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Dielectric and geometric properties of plasmonics in metal/dielectric nanowires composites used in surface-enhanced Raman spectroscopy

O.J. Glembocki[a], R.W. Rendell[a], S.M. Prokes[a], D.A. Alexson,[a] M.A. Mastro[a], S.C. Badescu[a] and A. Fu[b]
[a]U.S. Naval Research Laboratory, Washington, DC 20375
[b]University of Maryland, College Park, MD 20742

Keywords: Surface enhanced Raman scattering, dielectric properties, geometric properties, electric field hot spots, Ag coated Ga_2O_3 nanowires, sensing.

ABSTRACT

Finite elements calculations have been performed of the surface enhanced Raman (SERS) activity of Ag coated dielectric nanowires. It is shown that the SERS fields and the angle of the peak field from intersecting nanowires can be changed through the angle of the nanowires. In addition, it is shown that the strength of the SERS enhancement and its spatial profile depend on whether the nanowires are in free space or on a substrate. Experimental data for benzene thiol on dielectric coated nanowires is shown to support the calculations. These results demonstrate the importance of geometry and local environment on electric field hot spots in the SERS process.

1. INTRODUCTION

Surface enhanced Raman scattering (SERS) has a long and rich history of detecting submonolayer coverage of roughened metal electrodes by adsorbing molecules.[1,2,3] 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 and particularly of nanosphere lithography has led to more reproducible SERS active substrates characterized by nanoparticles with well defined shapes, such as nanospheres, nanoshells and triangles.[6,7,8] 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.

Furthermore. Garcia-Vidal and Pendry[12] have shown that when two Ag semi-cylindrical 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 Martin of two parallel Ag nanorods.[11] Their calculations indicated 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 operational for Ag coated Ga_2O_3 nanowires and for Ag coated SiO_2 spheres. This work demonstrated that enhancements as high as 10^7 can be attained with randomly oriented and intersecting nanowires.

In this paper we treat the nanowire problem theoretically and report on three key issues that are at the heart of interacting nanowires placed on a substrate. We show that the angle of crossed nanowires can be used to tune both the SERS enhancement and the wavelength at which the peak enhancement occurs. For all angles, the SERS hot spot extends spatially well beyond the region where the nanowires are crossed. When the nanowires are placed on a substrate, the SERS enhancement is shown to change 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. All

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of these results when taken together allow us to suggest optimal geometries for maximizing SERS hot spots and thus SERS sensitivity.

2. 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 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 as:[12]

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

where $E_{inc}(\omega)$ is the incident electric field and $\boldsymbol{E}_{total}(\mathbf{r}_m.\omega)$ 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. More complex geometries and interacting nanoparticles, must be treated with a numerical solution of the time dependent Maxwell's equations. Within the quasistatic approximation, which is appropriate when the the geometries of the scattering aggregates are much smaller than the wavelength of light, Maxwell's equations reduce to:

$$\nabla \cdot \left(\sigma(\vec{r})\left[-\nabla\phi(\vec{r}) + E_0\right]\right) = 0, \qquad (2)$$

where σ is the conductivity, and ϕ is the vector potential. In this paper we will solve this equation numerically using the Comsol package. The following cylindrical geometries were simulated: a) 300nm long solid Ag nanowires having a 50nm diameter; and b) 300nm long dielectric nanowires having a 60nm diameter and a 5nm Ag coating. Calculation were performed for individual and crossed nanowires in air, on a Si substrate and on a 5nm Ag coated Si substrate. These circumstances cover the possible experimental situations that can be encountered during a typical SERS experiment.

3. EXPERIMENTAL DETAILS

3.1. Nanowires and chemical exposure

The Ag coated nanowires used in our experiments were fabricated using the vapor solid liquid (VSL) method.[14] The dielectrics that were used included: Ga_2O_3, ZnO, InAs and GaN. In this paper we report only on the results for Ga_2O_3. Subsequently, 5nm of Ag was e-beam deposited and the samples were immediately vacuum sealed to protect from oxidation. Chemical exposures were limited to 10^{-6}M benzene thiol (BT), which is stable during exposure to green laser light at the power levels used. All samples, which were typically 1cm^2 in size were exposed to 10µl of BT prior to the Raman measurements.

