

Surface Enhanced Raman Scattering by 2D Photonic Crystals: Enhancement and Reproducibility

M.C. Netti^{*}, S. Mahnkopf^{*}, J.R. Lincoln^{*}, M.D.B. Charlton^{*}, S.J. Cox^{*}, P. Ayliffe^{*},
M.E. Zoorob^{*}, J. S. Wilkinson^{*}, J.J. Baumberg^{*}, N.M.B. Perney^{**}, S.L. Jaiswal^{**}

^{*} Mesophotonics Ltd., 2 Venture Road, Chilworth Science Park,
Southampton, SO16 7NP, United Kingdom, j.j.baumberg@soton.ac.uk

^{**} School of Physics and Astronomy, University of Southampton,
Southampton SO17 1BJ, United Kingdom

ABSTRACT

Surface enhanced Raman scattering effects are investigated for novel substrates based on a Gold coated photonic crystal structure with square lattice geometry.

Enhancement factors of over 10^6 are presented for several different analytes, (measured with respect to signals from a flat Au surface) with chip to chip and sample to sample repeatability of 7% and 5% respectively.

Keywords: SERS, Raman, photonic crystals

1 INTRODUCTION

Surface Enhanced Raman Scattering (SERS) is a widely used technique for the enhancement of otherwise weak Raman signals from specific molecular species, enabling detection and identification of ultra-low concentrations. However, extreme fluctuations in SERS signals from existing substrates (consisting of a roughened gold surface) have prevented large scale deployment of Raman sensing for clinical applications. Other substrates have been proposed which are not compatible with large scale production methods. In this paper, we show that SERS substrates based on 2D photonic crystals (PCs) fabricated from metal-coated dielectrics can produce SERS enhancements greater than 10^4 . These novel PC SERS substrates [1] exhibit extremely good reproducibility enabling a quantification of the adsorbed molecular concentration, and low-cost widely-applicable SERS devices. The devices can be fabricated for example on silicon by standard VLSI fabrication techniques.

Surface plasmons play an important role in the mechanism of operation of PC-BIOSERS substrates, as they mediate the interaction between incident electromagnetic radiation and vibrational modes of the molecules. Understanding plasmon properties is therefore essential for the optimization of the SERS process for a given analyte.

In contrast to other works on metal colloids and nanoparticles, metallo-dielectric photonic crystal substrates presented in this paper have cylindrical air cavities which are considered favorable for plasmon-enhanced electromagnetic fields [6]. The metal coating causes the

properties of photonic crystals to be modified in the form of “plasmonic” band-structure as opposed to “photonic” band structure. That is to say, incident light can couple into a set of discrete plasmon modes resident on the metal surface which then couple to molecules placed in close proximity to the surface. Interactions between incident light, surface plasmons, and bio-molecules is complex, further details of these interactions will be published elsewhere.

2 DEVICE FABRICATION

Our PC SERS substrates are based on a 2D photonic crystal with a square lattice geometry etched into a waveguide structure. These devices have previously been shown to demonstrate photonic bandgaps [2], slow light [3], superprism operation [4], and tri-refringence [5].

Fig 1(a) shows the schematic of the structure. Data is presented in this paper for structures based on a square lattices of holes, with lattice pitches in the range 500 nm-6 μ m, and hole diameters of 300 nm-4 μ m. The aspect ratio (depth : width) of the holes varies from of 1:1 to >10:1. The dielectric structures are then gold or silver coated by radio frequency sputtering to produce the final SERS substrates.

Figure 1(b) shows an SEM cross-section of a fabricated device. In this example, the substrate features a square lattice with lattice pitch of 610 nm, pore radii of 400 nm, and etch depths of about 200 nm. The substrate has been subsequently coated with a 300 nm thick Au layer. As one can see, the Au attaches well to the substrate surface as well as the sidewalls of the holes.

3 EXPERIMENT

3.1 SERS signature from Benzenethiol

The SERS substrates were coated with benzenethiol by leaving the sample in a benzenethiol bath for about 30 minutes and subsequent rinsing using ethanol. Standardized Raman experiments were then performed using a commercial Raman instrument (Renishaw RM1000). Excitation of surface plasmons was accomplished by focusing laser light onto the sample surface (nominally at normal incidence) using a microscope objective. The lasers

had emission wavelengths of either 632.5 nm or 785 nm and maximum powers of 3 mW and 22 mW, respectively.

