Simulation and Nanofabrication for Tip-Enhanced Raman Spectroscopy

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Abstract and Introduction:

Tip-enhanced Raman spectroscopy (TERS) is a fast-growing branch of spectroscopy using inelastic light scattering to characterize and analyze materials with nanoscale spatial resolution. By placing a metal coated tip or probe in close proximity to a sample, incident laser radiation creates a surface plasmon on the surface of the probe, which generates a high intensity localized electric field that produces greater signal strength when compared to conventional Raman spectroscopy as well as achieving resolutions below the diffraction limit.

The goals of this project are to; (1) realistically model and simulate the TERS set-up for gold-coated AFM tips, and (2) explore the use of nanosphere lithography (NSL) to fabricate periodic plasmonic gold nanotriangles (AuNTs). Much effort was placed into creating realistic tip models and simulations that are lacking in the literature. This was achieved using RSoft's DiffractMod software package and agreed with both theoretical intuition and experimental results. NSL techniques were then used to create AuNTs that can be used for TERS experiments in the future.

Experimental Procedure:

Rsoft and DiffractMod were used to build and perform computational electrodynamics simulations for TERs experiments. Due to RSoft's limited drawing capabilities it was decided that as a first approach in realistic TERs simulations to model the gold-coated AFM tip as a cone with a rounded tip. Though AFM tips are generally much more complicated and angular the additions made to the typical simple-sphere model are suspected to be a valid first approximation.

Three simulations were performed including; (1) no-tip, (2) a simple-sphere tip, and (3) a realistic tip. Using parameters previously optimized by Dr. Edward Yu's group, the simulations were set up using incident light polarized perpendicular to the samples (Ge-$Si_{0.5}Ge_{0.5}$ core-shell nanowires, CSNWs) at a wavelength of 633 nm and an incidence angle of 30°. All simulations were performed for a CSNW with a core radius of 40 nm and a shell thickness of 5 nm. The realistic tip was modeled as a cone 125 nm in height with a rounded tip of radius 50 nm. The simple-sphere was also 50 nm in radius and both tip models were modeled as pure gold with the tip at a distance of 3 nm from the sample surface. As with previous work, the quantity of interest is the Electric Field Density, U, which was calculated for each of the three set-ups [1,2].

The nanofabrication portion of this project focused on the creation of AuNTs using nanosphere lithography (NSL), which is a quickly emerging technique due to its low cost, quick production time and the quality of the structures formed. This method offers a more flexible in-house alternative to commercially produced AuNTs.

The first step in the NSL process is to deposit a monolayer of polystyrene (PS) nanospheres onto a glass substrate. This was achieved by pipetting a 1:1 nanosphere:ethanol solution into a shallow water bath. After adding the nanospheres, the substrate was used to scoop up the nanospheres. After drying, the substrate was then coated with 300Å gold on a 50Å adhesion layer of titanium using electron beam physical vapor deposition (EBPVD). After depositing the gold, the nanospheres were lifted off by sonicating the substrate in a toluene bath.

Results:

The electric field density (EFD) for each of the three simulations is shown in Figures 1-3. Immediately obviously is the drastic difference in the EFD produced by adding a tip — roughly a 500% increase in intensity. This serves to show that the modeling software correctly predicts intensity changes found in TERS experiments. The more interesting difference is that between Figures 3 and 4. Here it is noted that though the simple-sphere model has a greater maximum intensity the realistic tip model has a greater overall sample penetration with slightly more localization near the tip. This suggests that the simple-sphere model is not appropriate for TERS simulations and that more realistic tip modeling is necessary to ensure accurate results.

