

Plasmonic behavior of Ag/dielectric nanowires and the effect of geometry

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Recently, the authors have shown that dielectric/metal composite nanowires exhibit very strong surface enhanced Raman (SERS) signals when arranged in a random three-dimensional geometry. Since they believe that the intersections of nanowires are critical in generating the high electric fields necessary for this enhancement, they have investigated the effect of crossing geometry under more controlled conditions. Thus, they will discuss the formation of nanowire arrays by *in situ* growth achieved by the control of nanowire material/substrate combination, as well as *ex situ* nanowire array formation involving e-beam lithography. They have examined the plasmonic effects, both longitudinal and transverse, due to changes in crossing geometry by specific placements of dielectric/metal nanowires on the fabricated arrays. The effects of nanowire geometry and the resulting SERS behavior show the importance of the dielectric/metal configuration, as well as the importance of nanowire angular geometry in the SERS enhancement. © 2009 American Vacuum Society. [DOI: 10.1116/1.3130150]

I. INTRODUCTION

Optically based sensing provides advantages over electronic sensing because optical spectra can uniquely fingerprint a chemical compound, eliminating false alarms and simplifying the detection process. In Raman scattering (RS), light is scattered from a chemical of interest, and the vibrational modes in the chemical redshift the frequency of the scattered light, producing a spectrum of lines that are characteristics of that molecule. Since this fingerprint is unique to a given material, precise chemical identification is possible.

The problem in ordinary Raman scattering is that its cross sections are very small resulting in low sensitivity, but the Raman signal can be enhanced by many orders of magnitude by the use of various metal-based nanoparticles.^{1,2} This enhancement is thought to be the result of local electromagnetic fields that are created by the laser excitation of surface plasmons at the metal surface. Even though enhancements of as high as 10^8 – 10^{12} have been reported,³ the underlying mechanisms are not fully understood.

Thus, understanding the surface enhanced Raman (SERS) mechanism and how it relates to the geometric properties of a SERS substrate is critical to any possible future applications in highly efficient sensors and taggants. Current research suggests that the size, shape, alignment, and chemical effects are important parameters in the SERS effect.^{3–6} For example, it has been shown that Au nanorods exhibit a stronger SERS effect than Au nanoparticles,⁷ and the plasmon resonance can be tuned in a dielectric core/metal shell nanosphere geometry,² as well as in metal/dielectric nanodisks.⁸ In addition, special alignment or close proximity also resulted in higher SERS intensity.^{2,9,10}

We have developed a highly sensitive SERS substrate based on a random distribution of dielectric core/metal shell nanowire (NW) geometry,^{11,12} which can reliably detect 0.2 pg of rhodamine 6G (a standard SERS-active dye). The SERS enhancement for these experiments was greater than 10^7 , with the fluorescence being three to five orders of magnitude greater.¹² We believe that the random distribution of Ag/dielectric nanowires is important because it maximizes the density of hot spots (high electric field regions) and allows molecules to have more access in depth than nanoshell geometries.

In this work, we have tried to elucidate the role of these hot spot in the crossing geometry, and we have investigated various nanowire crossing geometries, including random, parallel, and nearly crossed arrays. We have also measured the strength of the SERS effect as a function of these various geometries using our micro-Raman system. The results show the importance of the cross-over geometry, the angular dependence of the SERS effect, as well as the importance of the dielectric core/metal sheath geometry.

II. EXPERIMENTAL PROCEDURES

Several different nanowire systems have been grown, including random Ga₂O₃ nanowires, ZnO nanowires, as well as Au lines produced by e-beam lithography. The growth of the Ga₂O₃ nanowires was achieved by the controlled oxidation of pure Ga metal in a vacuum tube furnace.¹³ A schematic of the growth system is shown in Fig. 1. The source material was placed at one end of a 4 in. alumina boat, with the substrate (which includes the Si wafer and Au catalyst) at the opposite end. The boat was then inserted into a quartz tube inside a tube furnace, which was evacuated to a base vacuum of 40 mTorr using a mechanical pump. The furnace was then heated to 900 °C. Several gas feed valves and flow controllers were connected to the other end of the tube, allowing a controlled flow of argon and oxygen gas to pass over the alumina boat. Once at temperature, the growth was

