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Observing Plasmon Damping Effects of Metallic Adhesion Layers in E-Beam Synthesized Nanostructures Using STEM-EELS and Raman Spectroscopy

Steven Madsen[1], Paul Kempen[1], and Robert Sinclair[1]

[1]Stanford University, Department of Materials Science and Engineering, Stanford, CA 94305-4034 USA

Plasmonics is a rapidly growing field with many potential applications, including biosensing and cancer detection [1]. Electron beam lithography (EBL) is often used to pattern gold or silver nanostructures onto silicon substrates. A thin layer of either Cr or Ti is used to promote adhesion, but has recently been shown to damp plasmonic resonance [2]. 3-mercaptopropyltrimethoxysilane (MPTMS), which forms a silane monolayer, has been proposed as an alternative [2]. The present study aims to compare MPTMS with Ti as an underlayer for plasmonic nanostructures using scanning transmission electron microscope electron energy loss spectroscopy (STEM-EELS) and surface enhanced Raman spectroscopy (SERS).

EBL was used to fabricate arrays of nanoholes in a resist film spun onto Si (for SERS) or 35nm SiN membranes (for STEM-EELS). At this point, an adhesion layer was formed either by vapor depositing MPTMS or evaporating 2nm Ti. Finally, 30nm of Au is deposited to give the structure shown schematically in Fig. 1. Because fast electrons can excite plasmons by transferring a small fraction of their energy to the sample, EELS can be used to measure plasmon resonances. Spectrum images were collected using a Gatan Quantum GIF connected to a monochromated FEI Titan 80-300 at 300kV, with 0.13eV energy resolution and 2.5nm pixel size. Raman spectra were acquired using 4-mercaptopyridine (4-MP) dye in a Renishaw InVia system equipped with a 785 nm laser (1.57 eV), using the 50x objective with a 1 second collection time.

Spectrum images were collected from samples with Ti and MPTMS and compared. Summing EELS data over several nanoapertures (Fig. 2) yields the plot shown in Fig 3. These spectra show a peak at 1.3 eV which is present only in the MPTMS/Au sample. Spectrum images of the regions shown in Fig. 2 were integrated from 1.4 to 1.5 eV and normalized to generate the maps in Fig. 4. The MPTMS/Au sample has bright contrast localized inside the apertures, indicating the presence of localized plasmons in the 1.4 to 1.5 eV range which are not measured in the Ti/Au sample. The damping effect has been claimed to result from the optical absorbance (imaginary dielectric function) of Ti, which is much greater than for Au [2].

SERS relies on the excitation of plasmons in metal structures to enhance the local electric field at the frequencies corresponding to the excitation frequency and the emission frequency. Therefore, it can be expected that the MPTMS/Au sample will provide greater signal enhancement as compared to the Ti/Au sample when using a near infrared 1.57 eV laser. As predicted, the measured signal is dramatically higher in samples without Ti, shown in Fig. 5.

This study demonstrates the ability of EELS to detect the damping effect of metallic adhesion layers on plasmonic nanostructures. Additionally, EELS mapping provides the spatial resolution needed to determine the locations of particular plasmonic resonances within the structure. The SERS enhancement qualitatively changes consistent with the EELS data, demonstrating the utility of this technique to assist in tuning and optimizing SERS structures.

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[2] TG Habteyes, S Dhuey, E Wood, D Gargas, S Cabrini, PJ Schuck, AP Alivisatos and SR Leone, ACS Nano, **6** (2012) 5702-5709.
[3] This research is supported by the Center for Cancer Nanotechnology Excellence and Translation (CCNE-T) grant funded by NCI-NIH to Stanford University U54CA151459.

Figure 1: Cross section schematic of fabricated structures. The adhesion layer is either 2nm Ti or vapor deposited MPTMS.

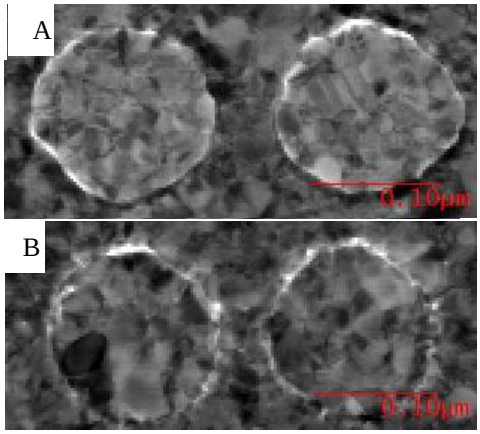

Figure 2: STEM brightfield images of Ti+Au (A) and MPTMS+Au (B) nanostructures.

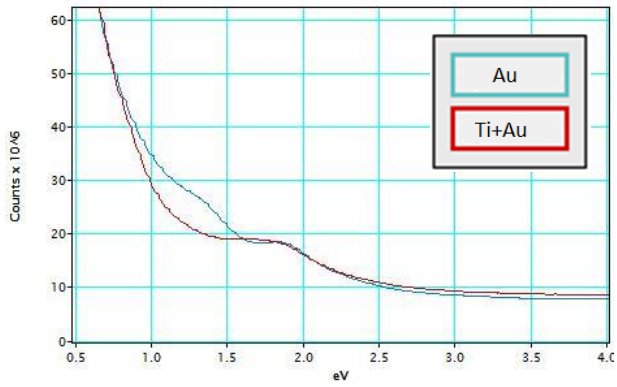

Figure 3: Spectra were integrated over several nanostructures to form the EELS spectra shown. Note the peak at 1.3 eV which is absent in the Ti sample.

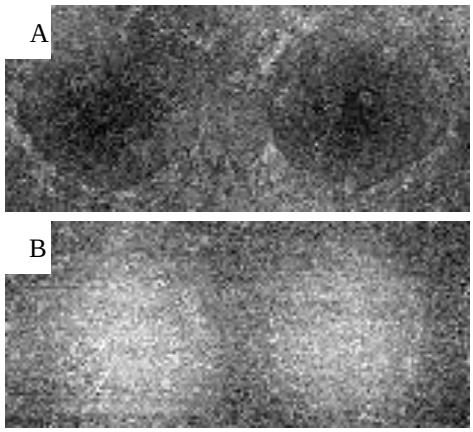

Figure 4: Normalized EELS spectrum image integrated over the 1.4 to 1.5 eV range for Ti+Au (A) and MPTMS+Au (B).

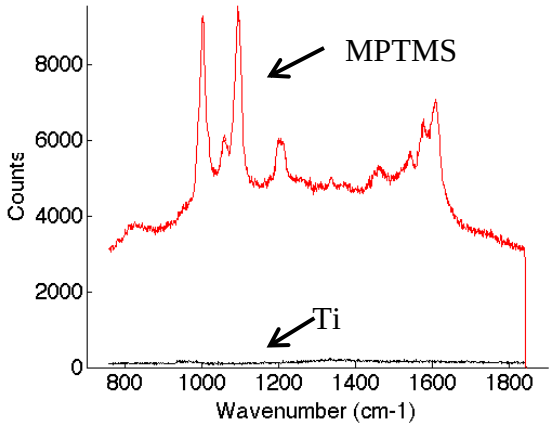

Figure 5: Raman signal from 4-MP on MPTMS (red) and Ti (black) adhesion layer samples. Ti dramatically lowers signal enhancement.

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