An AFM image of the AuNTs created through NSL is presented in Figure 4. Though there appears to be a somewhat periodic array of AuNTs, there are very clearly

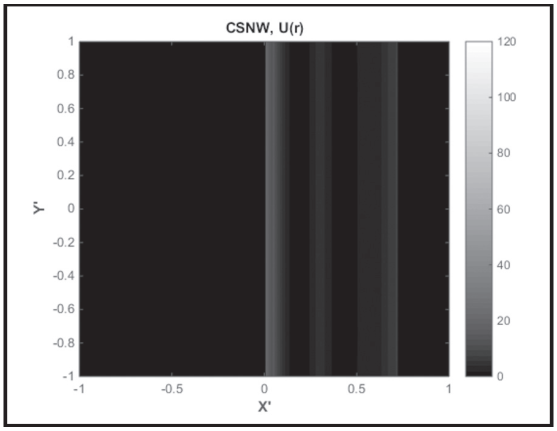

Figure 1: *EFD for a CSNW sample without tip.*

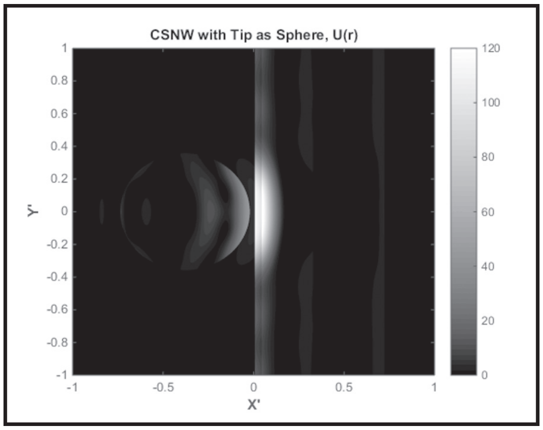

Figure 2: EFD for a CSNW with a simple-sphere tip.

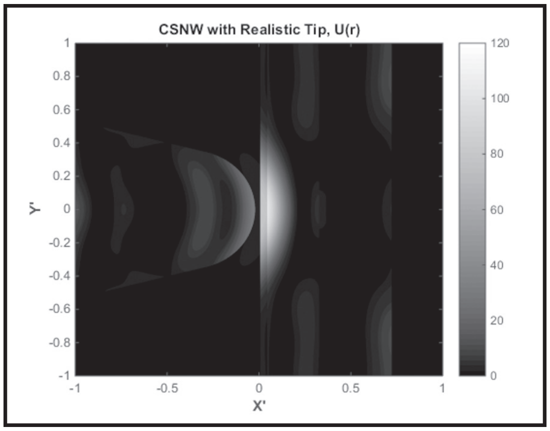

Figure 3: EFD for a CSNW with a realistic tip.

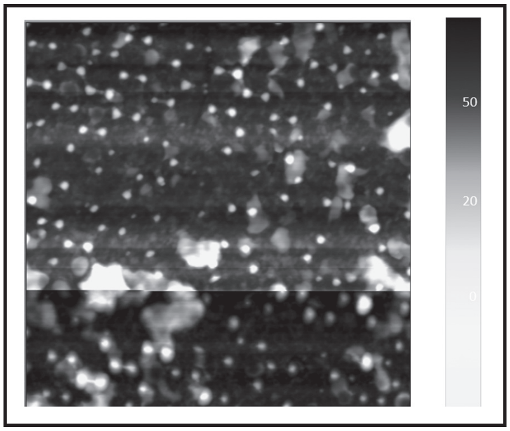

Figure 4: AFM of AuNTs deposited onto glass substrate.

defects and imperfections. There also appears to be debris or other substances on the substrate. Though AuNTs were created using them in tip- and surface-enhanced Raman spectroscopy (SERS) experiments is required to verify the viability of this procedure.

Future Work:

In future simulations it may prove fruitful to model a more angular tip. Electric fields concentrate around edges and thus more accurate results may be obtained from an angular tip model [3]. Similarly in the simulations for this project, the tips were modelled as solid gold even though the tips were actually gold-coated Si tips. Future simulations should incorporate this material layering (though it is believed that with a ~ 120 nm Au coating the effects of this addition would be minor).

In future AuNT fabrication using NSL, it will be necessary to perfect the NS monolayer deposition as this is the step that determines the quality of the structures. One way this can be achieved is through evaporating the water from the bath allowing the monolayer of NS to deposit uniformly instead of using the scoop technique. Also other substrates should be explored to determine the best fit for the process.

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