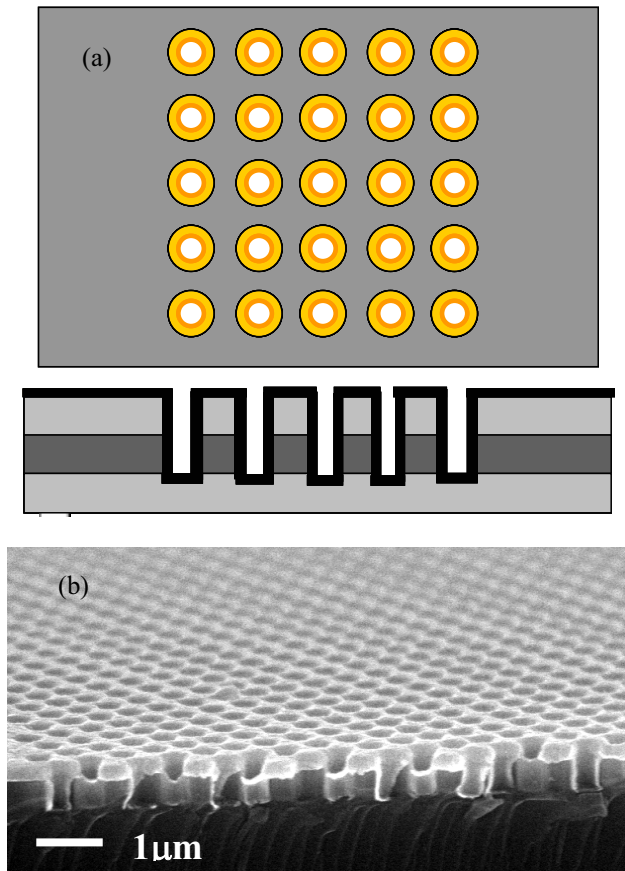


Figure 1: Schematic design and SEM of a SERS substrate (pitch 560nm, hole diameter 420nm, Au thickness 300nm)

Fig. 2 shows SERS spectra obtained from the square lattice devices with lattice pitch $a=2 \mu\text{m}$. The spectra exhibit the well-known five main Raman lines expected

from the benzenethiol at 996 cm^{-1} , 1020 cm^{-1} , 1071 cm^{-1} , 1571 cm^{-1} , and 3055 cm^{-1} . These lines correspond to the $\beta(\text{C-C-C})$, $\beta(\text{C-H})$, $\nu(\text{C-S})$, $\nu(\text{C-C})$, and $\nu(\text{C-H})$ bonds of the benzenethiol molecule, respectively. The absence of the S-H bond implies that the benzenethiol has formed a monolayer with the Au surface of the SERS substrate. From the measured signal, the peak amplitudes (measured from the bottom of the background) were extracted. The SERS signal was found to be enhanced at least by a factor of 10^4 compared to a reference SERS signal obtained from a neighboring unpatterned flat Au surface. Fig. 2(b) shows the SERS spectra acquired using microscope objectives of different magnifications.

3.2 SERS signatures from Phenylalanine and Urea

Fig. 3(a) shows the SERS spectrum obtained from phenylalanine upon excitation at 785 nm with a power of 22 mW after subtraction of the background. One can observe a series of characteristic peaks at 407 cm^{-1} , 621 cm^{-1} , 1002 cm^{-1} , 1029 cm^{-1} , 1445 cm^{-1} , and 1600 cm^{-1} . The ring breathing mode at $1,002 \text{ cm}^{-1}$ is the dominant mode exhibiting the largest SERS amplitude.

Fig. 3(b) shows the SERS signature from urea after background subtraction obtained under the same measurement conditions. The SERS spectrum exhibits modes at 546 cm^{-1} and 1010 cm^{-1} the lines characteristic to the bond excitations of urea.

