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Effects of Adhesion Layers in Silver Plasmonic Nanostructures for Surface Enhanced Raman Spectroscopy

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Abstract:

Surface enhanced Raman spectroscopy (SERS) of plasmonic nanostructures can be useful in biomedical practices, including cancer detection, because of these particles' low detection limits. Lasers at certain wavelengths excite localized plasmon resonances that enhance local electric fields and result in higher Raman intensities — this makes the particles easier to detect. Electron energy loss spectroscopy (EELS) spectra of these nanostructures taken with a transmission electron microscope (TEM) have peaks at energies corresponding to plasmon resonances. Previous work with gold nanostructures has shown that Raman wavelengths with energies corresponding to EELS energy peaks result in higher Raman enhancement. We fabricated silver plasmonic nanostructures via electron-beam lithography on silicon wafers with titanium and mercaptopropyltrimethoxysilane (MPTMS) adhesion layers. Raman spectra of the silver nanostructures revealed no enhancement with titanium layers and high enhancement with MPTMS layers, agreeing with gold results. Plasmon peaks in silver EELS spectra did not correlate with enhancement as well as gold EELS spectra. Further investigation is needed to determine a correlation between strong plasmon resonance peaks in EELS spectra and high SERS enhancement factors.

Introduction:

Metallic nanostructures that exhibit SERS properties, such as gold and silver, are coated with a Raman active dye and are injected into the bloodstream where they can then enter a tumor. The nano particles are detected by their Raman signal, which is enhanced by several orders of magnitude due to the properties of the metal. The enhanced Raman signals can be explained by the presence of surface plasmons, which are oscillating electron clouds on the surface of the metal. They can couple with electromagnetic radiation to create enhanced localized electric fields on the surface. The intensity of electric field in these regions is a superposition of the metal field and the incoming field [1].

Raman spectroscopy detects the Raman scattering process occurring at the surface of the nanostructures. Raman scattering is the inelastic scattering of light from a substrate. When the Raman dye is located in a region on the metal where there is an enhanced electric field, both the incoming and exiting photon intensities are enhanced resulting in an overall signal enhancement [1]. Factors that affect the Raman intensity are size, shape, and material of the metal nanostructures.

Another spectroscopic technique used to gain more insight into the location of surface plasmons and their contribution to enhanced Raman signals is electron energy loss spectroscopy (EELS). EELS is done in a transmission electron microscope (TEM). Electrons passing through a sample are sometimes inelastically scattered and lose some energy. The TEM measures the energy loss of incoming electrons at each point on the sample resulting in a data cube that can be analyzed in two ways. An x,y position of an EELS data cube gives a spectrum that shows the frequency of energy loss at that point. An energy range of an EELS data cube gives an image where bright pixels indicate a higher frequency of energy loss. Bright regions correspond to the excitation of a plasmon.

Experimental Procedure:

Nanostructures were fabricated via electron-beam lithography on three-inch silicon wafers spin-coated with poly(methyl methacrylate) (PMMA) resist. The wafers were developed in a 1:3 methyl isobutyl ketone to isopropyl alcohol solution. A 2 nm layer of titanium was deposited with electron gun evaporation on one set of nanostrucures. A monolayer of MPTMS was deposited on another set of structures with vapor deposition in a vacuum chamber. A 30 nm layer of silver was deposited with electron gun evaporation on both sets of nanostructures. For Raman spectroscopy, a Raman active substrate 4-mercaptopyridine dye was deposited by submerging the wafers in a 1 mM solution of the dye. For EELS, the same procedure was replicated on TEM silicon nitride instead of silicon wafers.

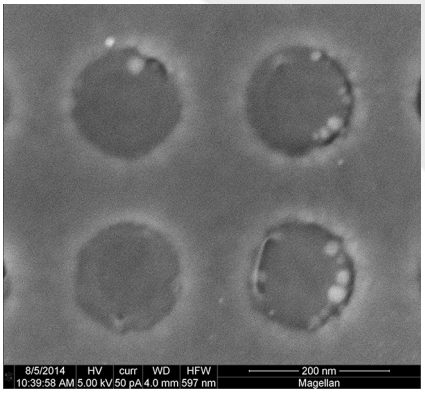

Figure 1: 144 nm diameter apertures with 100 nm spacing.

