

Enhanced plasmon coupling in crossed dielectric/metal nanowire composite geometries and applications to surface-enhanced Raman spectroscopy

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(Received 11 December 2006; accepted 25 January 2007; published online 27 February 2007)

Surface-enhanced Raman spectroscopy (SERS) was performed on Ga₂O₃/Ag and ZnO/Ag nanowires, which were arranged in either a crossover or noncrossing geometry. Results indicate a high SERS sensitivity (near 0.2 pg) for nanowires arranged in a crossing geometry. It is suggested that this is due to the dielectric core/metal shell structure, as well as to the nanowire crossings, which are regions of very high electric fields. Finite element simulations of the electric field near two crossed wires confirm an enhanced plasmon resonance in the vicinity of the crossing, which extends spatially in the crossings and around the nanowires. © 2007 American Institute of Physics. [DOI: 10.1063/1.2709996]

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. Light can also easily be directed over long distances, enabling remote sensing. Although Raman scattering can provide a fingerprint which is unique to a given material, a major issue for ordinary Raman scattering is that its cross sections are very small, resulting in low sensitivity (1×10^{-8} of the exciting laser). However, the Raman signal can be enhanced by many orders of magnitude by the use of metal nanoparticles¹ and metal shell/dielectric core nanoparticle composites.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 surface enhanced Raman spectroscopy (SERS) enhancements as high as 1×10^8 – 1×10^{12} have been reported for different nanostructures,³ the underlying mechanisms are not yet fully understood. This is evidenced by theoretical calculations which predict SERS enhancements that are many orders of magnitude greater than have been experimentally attained.² Thus, understanding the SERS mechanism and how it relates to the geometric properties of nanostructures is critical to the optimization effect and any possible applications to highly efficient sensors.

Current research with metallic nanoparticles suggests that the size, geometry, shape and alignment are important parameters in the enhancement effect.^{4–6} For example, it has been shown that Au nanorods exhibit a stronger SERS effect than Au nanoparticles,⁷ and the plasmon resonance and the strength of the electric field can be tuned in a dielectric core/metal shell nanosphere geometry,² as well as in metal/dielectric nanodisks.⁸ In addition, special alignment also resulted in higher SERS intensity,⁹ as well as close proximity of the nanostructures to each other.^{10,11} It was empirically shown¹¹ that closely packed and touching metal nanoshells and nanospheres have a much stronger SERS signal than isolated nanostructures of similar geometries.

In this letter, we show that the intersections of nanowires are critical in generating high electric fields. We do this by

comparing the SERS from rhodamine on metal/dielectric composite nanowires that are either intersecting or isolated. Our results indicate a significantly enhanced SERS in the case of crossing metal/dielectric nanowires arranged in a three-dimensional (3D) network. We believe that the enhancement in the SERS signal is not only due to the dielectric/metal shell nanowire geometry but also due to the crossover geometry, in which “hot spots” of the electric field occur at the crossings of the nanowire composites. Due to the oblique angle of the crossings, a large electric field enhancement can be realized in two regions near the crossing, as well as regions surrounding the crossed wires.

The growth of the Ga₂O₃ nanowires was performed by the vapor-liquid-solid (VLS) growth mechanism,^{12,13} using Si(100) and Si(111) substrates¹⁴ and a 20 nm Au film. Ga (99.995% purity) and oxygen were used as the source materials and the growth was performed at 900 °C. The ZnO nanowires were grown at 550 °C in a tube furnace under atmospheric conditions,¹⁵ using Zn pellets (Alpha-Aesar) as the source material. No metal catalyst was used for the growth of the ZnO nanowires. Both types of nanowires were examined using a Leica Cambridge Stereoscan 360FE scanning electron microscope (SEM) with energy dispersive x-ray (EDX) capabilities, a Hitachi high resolution transmission electron microscope (HRTEM), and Raman spectroscopy. SERS spectra were obtained using a micro-Raman system, which consisted of a Mitutoyo microscope and a SPEX Triplemate spectrometer equipped with a charge coupled device. The 514.5 nm line of an Ar ion laser was used as the excitation source.

The VLS growth resulted in Ga₂O₃ wires with a large number of crossings, as shown in Fig. 1(a), with diameters ranging between 40 and 80 nm. The nanowires were single crystal, as determined from fringes in HRTEM [insert in Fig. 1(a)] and consisted of β -Ga₂O₃, as determined from Raman spectroscopy. The Raman lines obtained from the nanowires were similar to those for bulk β -Ga₂O₃ reported by Zhang *et al.*¹⁶ and Sulikowski *et al.*¹⁷ From these results, we conclude that these nanowires consist of stoichiometric monoclinic Ga₂O₃.