3.3 Repeatability

In order to assess the quality of the photonic crystal SERS substrates, a rigorous test was undertaken to determine the repeatability of the SERS signal across the chip and from chip to chip. The repeatability is defined here to be the relative standard deviation (RSD) between the main peaks of the analyte, in this case benzenethiol. The measurements are done on a 3×3 grid spaced 1mm apart

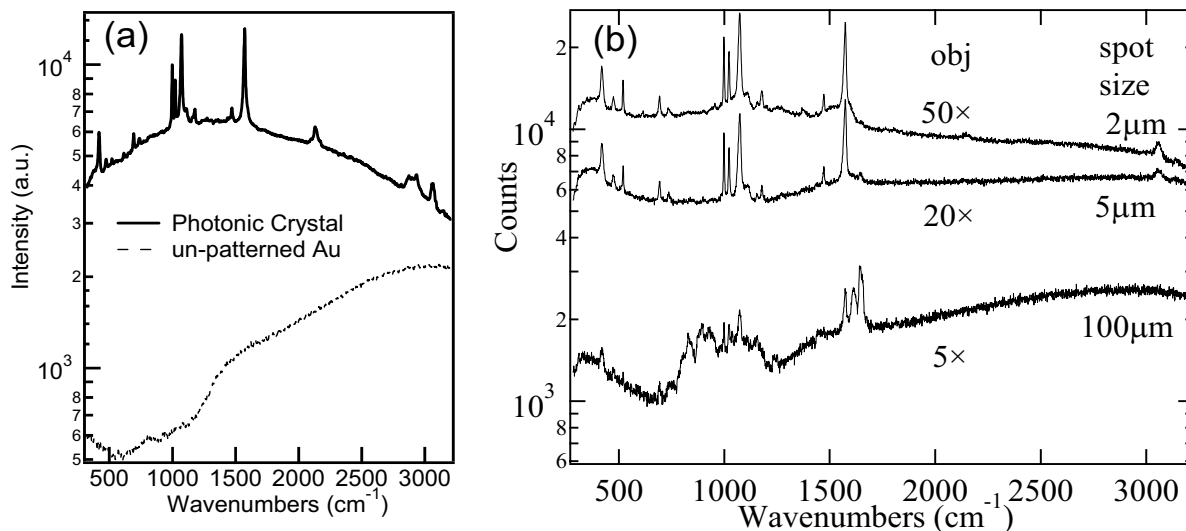


Figure 2: SERS spectra (633nm 3mW pump source) on benzenethiol coated metallo-dielectric Photonic Crystal

across the whole chip area.

Benzenethiol peak (cm ⁻¹)	Average amplitude (a.u.)	RSD (%)
996	11,273	3.8
1020	5,426	4.5
1071	7,536	5.1
1571	10,575	5.2
3055	2,284	5.5

Table 1: Average amplitude and relative standard deviation (RSD) of above measurements for the five main benzenethiol peaks: RSD across the chip varies between 3.8% and 5.5%.

Fig. 3(a) displays the measured SERS signal from benzenethiol without any background subtraction. As one can see, the signals strongly overlap. From the measured SERS spectra the various peaks amplitudes are extracted through a fitting algorithm. The results are displayed in Fig. 3(b) as a function of scan number. The SERS amplitudes fluctuate in narrow intervals around the respective peaks' amplitudes. Table 1 summarizes the resulting RSD for the five main benzenethiol bonds. The RSD is in the range of 5% with the β (C-C-C) exhibiting the smallest RSD of 3.8% and the ν (C-H) bond exhibiting the largest RSD of 5.5%.

