

Dielectric-substrate-induced surface-enhanced Raman scatteringO. J. Glembocki, R. W. Rendell, D. A. Alexson, S. M. Prokes, A. Fu,* and M. A. Mastro
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It is shown through experimental mapping of surface-enhanced Raman scattering (SERS) from dielectric core nanowires exposed to benzene thiol that any dielectric substrate plays a critical role in the SERS enhancement. Theoretical calculations of the plasmonic enhancement using finite element methods confirms the role that the substrate plays in increasing the intensity and spatial extent of the SERS enhancement. It is shown that because of the cylindrical shape of the nanowires, significant SERS hot spots form not only between crossed nanowires but also at the point of contact between the nanowires and the substrate on which they are placed. This result also applies to any structure whose geometry results in a point or line contact with an underlying substrate.

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I. INTRODUCTION

Surface-enhanced Raman scattering (SERS) has a long and rich history of detecting submonolayer coverage of roughened metal electrodes by adsorbing molecules.¹⁻³ The enhanced sensitivity of the Raman signals, sometimes by as much as 10^{12} has been attributed to light-mediated plasmonic interactions between the incident and scattered radiation with plasmons created in the tips of the roughened electrodes.^{4,5} An accurate accounting of this effect for many chemical species that have different enhancement factors and even in some cases no enhancements is difficult because the scattering is very sensitive to nanoparticle shape and geometry.

In recent times, lithography, particularly nanosphere lithography has led to more reproducible SERS active substrates characterized by nanoparticles with well-defined shapes, such as nanospheres, nanoshells, and triangles.⁶⁻⁸ These substrates result in better control over the plasmonics and have led to reports of single-molecule detection.^{9,10} Furthermore, it has been shown that closely spaced metal nanoparticles will exhibit coupled plasmon modes that further increase the SERS enhancements. Garcia-Vidal and Pendry¹¹ have shown that when two Ag semicylindrical nanostructures are brought together, the field in the region close to the intersection of the two nanostructures is significantly enhanced. Similar results were obtained in the calculations by Kottman and Martin¹² of two parallel Ag nanorods, which showed that the regions between the nanorods had very high fields. These fields are commonly referred to as “hot spots.” Both Glembocki *et al.*,¹³ and Prokes *et al.*¹⁴ have shown experimentally that this effect is also prevalent in the SERS for Ag coated Ga₂O₃.

Despite the significant focus on the geometric and material properties of metal nanoparticles, the substrate on which they are placed has received little attention. The role of thin metallic films in the proximity of nanoparticles has been shown to play a role in the enhancement. This result can be understood in terms of interacting plasmons in the film and the nanoparticles.^{15,16} However, there is no clear understanding of the influence of the role that a dielectric substrate plays in the overall behavior of a plasmonic nanoparticle, that is, placed in the vicinity of the substrate. Clearly the

solution of Maxwell’s equations places a new boundary condition on the electromagnetic fields at the surface of the dielectric that must be included in the solution.

In this paper we have observed that dielectric or insulating substrates can play a significant role in the SERS process. This result is unexpected because the dielectric or insulating layer has no free mobile charge to respond to the plasmons and should not interact with the plasmons in the nanoparticles. We show that dielectric or insulating substrates or films represent a change in dielectric constant that the electromagnetic fields must experience and thus the field distributions are dramatically influenced. This effect is strongest when dealing with spherical or cylindrical SERS nanoparticles on a dielectric or insulating substrate because the fields from the nanoparticle are strongly focused in the regions between the nanoparticle and the substrate.

In order to demonstrate this effect, we have chosen to use nanowires randomly distributed on a Si substrate. These wires can be many microns long and the random distribution contains isolated wires as well as crossed wires. The crossed wires are very important because it is known that they form hot spots. We can use these hot spots as a basis for comparing the enhancement from the crossing to the enhancement of the same wire on the Si surface but many microns away from the crossing. This approach allows us to compare directly to theoretical predictions of the SERS enhancement at a hot spot and from a nanowire in contact with the dielectric substrate. We demonstrate that for nanowires that are placed on a substrate, the SERS enhancement changes both in magnitude and in the location of the hot spots. Experimental data of SERS maps from crossed nanowires is presented and is in excellent agreement with the theory.