3.2. Sample characterization

The metal coated dielectric nanowires were characterized by a scanning electron microscopy (SEM) for obtaining structural information and also in a Nanaonics Multiview 2000AFM system that is directly mounted on the stage of our Raman microscope. Figure 1. shows SEM and optical microscope images of a Si substrate containing Ag/Ga2O3 nanowires. Note that in the dense regions there are many nanowires and nanowire crossing. The more sparse regions shown in Fig. 1b are suitable for Raman mapping.

The confocal µ-Raman system consisted of a Mitutoyo Microscope and an Ocean Optics QE65000 cooled CCD spectrometer. The 514.5 nm line of an Ar ion laser was used as the excitation source and the laser had a power of 5mW

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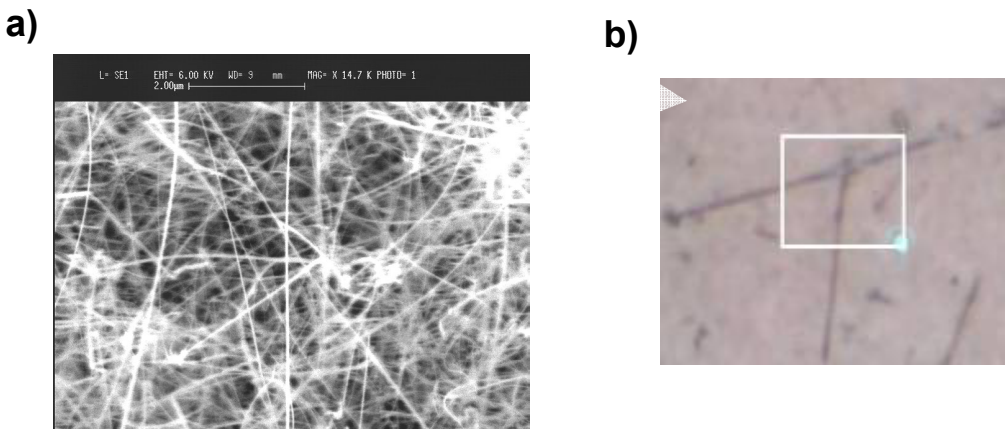

Figure 1. a) SEM and b) optical microscope images showing the dense and sparse regions of a Si substrate with Ag/Ga_2O_3 nanowires

or less. We usually used less than 1mW, focused into a half micron diameter spot with the 100x, NA=1 objective. The microscope had 10X, 50X and 100X objectives for focusing the laser light and was coupled to the spectrometer through a fiber. The laser light from the microscope was filtered by a 514.5 nm notch filter. In this configuration, we achieved a lateral spatial resolution of 0.7 µm.

This microscope system is equipped with a scanning Prior stage that had better than 0.1 micron step sizes. The Nanonics Multiview 2000 AFM was mounted on this stage and is capable of better than 5 nm resolution. The AFM is equipped with special tips that allow us to focus the light right at the tip and to recover scattered Raman light from the region. This Prior stage and the Nanonics AFM were used for mapping the Raman intensity.

4. RESULTS

4.1. Theory for 50nm Ag nanowires

The simplest case to consider in order to build up an understanding of the behavior of dielectric core nanowires is the pure Ag nanowire. The results of the simulation for a pair of crossed nanowires at an angle of 30° is shown in figure 2. The nanowires had a diameter of 50nm and were 300nm long and were placed on a Si substrate. The complex index of refraction for Ag was taken from Palik's Handbook of Optical Constants.[15] Figures 2a and 2b show the spatial distribution of the SERS enhancement, It is clear that for intersecting solid Ag nanowires the SERS enhancement is not confined to the surfaces of the nanowires, as one might expect for an isolated nanostructure. In fact the SERS enhancement is distributed between the wires and over much of the wires. The spectral behavior of the enhancement or the surface plasmon resonance (SPR) is plotted in figure 2c. for a single Ag nanowires and for the two intersecting nanowires of figure 2a. The SPR develops two peaks rather than one and is significantly increased. This is true for both orthogonal polarizations of the incident light. Note that the strongest SPR is in the near IR.