The ZnO nanowires [shown in Fig. 1(b)] were single crystal, as determined from HRTEM, with diameters be-

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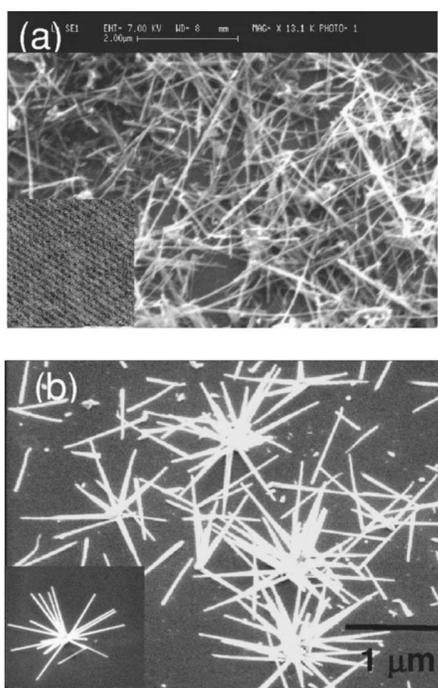


FIG. 1. (a) SEM image of single crystal (inset: HRTEM image) of Ga_2O_3 nanowires arranged in a crossover geometry and (b) SEM image of ZnO nanowires in parallel geometry.

tween 60 and 80 nm. In this case, the wire growth did not involve a metal catalyst, and straight, parallel wires, originating from single points, were formed, resulting in a series of noncrossing, starlike structures [shown in inset of Fig. 1(c)]. Thus, in this case, although the nanowire density is similar, most of the wires do not cross. The wires consist of stoichiometric ZnO, as determined from EDX analysis and Raman spectroscopy. Two features in the Raman spectrum were associated with ZnO lines, one at 434 cm^{-1} and the other at 577 cm^{-1} , which are similar to those reported by other groups.^{18,19}

Both sets of wires were subsequently covered with 5 nm of Ag, using high vacuum electron beam evaporation, resulting in $\text{Ag}/\text{Ga}_2\text{O}_3$ and Ag/ZnO nanowire composites. The thickness of the Ag shell (5 nm) and the radius of the dielectric core (40–80 nm) were chosen in order to maximize the plasmon electric field, as calculated by Jackson *et al.*² in the case of the spherical nanoshell geometry. The Ag layer on the nanowires was relatively smooth, as determined from SEM. Rhodamine 6G (R6G) dissolved in methanol (10^{-6} M) was used as the SERS-active molecule, which was deposited on the surface of the substrate using a micropipette resulting in a $10\ \mu\text{l}$ drop. The methanol was allowed to evaporate, which occurred in less than a minute, creating a 1 cm^2 drop area. An additional Si sample, which contained only 5 nm of Ag but no nanowires, was also examined, but no SERS signal was detected.

The SERS results were obtained using a $60\ \mu\text{m}$ spot size of the 514 nm Ar^+ ion laser line with a power of less than 1 mW. Based on the concentration and amount of liquid deposited and the area coverage of the substrate, we calculate the sensing capability of the crossed nanowire substrates to be about 0.2 pg. The only commercial technique which shows better chemical sensitivity is based on fluorescence quenching, such as sensors produced by Nomadics, Inc. However, it is more difficult to identify a specific molecule

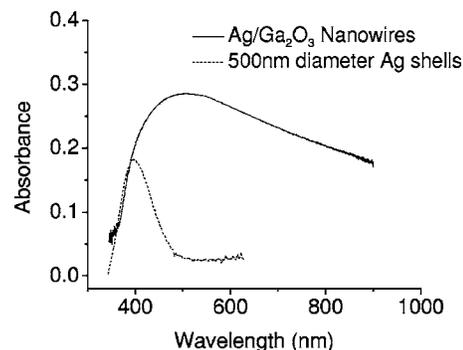


FIG. 2. SPR of $\text{Ga}_2\text{O}_3/\text{Ag}$ crossed nanowires and 500 nm Ag nanoshells.

by this technique, especially when in a real environment, due to environmental clutter.

An interesting feature of the Ga_2O_3 nanowires is their broad surface plasmon resonance (SPR), as shown in Fig. 2. In general, sharp SPRs have been reported in other SERS materials,²⁰ which require that the laser energy be carefully tuned in order to maximize the SERS enhancement. For example, this is shown in the case of 500 nm Ag nanoshells (Fig. 2), which exhibit a much sharper SPR. In the case of the nanowires, however, the very broad SPR allows one to obtain maximum SERS in a very large laser energy range. The broad SPR in the nanowires originates from the fact that they consist of a range of diameters (between 40 and 80 nm) and a range of randomly distributed crossing angles.