II. THEORETICAL CONSIDERATIONS

The Raman-scattering process depends on light scattered from molecular vibrations in a solid, liquid, or a gas. In SERS, the Raman scattering from molecules adsorbed on nanostructured metal substrates is significantly increased by the creation of surface plasmons.^{4,5} Theoretically, the enhancement factor for surface-enhanced Raman scattering has been shown to depend on the dielectric properties of the

molecule adsorbed on the metal nanostructure, as well as on the geometry and dielectric properties of the metal nanostructure. The enhancement factor, G , can be written as¹¹

$$G(\mathbf{r}_m, \omega) = \left| \frac{\mathbf{E}_{total}(\mathbf{r}_m, \omega)}{E_{inc}(\omega)} \right|^4, \quad (1)$$

where $E_{inc}(\omega)$ is the incident electric field and $\mathbf{E}_{total}(\mathbf{r}_m, \omega)$ is the total field at the location of the molecule, \mathbf{r}_m . It is important to note that the total electric field is a vector quantity and that it contains contributions from the incident field as well as the electric field, that is, excited by the plasmons when they are in the presence of the incident field. Equation (1) has an analytical form for the case of solid spheres and cylinders of infinite length. More complex geometries and interacting nanoparticles must be treated with a numerical solution of the time-dependent Maxwell's equations.

In this paper we will solve the full Maxwell's equations numerically using the finite elements method (FEM) through the RF module of the COMSOL Multiphysics package.¹⁷ We used FEM simulations because they are more appropriate for the complex geometries of crossed nanowires placed on a substrate.¹⁸ FEM approaches have been shown to agree well with finite difference time domain simulations.^{18,19} In addition, the FEM technique implemented via COMSOL has been shown to be capable of accurate simulation for nanoshell structures if sufficiently accurate meshing is used and appropriate absorbing perfectly matched layers (PML) are used on the boundaries.²⁰ This approach allows us to treat the scattering problem by bringing in plane waves of a specific polarization and then calculating the scattered fields. As another test of the numerical simulations, we find excellent agreement between the COMSOL results with the analytical Mie solutions for scattering from a Ag sphere.^{18,20}

The modeling of the nanowires in air above a Si substrate requires the construction of separate PML boundaries for both the Si and air regions. The dielectric constants of each PML matches its adjoining region, either Si or air. To avoid artifacts due to scattering at the boundaries between the Si and air regions of the PML's, the scattering at the air-Si interface is incorporated into the incident-polarized plane wave by means of analytical functions for the Fresnel coefficients. The resulting incident field is thus an exact solution in the absence of the nanowires. The numerical finite element solution for the scattered field is then calculated in the presence of the nanowires. This requires sufficient meshing to adequately resolve both the nanowires with shells and the PML boundaries.²⁰

In this study, we examined the following cylindrical geometries: 300-nm-long dielectric nanowires having a 60 nm diameter and a 5 nm Ag coating. Calculations were performed for individual and crossed nanowires in air and on a Si substrate.

III. EXPERIMENTAL DETAILS

In this study we used Ag-coated Ga₂O₃ and GaN nanowires. The core Ga₂O₃, dielectric nanowires were fabricated using the vapor solid-liquid method¹⁴ and the GaN nanowires were grown by vapor-phase epitaxy. The nanowires

were grown directly on Si substrates. After growth, 5 nm of Ag was e-beam deposited and the samples were immediately vacuum sealed to protect from oxidation.