Since the nanowire intersections significantly modify the SPR, one might expect the angle between the nanowires to play a critical role. Shown in figure 1d are plots of the wavelength of the peak in the SPR and its intensity as a function of angle. The first thing to note is that for light polarized along the length of the bottom wire, the enhancement can be varied from nearly 10^{12} for the parallel wires case to 10^4 for the wires at right angles. The SPR for light perpendicular to the length of the bottom wire is insensitive to the angle for most of the angular range. Finally the wavelength of the peak SPR is confined to 800nm to 900nm, except for the 0° and 90°, where it shifts back to the near UV. The behavior of the SPR peak at 0° is consistent with the work of Kottman et al., who also got the same result for coupled parallel wires.[11]

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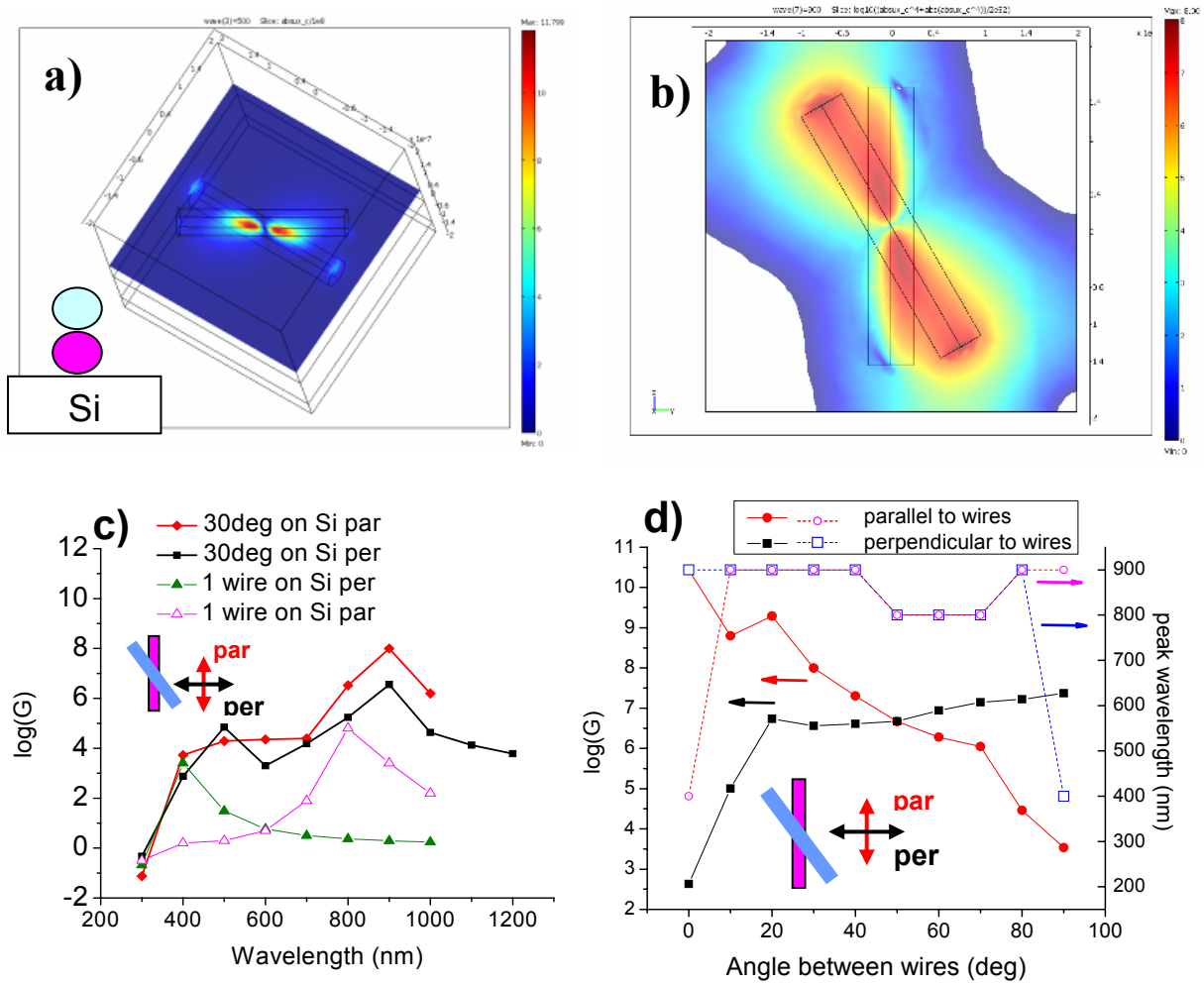

Figure 2. Spatial profiles as obtained from Comsol for crossed Ag nanowires on a Si substrate a) and b) showing the extent of the SERS enhancement. The surface plasmon resonance (SPR) spectra are shown in c) and the angular dependence of the peak in SPR is shown in d).

