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Report Title

Extending Usable Lifetime of Plasmonic Silver Structures Designed For High Resolution Chemical Imaging and for Chemical and Biological Sensing

ABSTRACT

The overall objective was to identify, from among different classes of coating schemes, the most fruitful approach for extending the lifetime of silver plasmonic structures used in high resolution optical spectroscopies for materials characterization or high sensitivity detection schemes. This enhanced durability will aid in Army efforts to develop high sensitivity, high selectivity schemes based on tip enhanced Raman spectroscopy (TERS) for chemical imaging and surface enhanced Raman spectroscopy (SERS) techniques for detection of explosives, chemicals, or biological agents. Protected plasmonic structures have been successfully prepared by sequential physical vapor depositions of silver and of SiO_x or Al₂O₃ layers at very low pressures. Our key result to date is the creation of a corrosion-protected, highly enhancing plasmonic structure on an SPM tip for the first time. For the protected metallized tip the enhancement factor is of the order of 10⁴. The vital advance made here, through materials design, is fabricating long-lasting metallized probes without compromising signal enhancement. This advance has been proven by measurements on thin films of a conductive polymer blend (PEDOT/PSS) and an inorganic material (CdS).

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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C. A. Barrios, A. V. Malkovskiy, R. D. Hartschuh, S. R. Hamilton, A. M. Kisliuk, A. P. Sokolov, M. D. Foster. "Extending Lifetime of Plasmonic Silver Structures Designed for High Resolution Chemical Imaging or Chemical And Biological Sensing", In: Chemical Biological Radiological and Explosives Sensing. Proceedings of the Society of Photo-Optical Instrumentation Engineers (SPIE) Meeting, Orlando, Florida, March 18-20, 2008.

Foster, M. D.; Barrios, C. A.; Malkovskiy, A. V.; Hartschuh, R. D.; Kisliuk, A. M.; M. D.; Sokolov, A. P. "Nanoscale adhesive characterization with scanning probe microscopy: adding resolution of chemistry", Proceedings of the Adhesion Society Annual Meeting, Austin, Texas, February 17-20, 2008.

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(c) Presentations

Barrios, C. A.; Malkovskiy, A. V.; Kisliuk, A. M.; M. D.; Sokolov, A. P.; Foster, "Chemical Imaging with Nanoscale Resolution: Extending the Lifetime of Plasmonics Probes". Ohio Nanotechnology Summit 2008, Cincinnati, Ohio, April 9-11, 2008.

Barrios, C. A.; Malkovskiy, A. V.; Hartschuh, R. D.; Kisliuk, A. M.; M. D.; Sokolov, A. P.; Foster, "Design, fabrication and protection of Nanoprobes for high resolution chemical imaging", The Microscopy Society of Northeastern Ohio Spring Meeting, Akron, Ohio, February 27, 2008.

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Barrios, C. A.; Malkovskiy, A. V.; Kisliuk, A.; Sokolov, A. P.; Foster, M. D. “Improving Stability of Plasmonic Structures for TERS”, Applied Physics Letters, 2008, Submitted.

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Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
Carlos Barrios	1.00
Shih-fan Wang	0.33
Gokce Ugur	0.33
Sewoo Yang	0.33
FTE Equivalent:	1.99
Total Number:	4

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

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Extending Usable Lifetime of Plasmonic Silver Structures Designed For High Resolution Chemical Imaging and for Chemical and Biological Sensing

Final Report for Grant # W911NF-07-1-0470

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Authors: Carlos Barrios, Mark D. Foster