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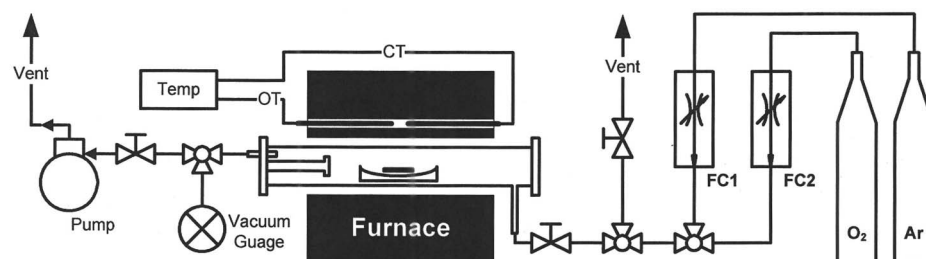


FIG. 1. Nanowire growth system consisting of a single zone furnace and evacuated quartz tube and gas flow controllers.

initiated by the flow of a 6:1 ratio of argon to oxygen. The ZnO nanowires were grown at 550 °C in a tube furnace under atmospheric conditions¹¹ using Zn pellets (Alpha-Aesar) as the source material. No metal catalyst was used for the growth of the ZnO nanowires. Finally, Au lines, 80 and 90 nm thick, with 186 nm spacing, were produced by e-beam lithography. Two types of lines were fabricated, those that were only 20 nm high and those that were 65 nm high. The Ag metal sheath was formed subsequently by e-beam evaporation and then the nanowire composites were removed off the substrate by sonication in a methanol solution. All the grown nanowires were analyzed using a LEO SUPRA 55 scanning electron microscope (SEM), JEOL 2010F 200 KV high resolution transmission electron microscope (HRTEM), and x-ray energy dispersive spectroscopy attached to the HRTEM, as well as Raman spectroscopy.

III. CROSSINGS OF NWS AND THE ANGULAR DEPENDENCE OF THEIR PLASMONIC PROPERTIES

As discussed above, we have developed a SERS substrate, consisting of Ga₂O₃ nanowire core/Ag metal sheath nanostructures, which have been shown to exhibit strong SERS enhancements. An example of such a nanowire network is shown in Fig. 2(a). A comparison of the SERS sensitivity for rhodamine 6G (Rh6G) for these nanowires and that of a commercial substrate from Mesophotonics (Klarite) is shown in Fig. 2(b). In order to compare these substrate, we have used 0.2 pg of Rh6G for these studies, and the nanowire arrays were covered with a 5 nm layer of Ag, creating dielectric/Ag nanowire composites. The Ag film on a flat substrate did not exhibit any SERS signal, which rules out

the effect of Ag roughness as the source of the SERS signal. As is evident, the nanowire composites are about two orders of magnitude more sensitive than the Mesophotonics substrate.

Since these Ga₂O₃/Ag nanowire composites can be very efficient SERS substrates, we have suggested that the nanowire crossings result in “hot” spots¹² in the electric fields, thus enhancing the SERS signal. The importance of plasmon coupling at nanowire crossings can be seen in Fig. 3(a), which is a result of a finite element simulation¹² of the electric field near two obliquely crossed nanowires separated by several nanometers in air, in response to 500 nm wavelength light polarized in the x-direction. An enhanced plasmon resonance is found in the vicinity of the crossing. However, the field maximum does not occur halfway between closest separations between the wires, as would be the case in the parallel wire or the nanosphere, shown in Fig. 3(b). Instead, the maximum is displaced away from the crossing angle in a much larger volume surrounding each crossing. This would not only enhance the SERS effect due to the strong coupling but also allow more molecules to enter this high electric field region, thereby enhancing the SERS sensitivity. Furthermore, the parallel wire geometry,¹⁴ as well as nanosphere geometries, requires a very specific spacing in order to maximize the enhancement due to coupling, which is not the case in crossed wires since an optimal spacing will always be present for every crossing angle due to the wire geometry. Randomly crossed wires would be expected to exhibit two such maxima in the vicinity of each of the crossings, as shown in Fig. 3(a).