Taken together the simulations allow us to better understand the behavior of the Ag coated dielectric core nanowires that have exhibited SERS enhancements as high as 10^7. These nanowires were randomly distributed and thus had a range of angles between the intersecting nanowires. From figure 2d., it is evident that for a uniform distribution of angles, one would achieve an average enhancement of approximately 10^7 for unpolarized light, in agreement with experiment.

4.2. Theory for Ag coated dielectric nanowires

Despite the encouraging qualitative agreement for solid Ag nanowires with experiments using Ag coated dielectric core nanowires, one must simulate the case of the Ag coated dielectrics to get a full understanding of the SERS results. In this case, we simulated 60nm diameter Ga_2O_3 nanowires that were coated with 5nm of Ag. For this simulation, we used the index of refraction from Palik.[16] The results for single nanowires in air and on a Si substrate are shown in figure 3a. The SPR for just a single nanowire exhibits a much more complex spectrum. The single peak that the solid Ag nanowires have is replaced by several peaks and periodic oscillations that appear to be interference like in nature. This behavior is due to the fact that the core is optically transparent at the laser wavelength and that the surface plasmons are now confined to the 5nm shell. Thus interference effects are possible from light within the dielectric core. The role of

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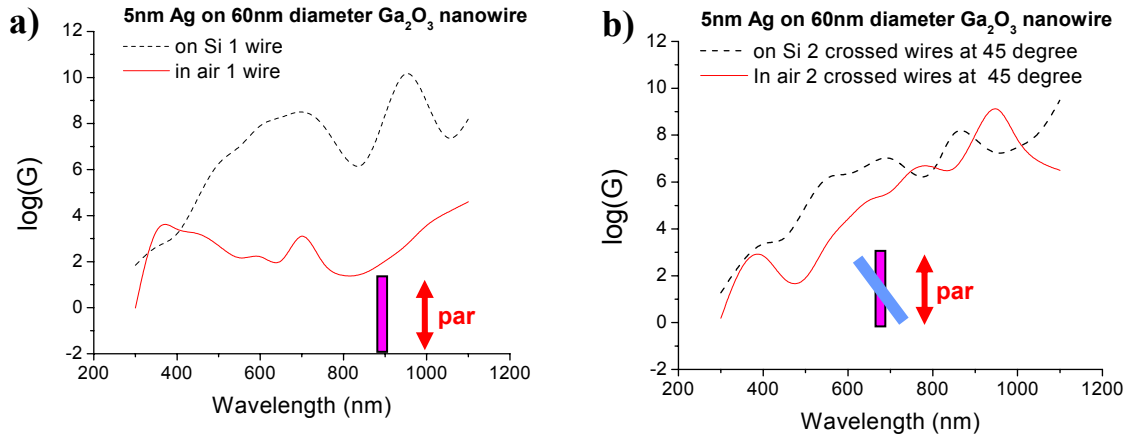

Figure 3 The surface plasmon resonance spectra for a) single wires in air(red) and on Si(black) and for b) crossed nanowires in air(red) and on Si (black). The light polarization is parallel to the bottom wire.

the dielectric core is further enhanced when the nanowires are placed on a Si substrate. The SPR for those nanowires is increased by 6 orders of magnitude and the positions of the more prominent SPR features are shifted. For the case of two Ag coated Ga_2O_3 nanowires at 45° angles, the SPR is shown in figure 2b. In this case, the differences between the wires in air and on Si are not as dramatic. In fact, the enhancement for the coupled system dielectric core system is similar in magnitude to that of the solid Ag system.

A better understanding of the role of the Si substrate can be obtained by examining the spatial distribution of the SPR. This is shown in figure 4 for the dielectric core cases simulated above in figures 3. All of the distributions were for 510nm light. In figures 4a and 4b we show the spatial profiles for a single nanowire in air or on a Si substrate. The first thing to note is that the SPR is very weak, uniformly distributed around the diameter of the nanowire and decreases from the edge to the center of the nanowire. The peak SPR, in fact comes from the sharp corners formed at the end of the cylinder. Placing the nanowire in Si changes the boundary conditions at the intersection of the wire with the substrate. The high dielectric constant of the Si tends to narrow the fields lines and changes the symmetry of the problem. The net result of this is the formation of high fields in the region where the nanowire touches the Si substrate. Figure 3b shows this clearly with the significant increase in SPR intensity at this point.