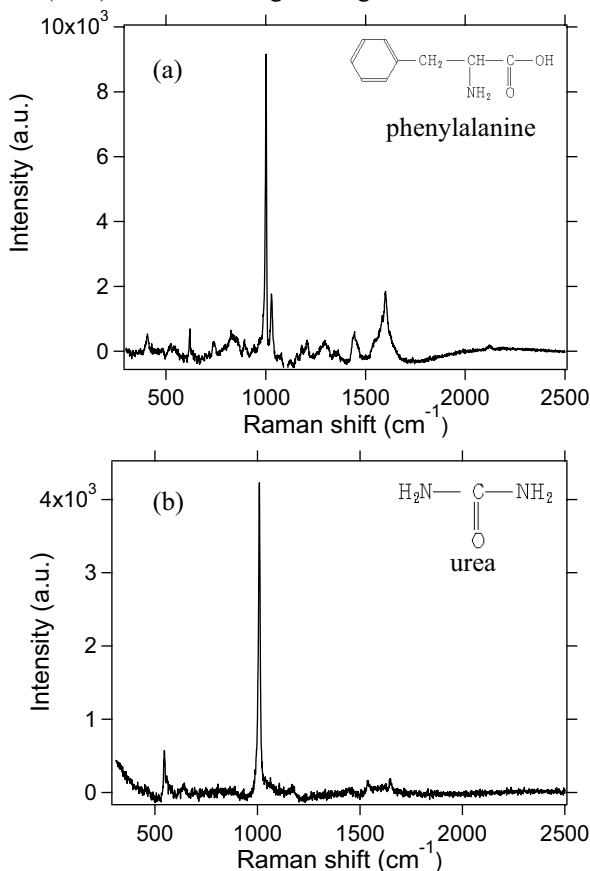


Figure 3: SERS spectra on (a) phenylalanine and (b) urea using 785 nm excitation, 22 mW pump source

The same analysis is undertaken for a second chip. The chip-to-chip RSD is found to be in the range of 7%.

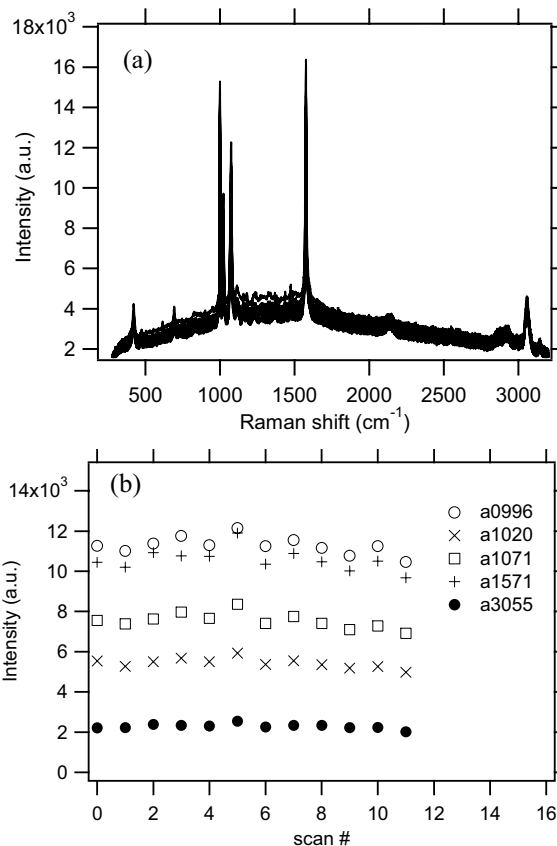


Figure 4: Repeatability of SERS signal from benzenethiol across 5x5 mm chip surface (633 nm, 3 mW pump source) (a) Measured SERS spectra without (b) Extracted signal amplitudes of the five main benzenethiol peaks as a function of scan number.

4 CONCLUSION

In conclusion, experimental measurements of surface enhanced Raman scattering (SERS) signals from various analytes such as benzenethiol, phenylalanine, and urea placed on the surface of a novel metallo-dielectric structure based on a photonic crystal structure were reported. The SERS enhancement compared to a flat Au surface is well in excess of 10^4 . The repeatability of the SERS signal was rigorously tested across the sample surface and was reported to be in the range of 5% across the chip surface and in the range of 7% across different chips. To the authors' knowledge, this repeatability is the best reported in the literature. The RSD is the critical parameter for use in applications which require quantitative measurements, and far improves on results obtained using electrochemically roughened substrates. Thus, the metallo-dielectric photonic crystals are extremely promising for widespread

application. In addition to allowing comprehensive engineering of the plasmons, they offer a test of SERS theories, allowing optimization and a way of making designer SERS substrates for specific applications.

Scanning the active area revealed strong SERS enhancements in the center of the Au-coated air cylinders while intermediate flat regions exhibit the lowest SERS enhancement factors.¹

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¹ Nanotech 2005, 696 San Ramon Valley Boulevard, Suite 423, Danville, CA 94526-4022, Ph: (925) 901-4959, Fax: (925) 886-8461, wenning@nsti.org