

## Photonic crystals with SiO<sub>2</sub>-Ag “post-cap” nanostructure coatings for surface enhanced Raman spectroscopy

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(Received 23 June 2008; accepted 16 September 2008; published online 9 October 2008)

We demonstrate that the resonant near fields of a large-area replica molded photonic crystal (PC) slab can efficiently couple light from a laser to SiO<sub>2</sub>-Ag “post-cap” nanostructures deposited on the PC surface by a glancing angle evaporation technique for achieving high surface enhanced Raman spectroscopy (SERS) enhancement factor. To examine the feasibility of the PC-SERS substrate, the simulated electric field around individual Ag particles and the measured Raman spectrum of trans-1,2-bis(4pyridyl)ethane on the PC-SERS substrate were compared with those from an ordinary glass substrate coated with the same SiO<sub>2</sub>-Ag nanostructures. © 2008 American Institute of Physics. [DOI: 10.1063/1.2998695]

Since the experimental demonstrations of surface enhanced Raman spectroscopy (SERS) (Ref. 1), it has been shown that many molecules display Raman cross sections that are several orders of magnitude greater when adsorbed upon roughened conducting surfaces than the corresponding quantity in solution or on an ordinary smooth surface. Due to the surface enhancement, small sample volumes can be detected with concentration resolution from the picomole to femtomole range, making the SERS technique potentially attractive for detecting trace quantities of explosives, drugs of abuse, environmental contaminants, and biological pathogens. The mechanisms by which the SERS effect occurs are currently a subject of debate, and two main enhancement routes have been proposed,<sup>2</sup> namely, the electromagnetic (EM) effect and the chemical enhancement effect. This work is concerned only with the EM effect in which the local EM field at the surface of a metal is significantly changed from that of the incident field and becomes more pronounced when fine metal particles or rough surfaces generate local surface plasmon resonances. The EM effect results in enhanced excitation of Raman vibrational modes due to highly localized EM fields that can be substantially higher than the electric field of the incident laser illumination. An extensive literature exists on the effects of metal surfaces for SERS and on the use of a variety of metal surface configurations (planar, corrugated, colloidal) or metallic particle types (spheres, shells, boxes, and triangles to name just a few) that involve plasmonic resonances to enhance EM excitation. Although enormous enhancement factors have been achieved using metal structures, further enhancement of Raman signals is still desirable to reduce laser power and accumulation time for detection of trace quantities of analytes. A previous publication described the use of a dielectric-based ring resonator for obtaining additional enhancement of the EM field around metal nanostructures for SERS.<sup>3</sup> In this paper, we demonstrate that the near fields of a photonic crystal (PC) slab optical resonator can also efficiently couple light from a laser to metal nanostructures on a PC surface.

The surface PC used in this work is a subwavelength periodic arrangement of dielectric materials that can support guided-mode resonances at designated wavelengths,<sup>4</sup> where the device reflects ~100% of incident light at the resonant wavelength while all other wavelengths are transmitted. Under resonant conditions, excited leaky modes are localized in space during their finite lifetimes, which enhance the near electric-field intensity of the PC structure<sup>5,6</sup> and thus enhance the SERS signal from adsorbed molecules on metal nanostructures in close proximity to the PC. We used the glancing angle deposition (GLAD) technique<sup>7</sup> to create a high density coating of electrically isolated Ag nanoparticles that are supported vertically from the PC surface on 50 nm-tall SiO<sub>2</sub> dielectric posts. The GLAD technique has been demonstrated to be a simple method for fabrication of metal structures with high SERS enhancement factor because the randomly distributed and sized Ag nanostructures have numerous interconnections and strong EM field within the gaps between the nanoparticles.<sup>8</sup> To examine optical coupling between resonant near fields from the PC and metal nanoparticles in close proximity to the PC surface, we performed computer simulations of the electric field distribution around a single exemplary metal particle. Experimental demonstration of additional enhancement of PC-SERS was performed by measuring the Raman spectrum of trans-1,2-bis(4pyridyl)ethane (BPE) on the PC-SERS substrate and by performing direct comparison with measurements from an ordinary glass substrate coated with the same SiO<sub>2</sub>-Ag structure (GL-SERS substrate).

