Metallo-Dielectric Photonic Crystals for Reproducible Surface-Enhanced Raman Substrates

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Abstract: Planar photonic crystals comprised of metals and dielectrics show huge enhancements in the surface-enhanced Raman scattering of attached molecules. Plasmon engineering is key to these properties including reproducibility (std.dev.<9%), beamed output, resonances and orientation.

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Surface Enhanced Raman Scattering (SERS) is a widely utilised technique to enhance the weak Raman spectrum of molecules, enabling detection and identification of ultralow concentrations of particular species. Discovered exactly 30 years ago,[1] it employs a roughened metal surface in the vicinity of a molecule to act as an antenna that couples laser light in and SERS photons out. However the major block to its application has been the extreme variability of the SERS signals from the substrates used to elicit this effect. Despite many experiments, there is still considerable debate over how the SERS enhancement arises on a metal, and no first-principle calculations can model the observed effect. We show both experimentally and theoretically how localised surface plasmons engineered on 2D photonic crystals (PCs) fabricated from metals and dielectrics can produce SERS enhancements $>10^4$. Our PC SERS substrates [2] exhibit extremely good reproducibility and will enable a new generation of applications based on quantification of the adsorbed molecular concentration, and low-cost widely-applicable SERS devices.

Our samples are based on 2D photonic crystal waveguide technologies, in which we have previously demonstrated photonic bandgaps [3], slow light [4], superprism operation [5], and tri-refringence [6]. High refractive index dielectric waveguides are sandwiched between silica buffer and cladding (all grown on silicon wafers), and e-beam lithography is used to pattern a variety of photonic crystal designs. Data is presented here on structures with square lattices of holes, of pitch varying from 500nm-6000nm, and hole diameters from 300-4000nm. The aspect ratio of the holes is varied from depth:width of 1:1 to >10:1. The dielectric samples are then gold- or silver-coated by rf-sputtering in an optimised process to produce the SERS substrates (Fig.1).

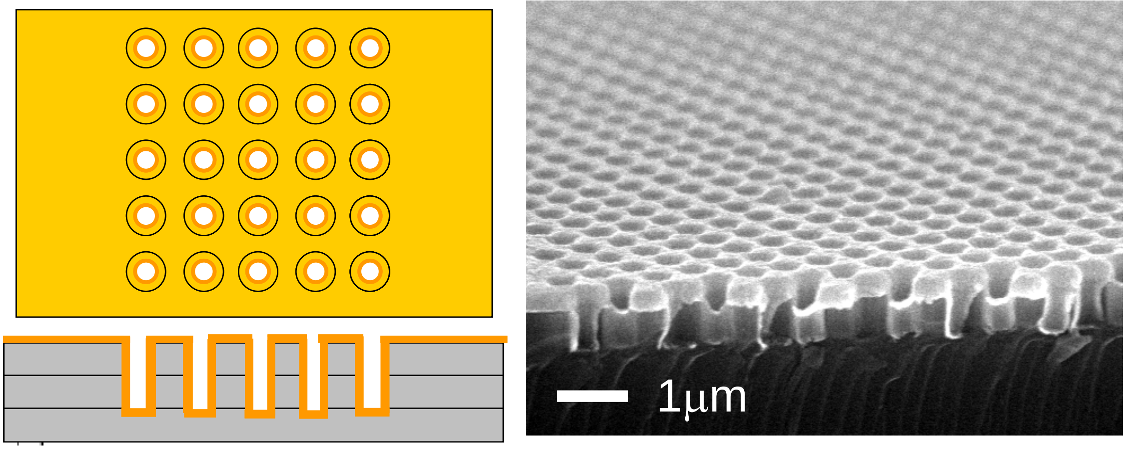

Fig.1: Schematic design and SEM of particular SERS substrate (pitch 560nm, hole diameter 420nm, Au thickness300nm on the surface and 75nm in the holes)

The spectroscopy of plasmons on flat metal films is well understood, however the plasmon engineering of nanostructured surfaces is a nascent field, so far concentrating on holes drilled in metal foils and weakly corrugated films. Understanding these plasmon properties is crucial to engineer and optimise the SERS scattering process which takes place between the incident light and the molecules, mediated by the plasmons. Other work in this area has focussed on measuring SERS at roughened metal surfaces (exhibiting extremely variable enhancements), and metal colloids and nanoparticles. In contrast, our metallo-dielectric photonic crystals have void-like structures which are much more favourable for plasmon-enhanced electromagnetic fields [7]. Our structures combine properties of both photonic crystals and plasmons, and exhibit a rich variety of different interactions with incident light.

To identify the different plasmons which are present in this nanostructured metallo-dielectric photonic crystal, we perform broadband reflectance spectroscopy using white-light lasers [3] varying the polar and azimuthal angles of the incident beams. Using a cross-polarised geometry allows us to concentrate on spectral features which rotate the plane of polarized light, identifying the different Bragg and Mie resonances as well as surface plasmonic bandgaps. Typical data are shown in Fig.2, for angles of incidence at 45 and 60 degrees, with the light impinging along the square lattice direction (Γ-X). By comparing spectra on uncoated and Au-coated samples, diffractive features can be identified, with typical dispersion in energy and wavevector matching the expected dispersion curves of square periodic structures. Additional features are present on the metallo-dielectric structures which correspond to both localised plasmons inside the cylindrical pores, and surface-plasmons which run on the top surface and scatter off the ring apertures of the pores.

