate to substrate. The application of Klarite surfaces to SERS sensing of explosive molecules with compact Raman platform was also demonstrated.

Experimental

Sample preparation

Delivering molecules in close proximity of a metal surface is a prerequisite for measuring SERS signals and because energetic molecules are commercially available only diluted in volatile solvents, they were analysed as evaporated films prepared by dropping a controlled volume of solution on the substrate. We used the following solution of explosives: PETN in methanol (Superchrom, 1 mg/ml, 100 μg/ml), RDX in methanol/acetonitrile (Superchrom, 1 mg/ml, 100 μg/ml), TNT in acetonitrile (Sigma, 1 mg/ml, 100 μg/ml) and KNO_3 (Aldrich) in water (1 mg/ml, 100 μg/ml) prepared in our laboratory.

Solvents will spread across the surface, even if small volumes are used, and selectively evaporate leaving the dried molecule adsorbed on the surface. Raman measurements were carried out across the deposited patch. In our procedure, the substrate was used as received without any chemical treatment of the surface and the solvent evaporated in the air. Quantitative studies require a uniform distribution of molecules on the surface, a known volume of analyte in the deposited area, and a sampling of area probed by the laser beam. Thus, it is possible to estimate the quantity probed by the laser as the analyte dropped mass multiplied by the ratio between the laser spot and the evaporated film area. As an example, a drop of 0.1 μL of 4.4. 10^{-4} M solution of TNT corresponds to about 10 ng of analyte deposited on an area of about 4 mm^2 (measured by optical microscope observations), but the molecules that contribute to the SERS signal are only those comprised in the laser beam spot (diameter = 90 μm). Therefore, the Raman signal comes only from an area of 6.4×10^{-3} mm^2, which corresponds to a probed mass of 16 pg.

Surface enhanced Raman spectroscopy

SERS and Raman spectra were collected using a Raman spectrometer (*i*-Raman 785, BwTek Inc.), equipped with a micro-positioning system for fine xyz adjustments and a video camera for sampling viewing. The system uses an air-cooled charge coupled device (CCD) detector. The 785 nm laser light was focused onto the sample using a 20× objective (corresponding to a laser beam diameter of 90 μm, as already mentioned). Samples were moved into position using the xyz translational stage. The Raman spectra were acquired in the wavelength range 789–1048 nm corresponding to Raman shifts of 75–3200 cm^{-1} (resolution better than 3 cm^{-1}). A portable spectrometer (HR-3000, Ocean Optics) system was also used to acquire SERS spectra. The Raman spectra were excited with a solid state laser with 785 nm light, a power of 500 mW, a laser beam diameter of 90 μm and were collected with a CCD system in the wavelength range 797–1004 nm corresponding to Raman shifts of 200–2700 cm^{-1} (resolution better than 6 cm^{-1}). The Raman system was coupled with a fibre optic probe. The SERS spectra reported in the following are the average of those acquired from 10 random spots on the same substrate.

In our experiments, we used commercially available, slide-mounted Klarite SERS substrates from D3 Technologies Ltd. The slides were individually packed and vacuum sealed, they were only used once and opened just prior to measurement to avoid any possible surface contamination.

The SERS substrate morphology was examined by high resolution electron microscope (HR-SEM), using a Leo 1525 hot cathode field emission microscope by Zeiss, with a resolution of 1.5 nm at 20 kV.

Results and discussion

In Figure 1 the HR-SEM images of Klarite SERS substrates used in our experiment are reported. The aperture size L of inverted pyramids is aligned along the [1 0 0] direction of Si wafer and is linked by the silicon crystal structure with the pyramidal void depth d: $L = 2d \cdot tg(\alpha)$, where $\alpha \approx 35.3°$ is the inclination to the normal of the pyramid's face for [1 0 0] silicon. The cross-section view shows that the gold layer deposited onto the internal walls of the pyramids has a thickness of about 300 nm, and a nanostructured roughness of about 20 nm.

Figure 2 shows SERS spectra from a PETN drop adsorbed on Klarite substrate with $d = (373 \pm 5)$ nm, acquired with the two spectrometers for 20 s. Each spectrum trace is the average of 10 random scans over the same substrate surface, repeated for three substrates with the same depth whilst the error bars represent the standard deviation of the Raman signal at each wavenumber. The standard deviations of bands and background intensities was below 10%.

In both the spectra, PETN can be identified by the ONO_2 rock at 624 cm^{-1}, ONO_2 stretching (866 cm^{-1}) and NO_2 symmetric (1290 cm^{-1}) peaks [13-15] whilst the vibration at 1450 cm^{-1} of nitro group asymmetric stretching is less intense. As evidenced by Figure 2, also with the lower resolution of the portable spectrometer it was possible to identify very well the main peaks characterising PETN. As expected, the regularity of the substrate surface gives a good homogeneity and reproducibility of the Raman/SERS signal.

The origin of SERS activity of Klarite surface was widely discussed in literature [16–18]. Theoretical models assume that the plasmons propagate on the pyramid's side walls and its crevice as on planar gold, forming a resonant standing wave that, when the pit depth is sufficiently deep, overlaps and interacts to produce localised plasmons bouncing up and down the inverted pyramid's faces. These localised plasmons are responsible for the Raman signal amplification when the molecules are adsorbed on the pyramid's walls. Following this model, only certain surface plasmon energies can fit into the concave edge – to – edge distance and the energy of resonant plasmons scales with the inverse of the individual pit depth, being independent from the incident angle of excitation light. As consequence, for each pump laser wavelength it is possible to select the substrate with the void depth appropriately matched which gives the highest SERS response.

To verify this model we compared the SERS activity of Klarite substrates with different void aperture size/depth by estimating the EFs of each surface through the following equation:

$$EF = \frac{\frac{I_{SERS}}{N_{SERS}}}{\frac{I_0}{N_0}} = \frac{N_0 I_{SERS}}{N_{SERS} I_0} \tag{1}$$

where I_{SERS} and I_0 are the intensities of the same band for the SERS and Raman spectra, N_0 is the number of molecules probed with the normal Raman scattering, and N_{SERS} is the number of molecules probed in the SERS measurement, estimated as discussed in the experimental section.

In our calculations, we used the intensities of the peak at 1290 cm^{-1} for PETN, 870 cm^{-1} (C–N–C ring breathing mode) for RDX, 1360 cm^{-1} (NO_2 symmetric stretching) for TNT [13,14] and 1044 cm^{-1} (NO_3 symmetric stretching) for KNO_3. We choose these bands because they were the strongest in the corresponding SERS/Raman spectra as shown in Figures 2 and 3, in which the SERS