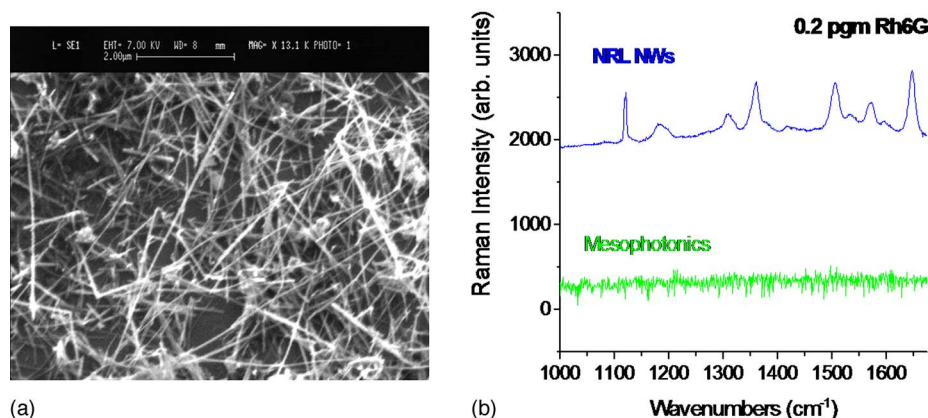


FIG. 2. (Color online) SEM image of (a) single Ga₂O₃ nanowires arranged in a random cross-over geometry and (b) SERS enhancement comparison to commercial substrate from Mesophotonics (Klarite).

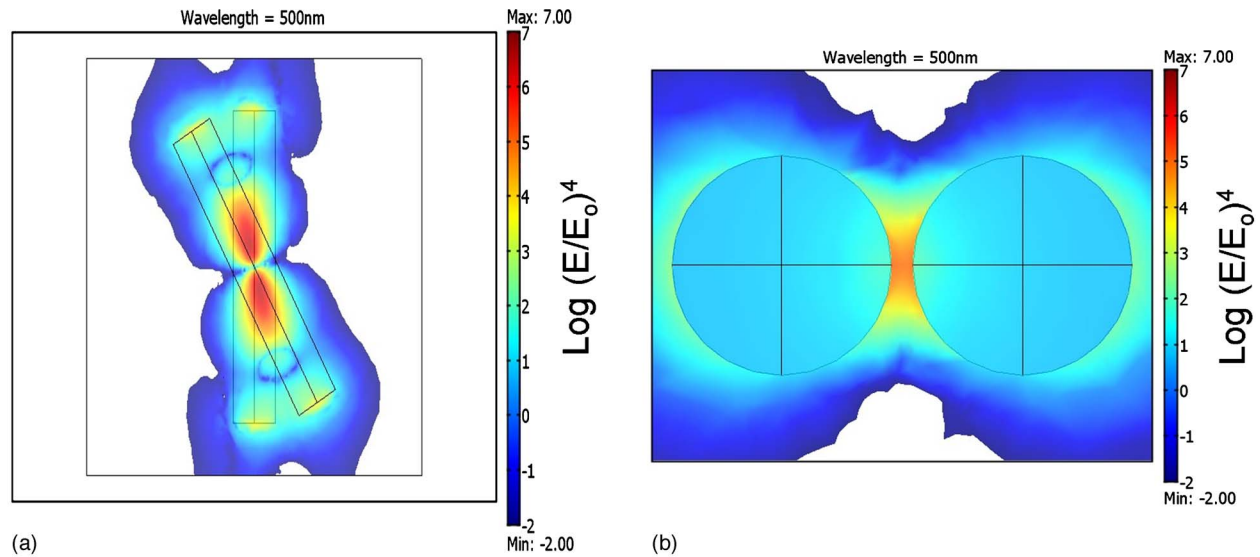


FIG. 3. (Color online) COMSOL electric field calculation of (a) crossed nanowires separated by several nanometers at the point of intersection and (b) similar diameter closely spaced nanospheres spaced less than 10 nm apart.

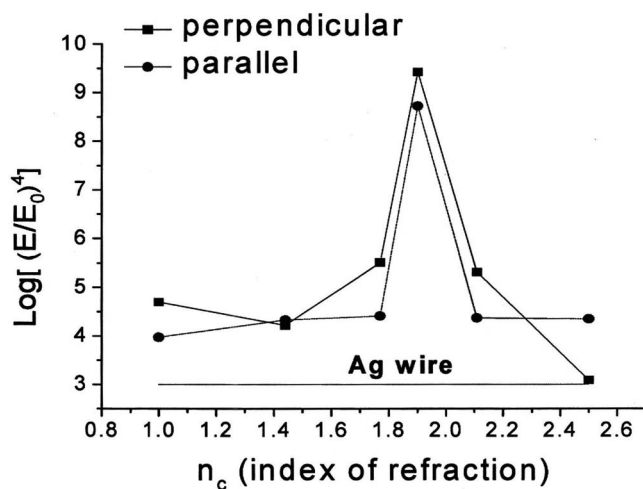


FIG. 4. COMSOL simulations of the enhancement vs core index of refraction for dielectric core/Ag sheath NWs and solid Ag NWs.