Figure 1(a) shows a cross sectional schematic of the PC-SERS substrate comprised of a one-dimensional PC slab and a SiO<sub>2</sub>-Ag “post-cap” nanostructure coating. To fabricate the PC, a polymer grating (period=360 nm, depth=60 nm) was fabricated using a nanoreplica molding process as described in previous work<sup>9</sup> from a silicon grating template. Following replication of the grating structure, a SiO<sub>2</sub> layer with a thickness of ~300 nm ( $n=1.46$ ) and a TiO<sub>2</sub> layer with a thickness of ~100 nm ( $n=2.25$ ) were subsequently deposited over the grating surface by sputtering. The resulting PC slabs have a resonant reflection for the laser used to

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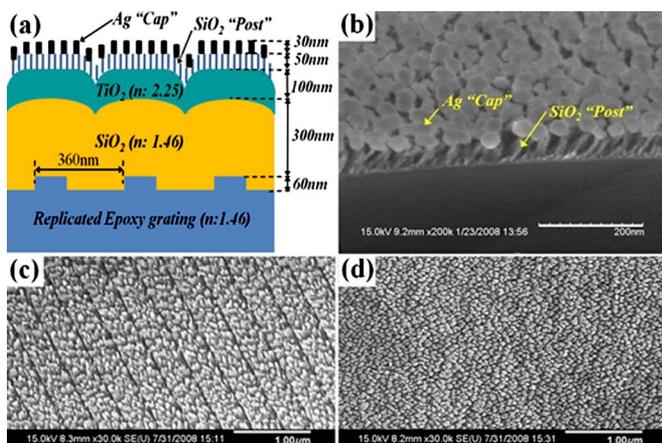


FIG. 1. (Color online) (a) Cross sectional schematic of the PC-SERS substrate, (b) cross sectional SEM image of  $\text{SiO}_2$ -Ag post-cap nanostructures, and top-view SEM images of (c) PC-SERS and (d) GL-SERS substrates.

excite SERS [ $\lambda=600$  nm, TE polarized (electric field parallel to the grating lines)] at an incident angle of  $\sim 13^\circ$ . Following PC fabrication, GLAD coatings of  $\text{SiO}_2$  and Ag were applied using an electron-beam deposition system (Temescal) at a deposition rate of  $5 \text{ \AA/s}$  for both materials. The angle between the incoming flux of evaporated material and the device surface was  $5.0^\circ$ . To minimize the shadowing effect of grating lines, the incoming flux was parallel to the grating sidewalls. The  $\text{SiO}_2$  post layer was used to prevent quenching of resonant near fields of the PC due to the high-loss metal structure. Since the resonance characteristic of the PC can be deteriorated by closely located metal nanostructures, a balance must be achieved between locating the Ag nanostructures too close to the PC surface while still positioning them within the PC evanescent field. Figure 1(b) shows the cross sectional scanning electron microscope (SEM) image of a  $\text{SiO}_2$ -Ag post-cap nanostructure with a  $\text{SiO}_2$  thickness of 50 nm and Ag thickness of 30 nm, which was fabricated upon a silicon substrate for SEM imaging. For comparison, an ordinary glass slide with  $\text{SiO}_2$ -Ag nanostructures was also prepared using the same GLAD process. Figures 1(c) and 1(d) show SEM images (top view) of a PC-SERS substrate and a GL-SERS substrate, respectively.

To examine the coupling effects of the enhanced near electric fields from the PC at resonance to the Ag nanostructure, software (RSOFT) utilizing the rigorous coupled-wave analysis algorithm was used to simulate the electric-field distribution around a single Ag nanostructure separated vertically from the PC surface by a narrow gap. Since the  $\text{SiO}_2$ -Ag post-cap nanostructure fabricated by the GLAD technique is a randomly distributed and sized structure, exact modeling of the nanostructured coating would require greater computational resources than are readily available, and a simplified structure was considered instead as a means of visualizing the electric field surrounding Ag nanoparticles. For the  $\text{SiO}_2$  nanopost layer, a uniform layer comprised of a 65:35 mixture of air: $\text{SiO}_2$  was used for simulation as described in our previous work using GLAD dielectric nanostructures.<sup>9</sup> For the Ag nanostructure, a cylindrical Ag metal nanoparticle with a diameter of 40 nm, height of 30 nm, and pitch of 60 nm was used for the simulation model because the measured diameters of Ag nanostructures from SEM images were 30–50 nm and the simulated transmission