April 30, 2008

Executive Summary

- 1.) We investigated the protection of enhanced Raman signal provided by three types of ultrathin coatings on silver plasmonic structures: self-assembled monolayers (SAMs) of thiols, thin silica layers created by sol-gel processes, and inorganic ultrathin SiO_x or Al_2O_3 layer fabricated by physical vapor deposition (PVD).
- 2.) Among the three types of ultrathin coatings tested, only inorganic ultrathin SiO_x or Al_2O_3 layers fabricated by physical vapor deposition (PVD) allowed controlled thickness variation and were extended to SPM tips.
- 3.) For the first time a plasmonic structure for SERS detection has been protected from chemical degradation without significant detriment to the signal enhancement. A PVD deposited 10nm thick SiO_x layer totally stopped degradation of the signal over time.
- 4.) For the first time a plasmonic structure on an SPM tip that can generate large enhancement in an optical spectroscopy signal has been protected from mechanical and chemical degradation without significant detriment to the enhancement.
- 5.) This protective coating is a physically deposited ultrathin inorganic SiO_x or Al_2O_3 layer with a thickness equal to or less than 3nm.
- 6.) Raman signal enhancement achieved using tips without and with the protective coating was measured on thin films of a conductive polymer blend (PEDOT/PSS) or CdS. The ratio of the signal intensity with the tip providing enhancement to the far field signal intensity obtained without the tip (= *contrast*), was only 10% lower when the structure was protected with SiO_x and remained unchanged when the structure was protected by Al_2O_3 .
- 7.) The decay in enhanced signal from either a SiO_x protected or unprotected tip is exponential in time. The decay rate is clearly slower for the protected structure.
- 8.) There was no decay in the enhanced signal from an Al_2O_3 protected tip. No decay was evident over a 40 day period.
- 9.) The contrast of the unprotected SPM tip decayed completely after 4 days of use.

1. INTRODUCTION

The objective of our work was to identify, from three different classes of coating schemes, the most fruitful approach for extending the lifetime of silver plasmonic structures used in high resolution optical spectroscopies for materials characterization or high sensitivity detection schemes. Self assembled monolayers (SAMs) of thiols, thin silica layers formed by sol-gel processes, and inorganic ultrathin SiO_x or Al_2O_3 layer fabricated by physical vapor deposition (PVD) were tested as protection schemes. Only the physical vapor

deposition technique allowed precise control over thickness and easy application on metallized SPM tips for TERS.

Extending the lifetime required slowing the tarnishing of the silver appreciably while minimizing unfavorable influences on the optical response of the structures and defining changes that occur. This enhanced durability will aid in Army efforts to develop high sensitivity, high selectivity schemes based on tip enhanced Raman spectroscopy (TERS) for chemical imaging and surface enhanced Raman spectroscopy (SERS) techniques with “hot spots” for detection of explosives, chemicals, or biological agents. Both plasmonic structures on tips and those on other sorts of substrates used for detection or sensing suffer reduced lifetime from mechanical, thermal and chemical degradation.

Resonant plasmon excitations in noble metal structures allow the localization and amplification of light in very small volumes and they are the basis of surface enhanced Raman spectroscopies (SERS) and tip enhanced Raman spectroscopy (TERS). TERS combines scanning probe microscopy with Raman spectroscopy, taking advantage of apertureless near-field optics, and has already achieved a remarkable lateral resolution of $\sim 10\text{-}20\text{nm}^1$. Bottom, top and side illumination optical schemes have been proposed²⁻⁴, the side illumination being the most flexible approach to analyze opaque and non-transparent samples. The key element of TERS, the apertureless tips, provides a high amplification ($\sim 10^3\text{-}10^4$) of the Raman signal by the surface plasmon resonance of the metal structure on the tip. These nanoprobe for optical applications use very rough thin metallic layers covering Scanning Probe Microscopy (SPM) tips or very sharp metal structures mounted on tuning forks. Tip characteristics such as radius, shape and roughness determine the spatial resolution and the enhancement factor. Maintaining the morphological, mechanical and chemical integrity of tips during scanning, i.e. keeping their optical properties unaltered, is crucial for obtaining undistorted optical images with nanometer scale resolution (TERS) or stable high sensitivity detection (SERS). It is essential to understand that this chemical imaging has a resolution very much superior to the resolution of commercially available “microRaman”, which is of order $1\text{ }\mu\text{m}$. Mechanical wear of tips and corrosion of the plasmonic structures limits the lifetimes of tips. This is especially problematic for silver-based structures that usually provide the best enhancements, but degrade very fast. Fabrication of highly enhancing plasmon-active probes with improved chemical and mechanical resistance is still a challenge.