In addition to the hot spot enhancements, further enhancement in the SERS signal should also be realized from the dielectric core/metal sheath configuration, as determined from the COMSOL simulations. Figure 4 shows the enhancement as a function of the index of refraction for the NW core. As can be seen, an enhancement of at least a factor of 10 is expected in the case of a dielectric core structure compared to a solid Ag nanowire. In addition, a much greater enhancement should be realized for materials that have index of refraction between 1.8 and 2.2. Since the indices of refraction of ZnO and Ga_2O_3 are 2.03 and 1.8 in the 514 nm wavelength range, one would expect an additional SERS enhancement due to the specific core material.

In terms of plasmon coupling, the advantage in crossings can be examined if one now considers the SERS results for two different nanowire geometries, one consisting of crossed wires and one that does not result in notable crossing, as shown in Fig. 5. In this case, the random $\text{Ga}_2\text{O}_3/\text{Ag}$ nanowire composites exhibit a high density of oblique crossings throughout the array, while the ZnO/Ag nanowires consist of a star-burst-type growth mode, with almost no crossing evi-

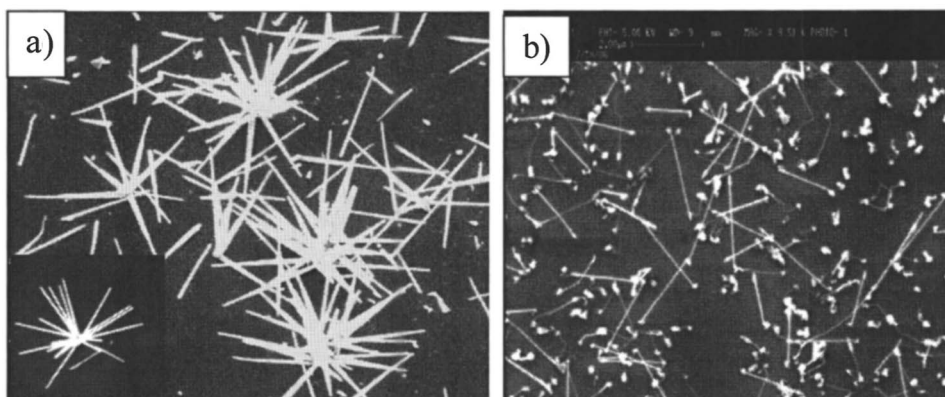


FIG. 5. (a) Nanowires grown in a "star-burst" morphology with minimal crossing and (b) nanowires grown in a cross-over geometry.

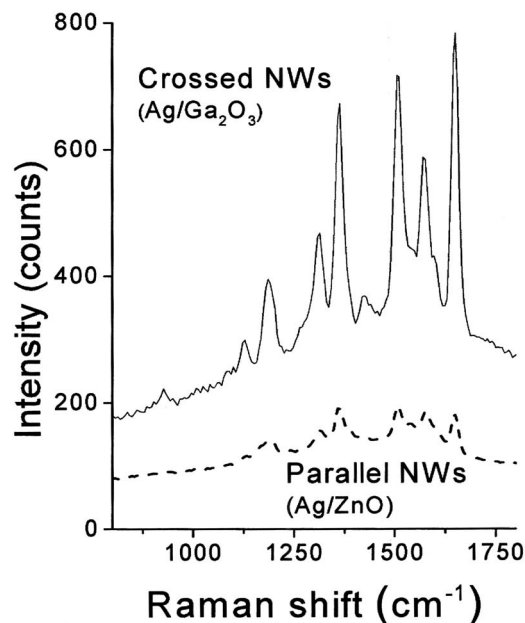


FIG. 6. SERS results of ZnO/Ag nanowire composites and Ga₂O₃/Ag nanowire composites using Rh6G.

dent. A comparison of the SERS signal is shown in Fig. 6. As can be seen, although the ZnO nanowire composites do exhibit a SERS signal, it is significantly weaker than that from the Ga₂O₃/Ag nanowire composites. This can be understood from the perspective of plasmon coupling since one would expect much greater coupling in the case of the crossed wires, as the calculations predict.