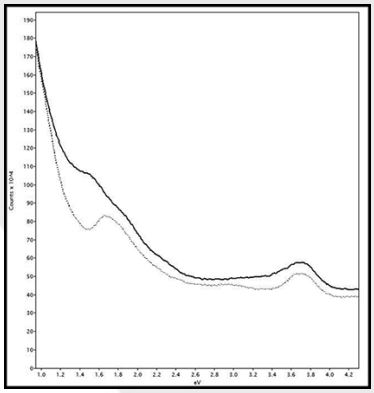

Figure 3: EELS spectra of 144 nm diameter apertures with 100 nm spacing with MPTMS adhesion layers (solid) and titanium adhesion layers (dotted).

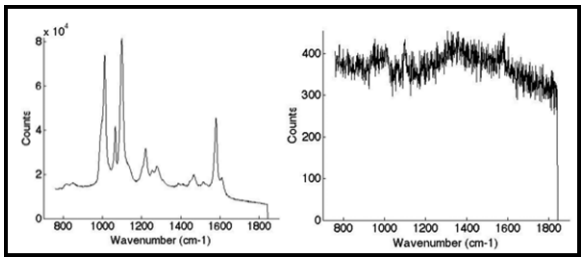

Figure 2: Raman spectra of 144 nm diameter apertures with 100 nm spacing with MPTMS adhesion layers (left) and titanium adhesion layers (right).

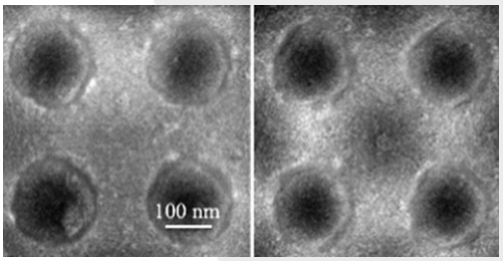

Figure 4: EELS energy slices from 1.5-1.6 eV of 144 nm diameter apertures with 100 nm spacing with MPTMS adhesion layers (left) and titanium adhesion layers (right).

We fabricated nanostructures of varying sizes, shapes and spacings to demonstrate the effects of these factors on the Raman signal enhancement and the location of surface plasmons. A scanning electron microscopy (SEM) image of nanoapertures is shown in Figure 1.

Results:

Raman spectra for silver nanostructures taken with a 785 nm (1.57 eV) laser agreed with gold results. In Figure 2, we see there was enhancement for silver structures made with MPTMS adhesion layers and no enhancement for structures made with titanium adhesion layers. These results were consistent for all silver nanostructures of various sizes, shapes and spacings.

EELS spectra of the same structures were less conclusive. For gold nanostructures, we saw strong plasmon peaks for MPTMS apertures at 1.57 eV and weak plasmon peaks for titanium apertures at 1.57 eV. Silver nanostructure EELS spectra taken in between apertures are shown in Figure 3. We see a weak plasmon peak at 1.57 eV for the MPTMS apertures and strong blue shifted plasmon peak for titanium apertures. Since MPTMS aperture peaks align better with the Raman laser energy, this may be the cause for the Raman enhancement.

Energy slices for silver nanostructures encompassing the Raman laser energy are shown in Figure 4. The brighter regions in between apertures for the titanium structure indicate more plasmon resonance for these structures than for MPTMS structures. It appears that the correlation between strong plasmon peaks and Raman enhancement is still unclear for silver nanostructures.

Conclusion and Future Work:

Titanium adhesion layers have negative effects on Raman signals for both gold and silver nanostructures. Although strong plasmon peaks align with high enhancement for gold, further investigation is needed for silver. This includes using different laser energies for Raman spectroscopy to determine if other plasmon peaks correlate to high enhancement.

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References:

[1] Pablo G. Etchegoin and Eric C. Le Ru, Principles of Surface Enhanced Raman Spectroscopy, Chapter 1, 2009.