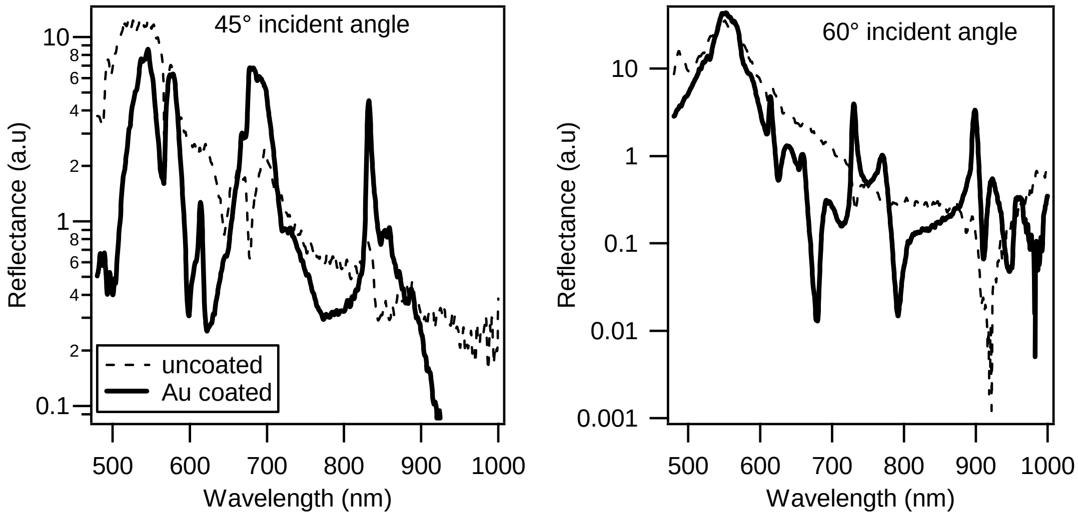

Fig.2: Cross-polarised reflection spectrum at several angles of incidence of metallo-dielectric PC, both uncoated and coated with 300nm of Au.

We perform standardised SERS experiments by attaching a continuous monolayer of benzenethiol to the gold, and using a standard Renishaw Raman instrument. To remove effects from any roughness of the metal film deposited, we compare SERS spectra from the photonic crystal and the nominally flat metal regions either side. Typically we see PC enhancements over that from the flat Au in excess of 100, and $>10^4$ above the signal from non-metallised surfaces. The SERS spectra show all the Raman lines expected from the benzenethiol (Fig3a), with enhancement of the background as well compared to the SERS taken on neighbouring unpatterned Au. The larger enhancement of the SERS at higher magnifications can be explained by the beaming effect of the plasmon mechanism, emitting the SERS photons into particular directions.

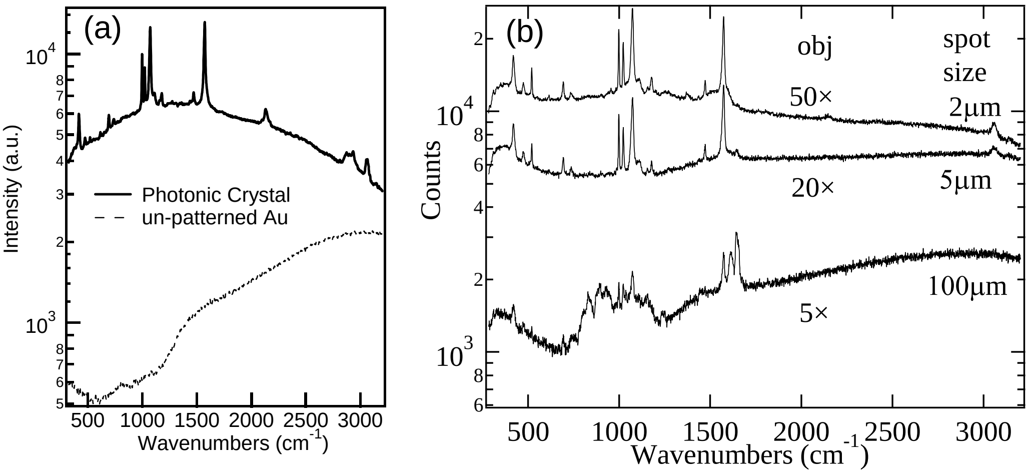

Fig.3: SERS spectra (633nm 3mW pump source) on benzenethiol coated metallo-dielectric PCs

The repeatability of the observed SERS amplitude on different samples (different regions and different wafers) is extremely good, better than 9% (standard deviation of peak heights, for x20 magnification) even in our non-optimised PCs. This is the critical parameter for use in applications which require quantitative measurements, and far improves on results using typical electrochemically roughened substrates. Thus these metallo-dielectric photonic crystals are extremely promising for widespread application. In addition to allowing comprehensive engineering of the plasmons, they offer a subtle test of SERS theories, a testbed for optimization, and a way of making designer SERS substrates for specific applications.

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