The importance of the nanowire crossings can be even clearer if one considers a single nanowire system, as shown in Fig. 7. In this case, the laser line was scanned across the nanowire in a horizontal direction, marked as 1, as well as a vertical direction, marked as 2, shown in an optical image in Fig. 7(a), with a corresponding SEM image shown in Fig. 7(b). The SERS spectra are shown in Figs. 7(c) and 7(d). What is quite evident is that in the horizontal direction, very little SERS signal is evident as a function of distance across the wire, while in the vertical direction, a strong SERS signal for Rh6G can be seen as the wire is intersected. The reason for this surprising difference becomes quite clear when this nanowire is examined in SEM, which allows for a more detailed examination of the nanowire structure and geometry [shown in Fig. 7(b)]. As can be seen, the horizontal scan involves a single large nanowire, while the vertical scan is over a nanowire crossing, as marked in Fig. 7(b). Thus, in this case, the crossing of the two nanowires leads to significantly enhanced plasmon coupling and to much enhanced electric fields and a much stronger SERS signal, as predicted from the finite element analysis.

A more ordered nanowire structure can also be produced by e-beam lithography, as shown in Fig. 8. In this case, both 80 and 95 nm wide Au lines, with 186 nm separation, were produced and examined for SERS using 10⁻⁶M Rh6G solution. The SERS results are shown in Fig. 9 and both structures exhibit SERS for Rh6G, with the 95 nm lines showing slightly stronger SERS signal. Interestingly, when identical width Au lines, having only 20 nm height, were examined, no SERS signal was evident. This suggests that the required

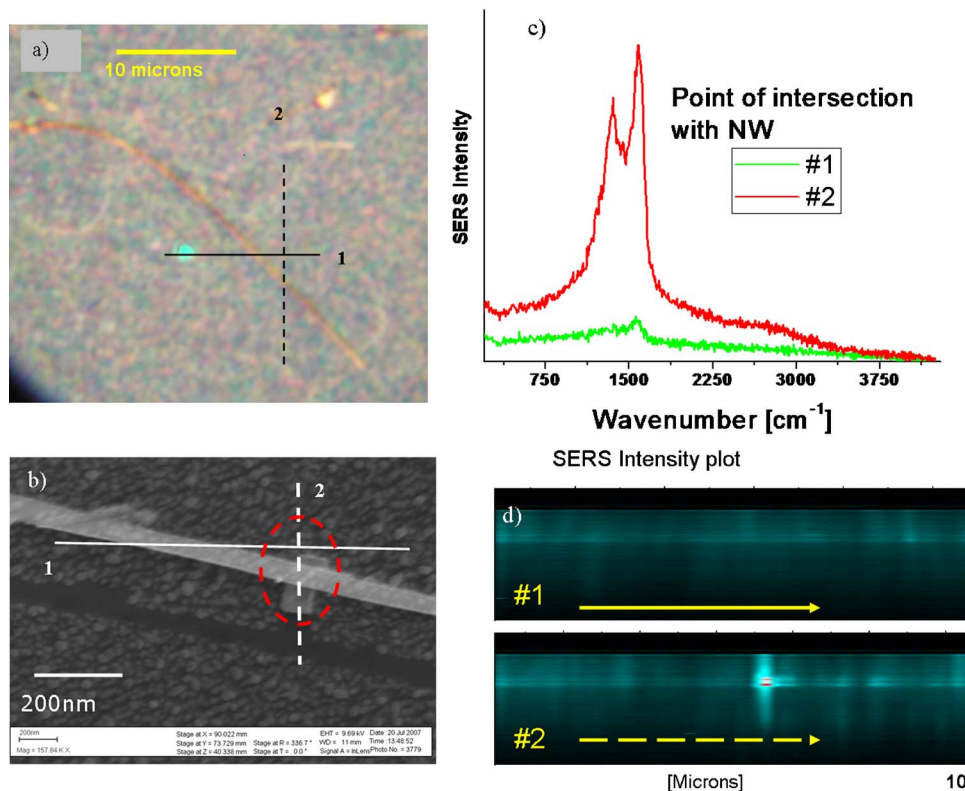


FIG. 7. (Color online) Optical micrograph and SEM image of a Ga₂O₃ nanowires indicating the scan direction of laser line. [(a)–(c)] SERS spectra for horizontal and vertical laser scan and (d) SERS intensity plot as a function of scan distance.