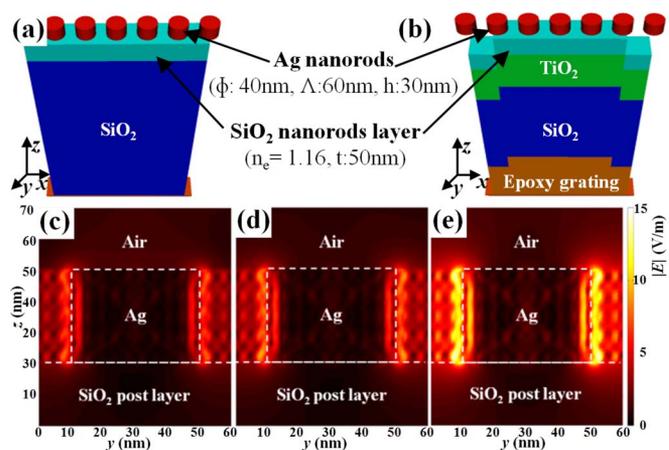


FIG. 2. (Color online) Simulation models for (a) GL-SERS and (b) PC-SERS substrates and  $y$ - $z$  plane cross sectional simulated electric-field distribution for a single Ag nanostructure on (c) GL-SERS and PC-SERS substrates at (d) off- and (e) on-resonance conditions.

spectra using these dimensions were similar to measured transmission spectra from GL-SERS substrates. Although this model cannot exactly predict the characteristics of real  $\text{SiO}_2$ -Ag post-cap nanostructures, we believe that this model can demonstrate the effect of guided mode resonance from the PC upon the electric-field distribution around Ag nanoparticles above the PC surface. Figures 2(a) and 2(b) show the three-dimensional simulation models for (a) GL-SERS and (b) PC-SERS substrates, where periodic boundary conditions were applied to the  $x$  and  $y$  extents. Figures 2(c)–2(e) show the  $y$ - $z$  plane cross sectional simulated electric-field amplitude distribution for a single Ag nanostructure on (c) a GL-SERS substrate and [(d) and (e)] a PC-SERS substrate illuminated with a TE polarized  $\lambda=600$  nm plane wave source (incident  $E$  field magnitude = 1 V/m) with an incident angle of (d)  $0^\circ$  (off-resonance condition) and (e)  $13^\circ$  (on-resonance condition), respectively. Figure 2(c) shows that the enhanced electric fields are located near the Ag nanostructure surface as expected due to the localized surface plasmon effect. We note that the shape of the electric field distribution around an Ag particle on the PC-SERS substrate is similar to that on the GL-SERS substrate, but the amplitude in (e) is about two times larger than that in (c). Since the Raman signal is proportional to  $|E|^4$ ,<sup>7</sup> the average value of  $|E|^4$  in the volume surrounding the metal particle was calculated, and the values were 2966, 7397, and 19 913 for GL-SERS substrate and PC-SERS substrate at off- and on-resonance conditions, respectively. The simulation demonstrates that an additional SERS enhancement factor of  $\sim 7\times$  may be obtained using the PC-SERS substrate.

For experimental verification of the enhancement effects of PC-SERS, Raman spectra of BPE on GL-SERS and PC-SERS substrates were measured and compared. The Raman detection instrument was comprised of a TE polarized Argon-dye laser excitation source (Coherent, INNOVA-90 and CR-500,  $\lambda=600$  nm, output power = 82 mW), a sample holder with a rotational stage, a power meter to measure laser transmittance through the sample, imaging optics, a spectrometer (SPEX-Triplemate), and a cooled charge coupled device (Princeton Instruments). Raman scattered light was collected from a  $235.4 \times 51.8 \mu\text{m}^2$  area, and the diameter of the laser beam spot was  $\sim 470 \mu\text{m}$ . A  $2 \mu\text{L}$