In preparation for use, the nanowires were removed from the Si substrate by sonication in a methanol solution. A drop of the methanol-nanowire solution was then applied to a clean Si substrate. Scanning electron microscopy was performed on the nanowires at all stages of processing and it was found that the Ag deposited on the nanowires in two-dimensional islands with a coverage of better than 70% while on the Si substrates the Ag formed three-dimensional islands with diameters less than 10 nm and widely spaced. Thus, even in the case of the substrates on which the nanowires were originally fabricated, they were in contact with Si only and not with an Ag film on the Si.

We used both saturated and 10⁻⁶ M chemical exposures of benzene thiol (BT), which is stable during illumination with green laser light at the power levels used. All samples, which were typically 1 cm² in size, were exposed to BT prior to the Raman measurements. The SERS enhancement for these nanowire systems was determined by comparison to the Raman spectrum of a neat solution of benzene thiol. We found that routinely these nanowire systems had enhancements in the range of 10⁶–10⁷.

The metal-coated dielectric nanowires were characterized by a scanning electron microscopy (SEM) for obtaining structural information and also in a Nanonics Multiview 2000AFM system, that is, directly mounted on the stage of our Raman microscope.

The confocal μ -Raman system consisted of a Mitutoyo microscope and an Ocean Optics QE65000 cooled charge-coupled-device (CCD) spectrometer. The 514.5 nm line of an Ar ion laser and a 532 nm diode laser were used as the excitation sources. We usually used less than 1 mW of laser power, focused into 0.75 and 50 micron diameter spots with the 100 \times , NA=1 objective. The microscope was coupled to an Ocean Optics QE65000 spectrometer through a fiber. The laser light from the microscope was filtered by a 514.5- or a 532-nm-long pass filter. In this configuration, we achieved a lateral spatial resolution of 0.7 μ m.

The microscope system was equipped with a scanning Prior stage that had better than 0.1 micron step sizes and a Nanonics Multiview 2000 AFM which is capable of better than 5 nm resolution. The microscope system also had an Olympus 730UZ digital camera that has 10 \times optical zoom and a 4 megapixel CCD. This arrangement allows us to image nanowires with diameters greater than 100 nm.

IV. RESULTS

The simplest case to consider in understanding the effect of a dielectric substrate is a simple sphere. However, the experimental verification of this effect for SERS from chemically coated spheres is difficult because of the fact that the nanoshell fabrication, that is, often used results in Ag-coated arrays of spheres restricting optical access to the contact points with the substrate. In addition, the spherical geometry provides no control situations because all of the spheres are either in contact with each other or with the substrate. A