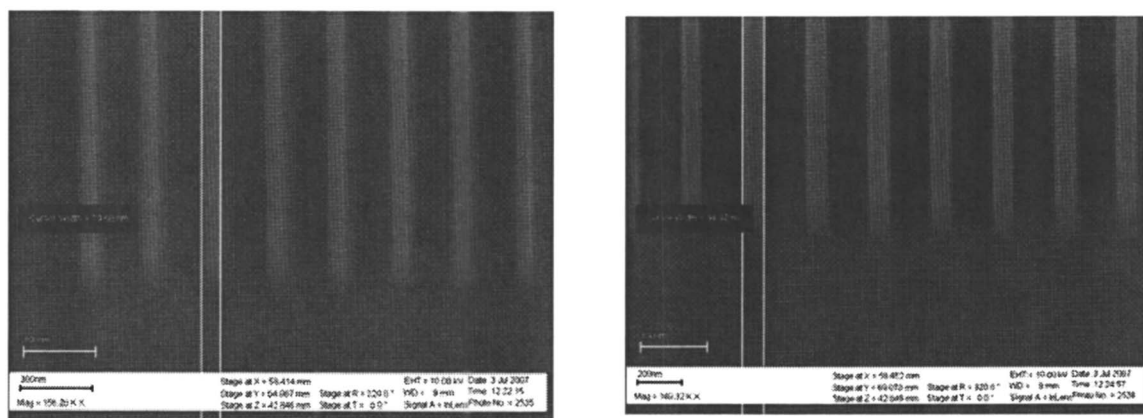


FIG. 8. Lithographically produced Au lines of 80 and 95 nm widths.

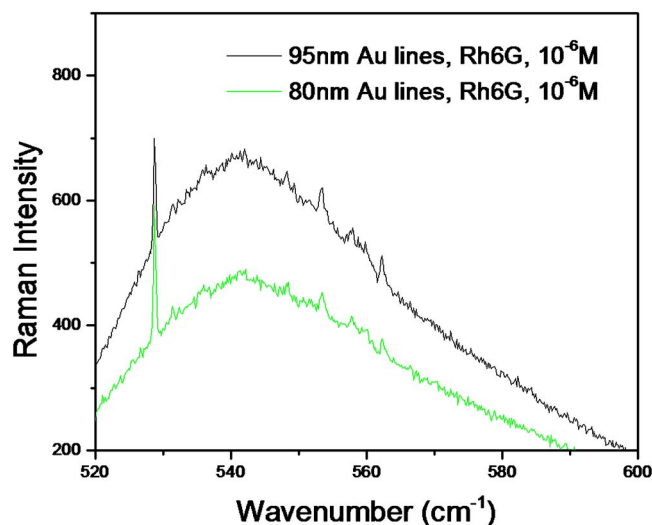


FIG. 9. (Color online) SERS signal for 95 and 80 nm wide Au lines produced by e-beam lithography. The molecule used for 10^{-6} M Rh6G.

dimensions for effective SERS are really in three dimensional and not just in two dimensional. Since the Au lines are spaced 186 nm apart, one would not expect effective plasmon coupling between the wires, and thus it is not surprising that the SERS signal is rather weak for Rh6G. We can, however, examine the effect of changes in geometry by the use of these Au lithographically produced lines and a solution of the $\text{Ga}_2\text{O}_3/\text{Ag}$ nanowire composites. In this case, in order to reduce the fluorescence, we have chosen to use benzene thiol (BZT), which does not experience excitation using the 514 nm laser line. However, BZT is not as easily detected using SERS. Thus, no SERS was detectable for the Au lines only, as shown in Fig. 10(a). If $\text{Ga}_2\text{O}_3/\text{Ag}$ nanowires are subsequently deposited on the substrate containing the 95 nm Au lines, a number of nanowire geometries can be seen, as shown in Figs. 10(a) and 10(b).