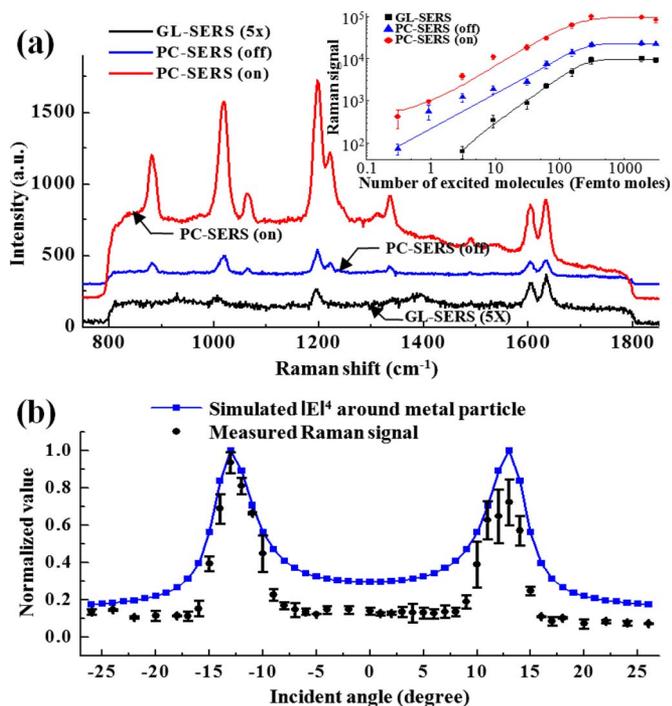


FIG. 3. (Color online) (a) Comparison of Raman spectra of BPE on GL-SERS and PC-SERS substrates at on/off resonance conditions and (right top) log-log plot of the Raman signal from GL-SERS and PC-SERS substrates against the estimated number of excited BPE molecules. (b) Comparison of measured Raman signal and simulated  $|E|^4$  for varying incident angles.

droplet of BPE dissolved in methanol ( $1 \times 10^{-4}$  M) was applied to each substrate by pipette. The BPE/methanol droplet spread out to form a circular region with a diameter of  $\sim 1.0$  cm on the substrate, resulting in a density of  $\sim 1.53 \times 10^{14}$  molecules/cm<sup>2</sup> and a number of excited molecules of  $\sim 31$  fmoles. For a laser wavelength of  $\lambda = 600$  nm, the PC resonance could be excited by illuminating at an angle of  $\sim \pm 13^\circ$ , and precise tuning to the on-resonance condition for any substrate could be achieved by the adjustment of the rotation stage to obtain a minima in laser transmitted intensity through the PC. Off-resonance conditions were obtained by detuning the incident angle from the transmission minima by  $\sim \pm 13^\circ$ . Figure 3(a) shows the Raman spectra obtained from BPE using both GL-SERS and PC-SERS substrates at on/off resonance conditions. The spectrum for GL-SERS substrate was enlarged by a factor of 5. The Raman signal was defined as the integrated intensity of the 1200 cm<sup>-1</sup> peak after subtraction of the background signal. The Raman signals obtained from GL-SERS and PC-SERS substrates at off- and on-resonance conditions were 531, 2762, and

18 702, respectively. Our results show that the Raman signal from the PC-SERS substrate increased significantly. Figure 3(b) compares the measured Raman signal and simulated  $|E|^4$  of the PC-SERS substrate for varying incident angles. The simulated  $|E|^4$  are maximized at the resonance angles of  $\pm 13^\circ$ , and at those incident angles, the Raman signal is also maximized. These results demonstrate that a PC-SERS substrate can substantially enhance SERS sensitivity and the enhancement factor was strongly correlated with the enhanced electric field around the Ag nanostructure due to the PC guided mode resonance. A Langmuir analysis (signal versus concentration) was also carried out to examine the additional enhancement effect attributable to the PC. The Raman signals from GL-SERS and PC-SERS substrates at on/off resonance conditions are plotted against the estimated number of excited BPE molecules in Fig. 3(a) (top right). The response is nearly linear over three orders of magnitude (0.3–300 fmoles) after which there is saturation of the signal. The enhancement effect on the Raman signal due to the guided mode resonance of the PC is observed throughout the entire concentration range with an enhancement factor of 10–30 $\times$  between GL-SERS and on-resonance PC-SERS.

In conclusion, we have demonstrated that a PC structure can effectively couple light to metal nanoparticles deposited on its surface when the incident light wavelength and angle are selected to match the PC resonant coupling condition. Using the PC surface, an additional SERS enhancement factor of 10–30 $\times$  was obtained resulting in a detection sensitivity of 0.3–3 fmoles for BPE deposited on the substrate surface.

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (Grant No. KRF-2007-357-D00015) and SRU Biosystems. The authors gratefully acknowledge the PC microscope slides provided by SRU Biosystems.

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