In the case of crossed nanowires, this effect produces a very interesting result. In figure 4c we see that the maximum SPR is located between the nanowires in much the same fashion as for the crossed solid Ag nanowires of figure 2. Placing these nanowires on Si moves the maximum SPR to the Si surface and increases it substantially (figure 4d). The SPR between the nanowires remains at approximately the same intensity as for the air case of figure 4c.

4.3. Experimental results for Ag coated Ga_2O_3 nanowires.

The two results from the Comsol simulations for the dielectric core nanowires has significant impact on our understanding of the behavior of the SERS from randomly distributed Ag coated Ga_2O_3 nanowires. The experimental results of references 13 and 14 are that the SERS signal is very strong and that it is very repeatable. This suggests that the SERS signal is weakly dependent on the clustering of the nanowires. In fact it has been reported that a factor of 20 decreases in nanowire density results only in factor of 3 decrease in SERS intensity.[14] This dilution was achieved by dissolving an original distribution of nanowires. The dissolution process might be expected to produce many more isolated nanowires.

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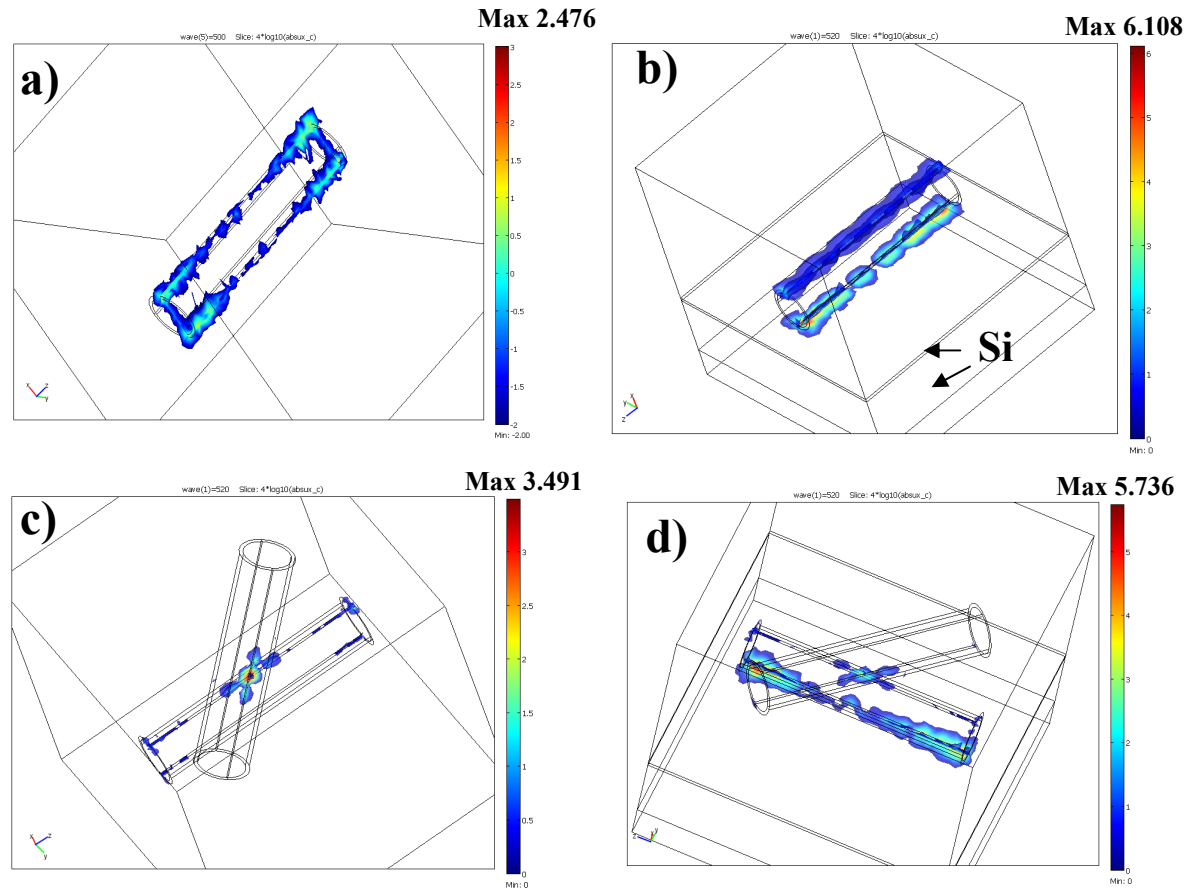

Figure 4. Log of the SERS enhancement maps for 510nm light for isolated wires in air (a) and on Si (b) and for crossed wires in air (c) and on Si (d). The bright yellow and red regions are where the SPR is greatest.