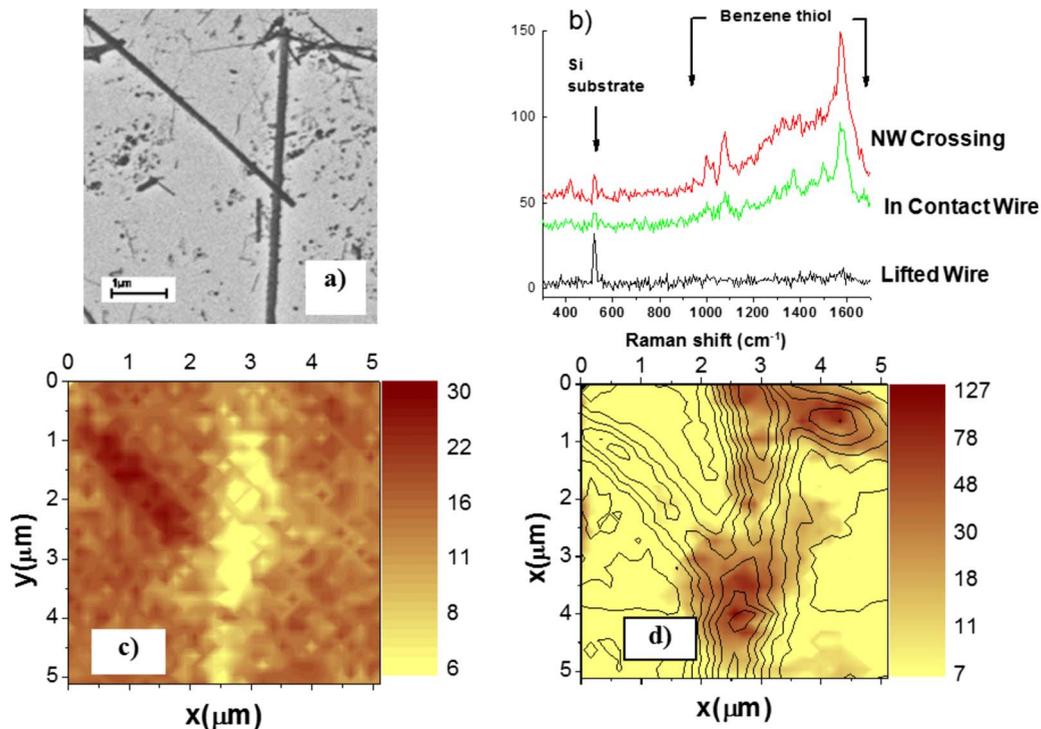


FIG. 1. (Color online) (a) SEM image of two crossed nanowires with the diagonal wire being suspended off the substrate and (b) shows the SERS spectra for BT and the Si substrate at the crossing and at midpoints of the two wires. In (c) is the Raman map if the 521 cm^{-1} of the Si substrate and in (d) is the SERS map for the 1576 cm^{-1} line of BT. The black lines overlaying the SERS map show the light scattering from the nanowires.

much better approach is to examine Ag-coated dielectric core nanowires because the nanowires can be fabricated to be many microns in length and can be randomly distributed, resulting in crossed and isolated nanowires, as well as nanowires that are off the surface because they bridge two other nanowires. The long lengths of these nanowires allows for examination at crossings and away from crossings. In addition, the advantage of using nanowires is that when they are crossed, easily detectable hot spots form between the nanowires.¹⁴ These hot spots can readily be used to compare the SERS from the whole wire to the crossing region to ascertain the relative strength of the dielectric substrate enhancement.

The experimental results of the substrate effect are shown in Fig. 1. The SEM image of two crossed nanowires is shown in Fig. 1(a). The nanowire running along the diagonal of the image is suspended between two other wires while the vertically oriented nanowire is in contact with the Si substrate. Figure 1(b) shows the SERS spectra from the middle of both wires and from the crossing. It is seen from the spectra that the wire in contact with the Si substrate and from the crossing show a strong BT line and virtually no signal from the underlying Si. This latter result is not surprising as the nanowire blocks light from penetrating into the Si substrate. In contrast to the results for the wire touching the Si substrate, the wire that is lifted from the surface shows no BT signal and a strong Si signal. The strong Si line is observed because the lifted nanowire allows EM fields to get around it. The lack of a BT signal is due to the fact that the SERS enhancement from this wire is significantly smaller

than for a wire in contact with the Si substrate.

Finally, Figs. 1(c) and 1(d) show Raman maps of the 521 cm^{-1} Si Raman line from the substrate and the 1576 cm^{-1} SERS line of the BT. These maps show in more detail the substrate effect for the increased plasmonic enhancement due to contact with the Si substrate. In addition, they also show us how the Raman of the Si line behaves in the presence of wires in contact with the substrate and lifted off the surface. This is useful in analyzing individual nanowires, where it is difficult to ascertain contact with the substrate.

Shown in Fig. 2 are an image of two long crossed wires and the SERS map of the BT line. In this case, both wires are in contact with the Si surface and are clearly imaged in the SERS map. Figure 3 shows the case of two isolated wires.