The interesting aspect of this type of geometry is that the “T” formation shown in Fig. 10(b) allows for the measurements of SERS using a nanowire, which is parallel or perpendicular to the underlying Au lines. An optical image of the two locations where SERS was obtained, along with the spectral images, is shown in Fig. 11. As is evident, the perpendicular wire shows extremely weak SERS for the BZT, while the parallel line has a strong SERS signal. Similar

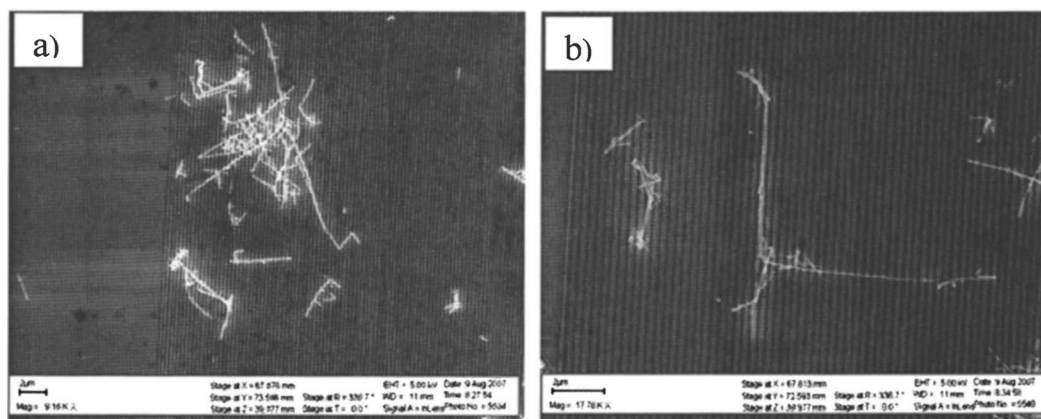


FIG. 10. SEM images of (a) clump of nanowires and (b) nanowire T placed on top of 95 nm Au lines.

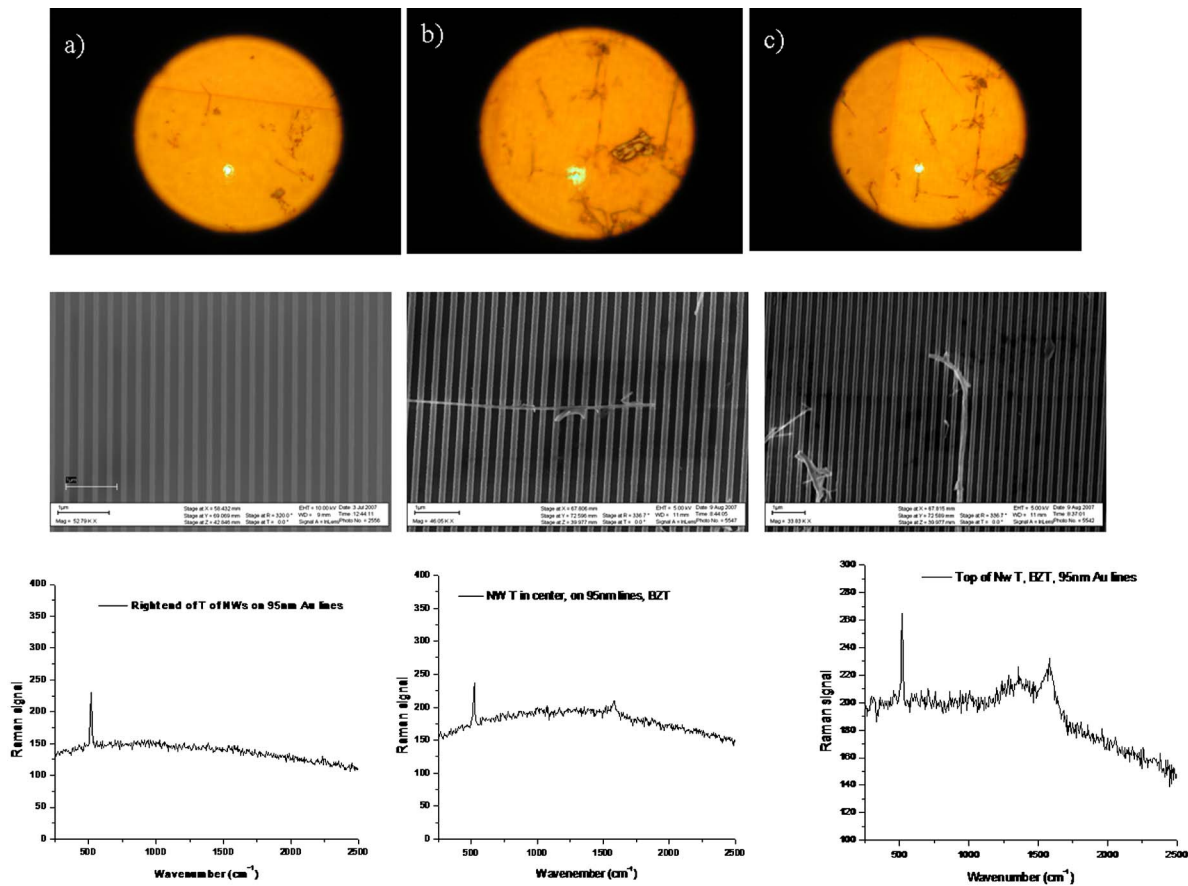


FIG. 11. (Color online) Optical and SEM images and corresponding SERS spectra for (a) grating only, (b) NW perpendicular, and (c) NW parallel.