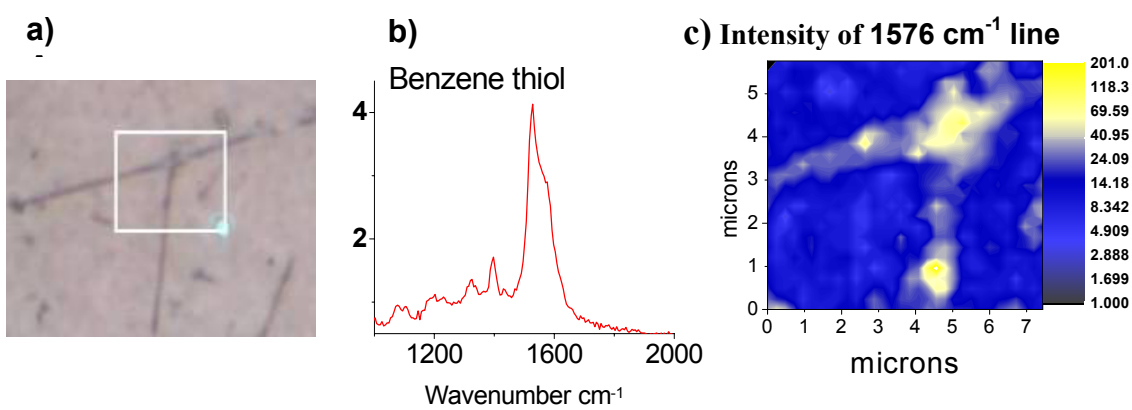

Figure 5. a) Optical image of crossed Ag/Ga_2O_3 nanowires that are approximately 100nm in diameter. B) the Raman spectrum of Benzene thiol from the nanowires and the c) the intensity map of the 1576 cm-1 line of BT..

The experimental results discussed above can be understood from the simulations. The key observation is that Ag coated Ga2O3 nanowires placed on a Si substrate exhibit enhanced SPR for both isolated and crossed nanowires. This

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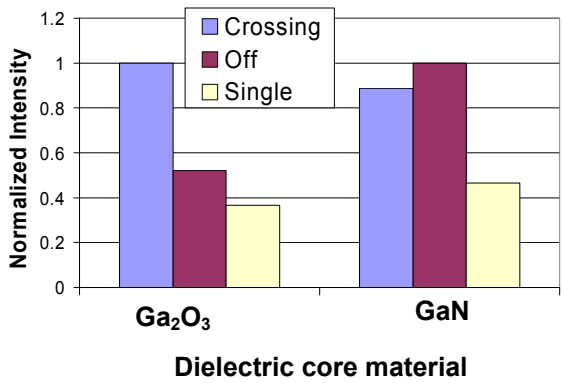

Figure 7. Normalized SERS intensities for benzene-thiol from 5 Ag/Ga_2O_3 samples and 5 Ag/GaN samples Data from isolated NW's (single) is shown in yellow..

leads to a significant increase in the SERS signal and much more uniformity for the case of randomly distributed nanowires. To test this, we have obtained SERS maps from two long and crossed nanowires that were exposed to benzene thiol. Figure 5a shows an optical image of the crossed nanowires. The SERS spectrum from the 1000 to 2000 cm^{-1} region is shown in figure 5b. The SERS map was obtained from the prominent peak at 1576 cm^{-1}. Note that the strongest signal comes from the region where the wires cross. However, the signal from the single wires many microns away from the crossing is decreased only by a factor of 5 at most. In fact, there are regions where the SERS signal from the single nanowires is comparable to that of signal from the crossings. The theory in figures 4 for an isolated wire in air compared to crossed wires in air shows at least 1 order of magnitude reduction in signal and that coming from the edges of the cylinder. The body of the cylinder has a SERS enhancement that is 2 orders of magnitude less than in the crossings. Since the experimental results are from the body of the crossed wires, we would have expected this signal to be barely detectable. The comparison of the SERS map to the simulation for nanowires on Si is much better.