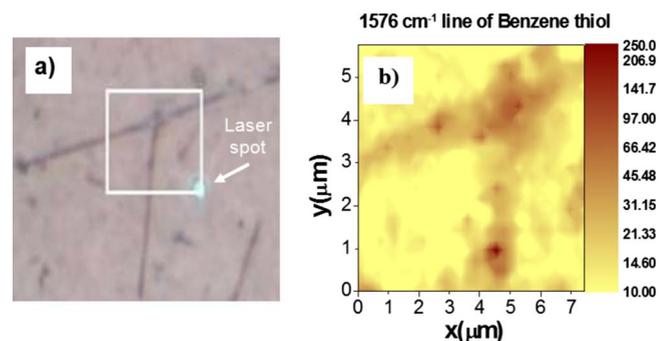


FIG. 2. (Color online) (a) Optical image of crossed Ag/ Ga_2O_3 nanowires that are approximately 100 nm in diameter. (b) The intensity map of the 1576 cm^{-1} of benzene thiol.

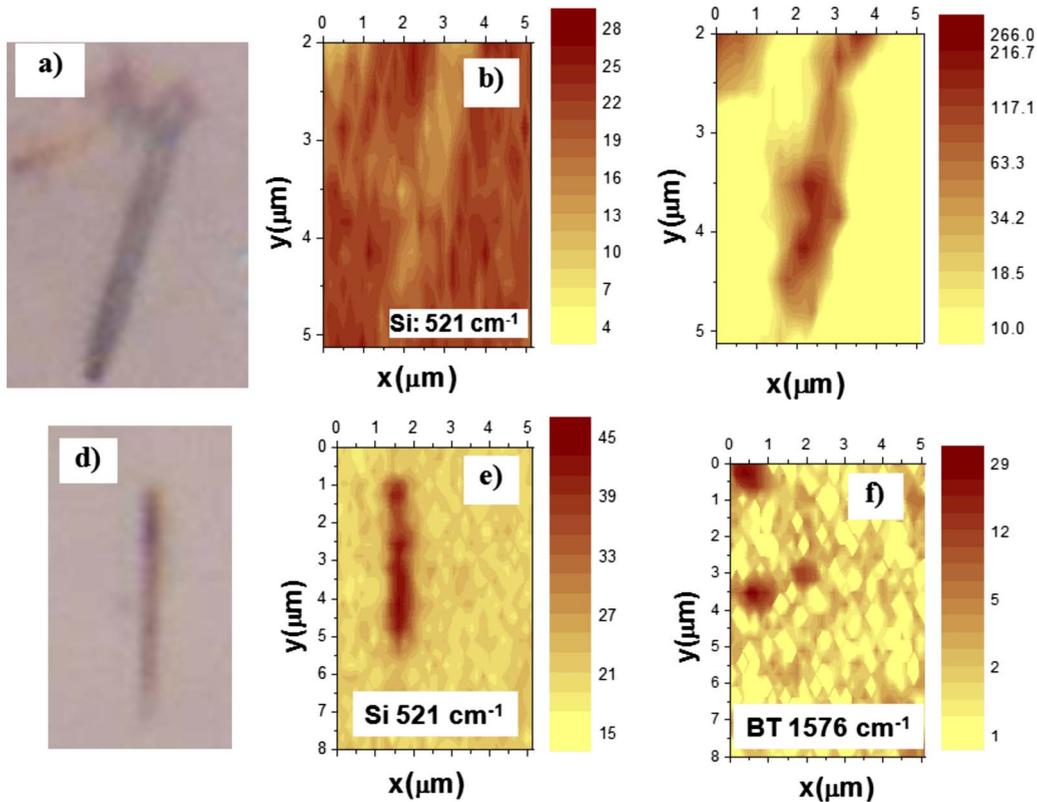


FIG. 3. (Color online) (a) Optical image of a single $\text{Ag}/\text{Ga}_2\text{O}_3$ nanowire in contact with the substrate and (b) the associated Raman map of the Si line, and (c) the SERS intensity map of the 1576 cm^{-1} of benzene thiol. In (d) is a nanowire raised for the Si surface and the associated (e) Si Raman and (f) BT maps.