A comparison of the SERS sensitivity for a similar density of the $\text{Ag}/\text{Ga}_2\text{O}_3$ and Ag/ZnO nanowire composites is shown in Fig. 3. As can be seen, under the same conditions, with the same R6G dilution, the $\text{Ga}_2\text{O}_3/\text{Ag}$ nanowire composites exhibit significantly enhanced SERS signal compared to those which consist of the ZnO/Ag composites. Although the two types of samples contain different core materials (Ga_2O_3 and ZnO), their dielectric constants are quite similar, as are the diameters and the density. The number of crossings is the most obvious difference between these two types of

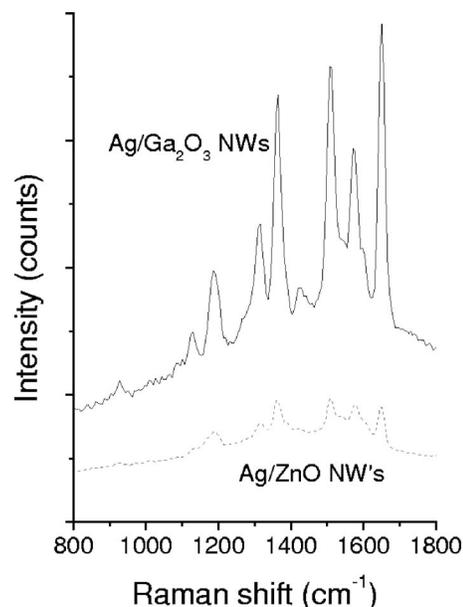


FIG. 3. Comparison of SERS signal for highly crossed $\beta\text{-Ga}_2\text{O}_3/\text{Ag}$ nanowires and ZnO/Ag nanowires, exhibiting few crossings. The Raman signal shown is for a similar nanowire density.

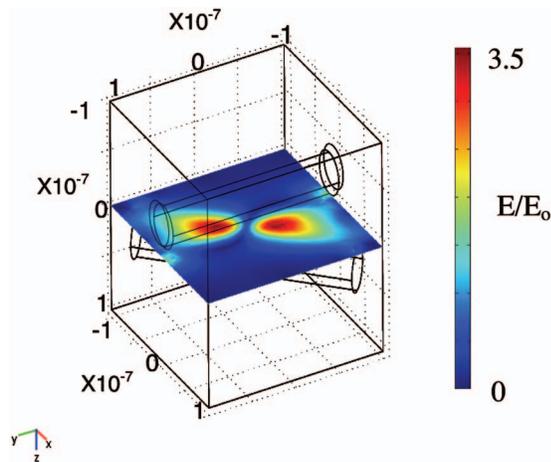


FIG. 4. (Color) Finite element simulation of the electric field near two 40 nm diameter Ag obliquely crossed wires separated by 10 nm in air, in response to 500 nm wavelength light polarized in the x direction.

substrates. In the case of the Ag/Ga₂O₃, the nanowires exhibit a high density of crossings, creating a 3D open structure, while the ZnO/Ag nanowires consist mostly of non-crossing nanowires emanating from single point sources.

The presence of crossings can lead to the formation of hot spots corresponding to very intense electric fields. Kottmann and Martin²¹ have shown the effects of geometry on the scattering cross section from two parallel metal nanowires. Their results indicate that coupled parallel wires, at a very short distance apart, lead to a significantly enhanced coupled plasmon resonance. These enhanced plasmon resonances also occur over a broader spectral range. The effect on the plasmon resonances by wire crossings can be examined using a simulation. Figure 4 shows a finite element²² simulation of the electric field near two 40 nm diameter Ag, (Ref. 23) obliquely crossed wires separated by 10 nm, 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 no longer occurs halfway between the closest separations between the wires, as in the parallel wire case. 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 allow more molecules to enter this high electric field region, thereby enhancing the SERS sensitivity. Furthermore, the parallel wire geometry, as well as nanosphere geometries, requires a very specific spacing in order to maximize the enhancement due to coupling. This 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. 4. The random 3D crossed wire geometry would thus be expected to show the most SERS enhancements due to the hot spots formation. Quantification of this effect will require

more detailed crossed wire simulations, to be published elsewhere.

One further point that should be made is that the core dielectric/metal shell wire structure also exhibits optical interference, since the laser light can penetrate into the core of the wire, leading to multiple reflections, which may also contribute to enhanced SERS signals.

Single crystal Ga₂O₃ and ZnO nanowires have been grown in an open growth system. These nanowires were then covered with a 5 nm Ag shell, forming a dielectric/metal composite nanowire structure. SERS measurements using rhodamine 6G have shown these substrates to be highly sensitive, and it is suggested that this enhancement is the result of the dielectric core/metal shell geometry, which leads to internal interference, as well as due to the formation of a large number of hot spots when arranged in a crossing geometry. Finite element calculations show significantly enhanced electric fields in the regions of the wire crossing, in support of the experimental results.

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