In Figure 7 we compare the results for Ga_2O_3 and GaN core Ag shells exposed to benzene thiol. The numbers in the chart are averages from 5 samples each and in this case we also examined isolated wires. The diameters of the GaN nanowires were a factor of 3 larger than the Ga_2O_3 nanowires. Note that the normalized SERS intensities from the crossings compared to regions away from the crossings and to isolated nanowires are similar. This is again verification of the dielectric substrate enhancement of the SERS effect. Finally, we note that similar calculations for pure Ag nanowires and for square faced box geometries do not have a very strong substrate effect.

5. SUMMARY AND CONCLUSIONS

We have presented Comsol simulations of the properties of obliquely angled Ag nanowires and Ag coated Ga_2O_3 nanowires. The simulations were performed using the quasistatic approximation and the nanowire geometries were chose so that the results were accurate. The results of the simulations were compared to SERS spatial maps for Ag coated Ga_2O_3 nanowires benzene thiol

The simulations indicate that the spatial extent of the SERS enhancement can be extended by using crossed nanowires. The SERS enhancement in these coupled systems extends for tens of nanometers beyond the point of intersection. The enhancement can be tuned by changing the angle at which the nanowires intersect.

The use of a dielectric core Ag shell system introduces interference effects in the SPR spectra and when combined with a Si (dielectric) substrate, further changes the spatial distribution. It was shown that the strongest SPR occurs not between crossed wires, but at the points of contact between the wires and the Si surface. In addition, it was shown that the SERS from a single nanowire can be dramatically enhanced by placing that nanowire on a Si surface. These observations were verified by performing SERS mapping from two long and intersecting nanowires and showing that the SERS signal from isolated regions of the nanowires was similar in intensity to the signal coming from the crossings.

The results reported here not only explain the behavior of randomly distributed nanowires systems placed on dielectric substrates, but they also have important ramifications on understanding the behavior of SERS nanoparticles in different environments. The clearly show that in order to properly account for the SERS enhancement the of a system of particles and substrate, that both the particles and the substrate must be taken into account in any simulation.

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Furthermore, the substrate effects reported here can provide a powerful tool in the design of new SERS substrates and also on the failure mechanisms of systems utilizing dielectric substrates for nanoparticle fabrication.

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REFERENCES

1. M. Fleischman, P. J. Hendra, and A. J. McQuillen, Chem. Phys. Lett. **26**, 163(1974).
2. D. L. Jeanmaire and R. P. van Duyne, J. Electroanal. Chem. **84**, 1(1977).
3. M.G. Albrecht, J.A. Creighton. J. Am. Chem. Soc., **99,** 5215(1977).
4. M. Kerker, D.-S. Wang, and H. Chew, Appl. Optics, **19**, 3373(1980).
5. M. Moskovits, Rev. Mod. Phys., **57**, 783(1985).
6. R. L. Moody, T. Vo-Dinh, and W. H. Fletcher, Appl. Spectrosc. **41,** 966 (1987).
7. J. C. Hulteen and R. P. Van Duyne, J. Vac. Sci. Technol. A **13,** 1553 (1995).
8. R. P. Van Duyne, J. C. Hulteen, and D. A. Treichel, J. Chem. Phys. **99,** 2101 (1993).
9. S. Nie, and S.S. Emory, Science **275**, 1102(1997).
10. Z. Wang, S. Pan, T. D. Krauss, H. Du, and L. J. Rothberg, PNAS, **100** 8643(2003).
11 . J.P. Kottmann and O.J.F. Martin, Optics Express, **8**, 655(2001).
12. F. J. Garcı´a-Vidal and J. B. Pendry, Phys. Rev. Lett., **77**, 1163(1996).
13. O.J. Glembocki, S.M. Prokes, H. Szemanski, J. Liu, F. Kub and C. Kub, Proc. SPIE, **6008,** 600809 (2005).
14. S.M. Prokes, O.J. Glembocki R. Rendell and M. Ancona, Appl. Phys. Letters. **90**, 093107 (2007).
15. D.W. Lynch and W.R. Hunter, in "Handbook of Optical constants in Solids", ed. E.D. Palik (Academic Press, Florida, 1985) p350.
16. D.F. Edwards, in "Handbook of Optical constants in Solids III", ed. E.D. Palik (Academic Press, Florida, 1998) p753.

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