The images of the wires are shown in Figs. 3(a) and 3(d). From these images it is difficult to determine contact with the Si. The Raman lines of the Si substrate shown in Figs. 3(b) and 3(e) show that the wire in Fig. 3(a) is in contact with the Si surface while the wire in Fig. 3(d) is not. The SERS from the BT shown in Figs. 3(c) and 3(f) indicates that for isolated nanowires contact with the substrate significantly increases the plasmonic enhancement.

In order to further verify this effect, we compared the results for Ag-coated Ga_2O_3 and GaN core shell nanowires exposed to benzene thiol. Fifteen measurements were performed for each sample; five at crossings, five at regions far away from crossings, and five at isolated nanowires. The relative SERS intensity average for all of these measurements agreed with the maps presented above and indicated that the SERS from any of the locations examined were within a factor of 3 of each other with the crossings being the strongest. Interestingly, the diameters of the GaN nanowires were a factor of three larger than the Ga_2O_3 nanowires and still showed similar results and comparable relative SERS intensities.

To explain the experimental results we have performed full-wave simulations of the SERS enhancement for a pair of crossed nanowires at an angle of 45° in air and on a Si substrate. The results of these simulations are shown in Figs. 4(a) and 4(b), respectively. The nanowires were cylindrical Ag shells with a Ga_2O_3 core that was 300 nm long and 60 nm in diameter. The shell thickness was 5 nm. The complex index of refraction for Si, Ag, and Ga_2O_3 were taken from

Palik.^{21,22} The incident plane wave was perpendicular to the Si substrate and wavelength of 515 nm and circular polarization to simulate unpolarized light. It is clear from the spatial distributions of $\log(G)$ that the SERS enhancement is not confined to the surfaces of the nanowires, as one might expect for an isolated nanostructure but that there is a large hot spot localized between the two wires as shown in Fig. 1(a), in the vicinity of the crossings. In addition, the maximum enhancement is many orders of magnitude higher than for the isolated wires.

Placing the nanowires on Si changes the electromagnetic boundary conditions for the scattering. The high dielectric constant of the Si pulls in the field lines and significantly increases the SERS enhancement in the vicinity of where the nanowire touches the Si substrate. As shown in Fig. 4(b), there is a significant enhancement region near the contact point between the base of the wire and the Si substrate. The magnitude of the enhancement is similar to that seen at the crossing of Fig. 4(a). Interestingly, as shown in the inset of Fig. 1(b), the region of the crossing maintains its high SERS enhancement.

This clearly shows the influence of the high-index substrate on the local electric fields near the contact point. The high index bends the fields toward the normal from the Si and creates a larger bunching of the field lines around the contact point. Similar results have been observed for electrophoresis of colloidal cylinders²³ and conducting spheres near dielectric planes.²⁴ The electric field patterns shown in Fig. 1(b) are analogous to what one might obtain from the case of