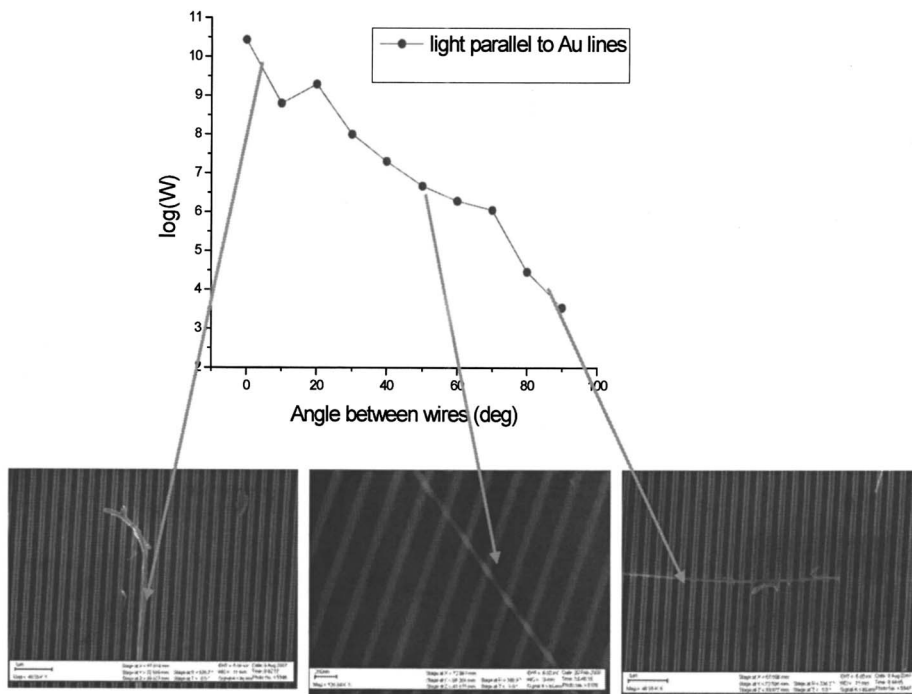


FIG. 12. COMSOL calculation of the expected SERS enhancements for wires as a function of crossing angle and SEM images of the parallel and perpendicular wires in the T configuration.

results can also be obtained for other NWs, such as one crossed at 45° , which exhibits a SERS enhancement in between the two extremes of 0° and 90° . In order to understand this result, let us briefly consider the expected SERS enhancement for wires as a function of angle between each other obtained from the COMSOL simulation, shown in Fig. 12, as well as the actual geometry, as determined from SEM, also shown in Fig. 12. As can be seen from the simulation, one would expect a much larger enhancement from nanowires, which are nearly parallel and very closely spaced, as is evident from the SEM image of the parallel wire. The perpendicular wire should exhibit much lower enhancement in this geometry, which is confirmed by the data in Fig. 10, in which the parallel nanowire geometry exhibits a noticeable SERS, while in the perpendicular case, no SERS is evident. As expected, the 45° crossing leads to an predicted enhancement in between the two extremes.

IV. CONCLUSION

In conclusion, we have addressed the effect of geometry on the electric field enhancement in the SERS effect using dielectric/metal nanowire composites, as well as Au lines produced by e-beam lithography. By appropriate choice of growth mechanism and substrate, we were able to produce nanowires that exhibit different array geometries. The results indicate that a crossed geometry leading to electric field hot spots can significantly enhance the SERS signal from target molecules, as does the dielectric core/metal sheath design. SERS measurements using rhodamine 6G have shown these

substrates to be highly sensitive, and it is suggested that this enhancement is the result of both the dielectric core/metal shell geometry and the formation of a large number of hot spots when arranged in an appropriate geometry. Finite element calculations support the angular dependence of the SERS enhancement results obtained experimentally.

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