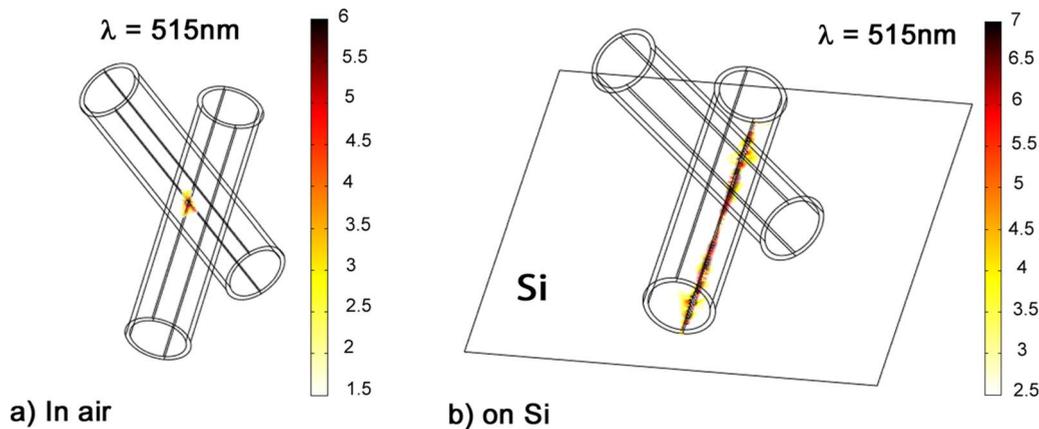


FIG. 4. (Color online) COMSOL simulations for the log of the SERS enhancement maps for 515 nm light for crossed wires. The map in (a) shows the case for two wires in air and (b) is for two crossed wires on a Si substrate.

the image charge problem, for a charged conductor near a grounded conducting plane and this analysis has been used in Ref. 21. In our case, however, there are no mobile charges in the Si to create an image charge. What we observe is the influence of the dielectric plane, which creates charge redistribution in the nanowires to satisfy the boundary conditions imposed by the dielectric substrate.

These results can be easily understood from the simulations and the fact that a molecule has to be able to adsorb in the region where the enhancement exists. Clearly the contact points are difficult to reach and few if any molecules can get to those points. Therefore the peak enhancements from the contact points would be difficult to observe. On the other hand, the regions 10–20 nm away from the contact points show theoretical enhancements that are comparable to the crossings and are readily accessible for molecular adsorption. We therefore, suggest that molecules move into the regions between the nanowire and the Si and that this is the source of the bulk of our signal from isolated nanowires.

V. SUMMARY AND CONCLUSIONS

In summary, we have performed SERS mapping from both long, intersecting nanowires, and isolated nanowires; and showed that the SERS signal from isolated regions of the nanowires, which were on a Si substrate, was similar in intensity to the signal coming from the crossings. In addition experimental data from crossed nanowires, where one of the nanowires was not in contact with the substrate had no measurable SERS along the isolated region and agreed well with calculations. We also examined isolated nanowires and showed that when the wires are in contact with the Si substrate, there is a significant increase in the SERS enhancement factor.

We also presented finite element simulations of the effects of dielectric substrates on the SERS enhancement from cylindrical nanowires and showed that the theory is in good agreement with the experimental results. The substrate acts to focus the field lines around the contact points and that the

SERS from a single nanowire or sphere can be dramatically enhanced by placing that nanowire on a dielectric surface. Previous theoretical work on the surface plasmons of spheroidal metal nanoparticles near a dielectric substrate show significant redshifts in the surface-plasmon resonance curves of the nanoparticles.²⁵ These changes would be large enough to shift the SERS enhancement away from what one would expect from a particle in air. Our simulations show that a bunching of fields occurs near the substrate and increase in the SERS enhancement. This is consistent with the image charge approach used in Ref. 25 to provide a simple model of the influence of the substrate on a sphere.

These results have significant implication in relation to SERS measurements from metal-coated nanoparticles in which the metal coatings are not uniform and have spherical or cylindrical islands.^{26,27} In this case, the coatings are typically smaller than the wavelength of the peak SERS enhancement. Coupling of these nanoparticles and interactions with the substrate significantly increase the SERS. In Ref. 26 enhancement factors of 10^6 – 10^8 are reported for 20–50-nm-diameter Si nanotips coated with silver nanoballs with radii 20 nm or less.

Finally, the results reported in this paper clearly show that, in order to properly account for the SERS enhancement of a system of particles and a dielectric substrate, both the particles and the substrate must be taken into account in any simulation. Furthermore, the substrate effects reported here can provide a powerful tool in the design of new SERS substrates that have large areas of enhancement when the nanoparticles with spherical cross sections are placed on a dielectric. This effect will also be present in nanoparticles with sidewalls that intersect the substrate at angles less than 90° .

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