A metallized apertureless tip usually consists of a silicon or silicon nitride tip covered with a thin (20-50 nm) structure of a metal such as gold (Au) or silver (Ag). Abrasive friction forces between the metal layer and the surface under analysis are the main reason for mechanical damaging of the metal structure during scanning. Wearing is a well-known problem for silicon or silicon nitride tips in conventional SPM imaging. Even stronger problems are expected with a metallized tip because the hardness of the metal layer is orders of magnitude lower than that of the bare tip. Metallized tips can also deteriorate irreversibly due to exposure to adverse environmental conditions⁵ or intense light⁶. SPM tips with 50 nm thick Ag structures no longer provide plasmon enhancement after 24 hours of continuous exposure in ambient to a $1\text{ }\mu\text{m}$ diameter confocal beam of power 1 mW. Others have shown that heating of SERS substrates caused by the enhanced field anneals the sharp structured metal films, reducing the plasmon resonance activity due to a decrease in roughness⁶. Similar effects are expected for apertureless tips. Atmospheric corrosion of silver, known as tarnishing, typically takes the form of sulfidation upon exposure to several gaseous sulfur-containing compounds in the atmosphere⁷, hydrogen sulfide (H_2S) and carbonyl sulfide (OCS) being the most important. For apertureless optics, the surface “plasmon resonance” of the metal coating on the tip is key. The surface plasmon resonance is destroyed as Ag structures are *sulfidized*. Prior to this work, the effect of protective coatings on the mechanical and optical properties of nanoprobe for TERS had not yet been systematically studied.

Wearing of silicon or silicon nitride SPM tips is a well-known problem in conventional SPM imaging. In an attempt to reduce the highly destructive forces between tip and surface when they are in contact, lubrication films^{8, 9}, and even new geometrical designs⁹ have been proposed. A similar problem is expected with a metallized tip, for which the hardness of the metal layer can be orders of magnitude lower than that of the bare tip. Changes in the plasmonic structure of the tip caused by wearing¹⁰, heating⁶, and/or chemical degradation⁵ can be responsible for unstable enhancement during imaging. For example, bending of sharp, etched silver tips has been demonstrated during AFM imaging, principally due to the high ductility of silver¹⁰. Heating of SERS substrates caused by the enhanced field has been shown to anneal the structured metal films, reducing the plasmon resonance activity due to a decrease in roughness⁶. All this evidence supports the need to protect the metal structures. An optically invisible protective coating brings wear resistance to the metal, while minimizing chemical reactions responsible for degradation and mitigating structural changes due to heating. Among the noble metals, silver and gold are of special interest for apertureless near-field optical applications because of their strong plasmon resonances, and we focus on silver due to its lower stability.

Protection against mechanical deformation, laser heating and chemical degradation is important for designing robust tips for TERS. The coating of metallic substrates with dielectric thin films for SERS has already received some attention. Walls and Bohn¹¹ showed that sputtering SiO₂ films thicker than 3nm on top of 5nm silver islands imparted resistance to chemical attack of the metal structures. Lacy et al.¹² have shown that the evaporation of SiO at 9×10^{-6} Torr results in complete and uniform SiO₂ films which are 5nm thick and able to completely cover 4.5nm thick Ag islands. In the case of alumina, Murray and Allara^{13, 14} have studied the effect on SERS of separating an analyte molecule from a silver substrate by layers of Al/Al₂O₃ and a polymer thin film. They suggested a synergistic effect of the aluminum with the silver increased the enhancement. During this project a publication by Van Duyne et al.¹⁵ appeared in which they reported that placing even a 0.2nm layer of aluminum oxide on a SERS substrate using atomic layer deposition (ALD) provided heat resistance and improved the preservation of sharp plasmonic structures. Also in the course of this work Zenobi et al.¹⁸ demonstrated theoretically that a SiO_x layer can be used to protect metallized tips for TERS. That work appeared at about the time we were investigating SiO_x coatings experimentally.^{16, 17}

The primary objective of this work was to identify a fruitful approach for extending the lifetime of plasmon-active structures used in TERS or SERS for materials characterization and high sensitivity detection schemes. We started by testing some of the coatings on flat surfaces and then extending the concept to tips for TERS. Our key result is the creation of a corrosion-protected, highly enhancing plasmonic structure on an SPM tip based on silver and silicon oxide or silver and aluminum oxide for the first time. The aluminum oxide protective coating completely stopped the enhanced signal decay for 40 days and did not alter the optical properties of the probes. For the protected and unprotected metallized tips the enhancement factors are of the order of 10^4 . ***The vital advance made here, through materials design, is achieving wearing resistance and corrosion protection without compromising signal enhancement.*** This has been proven by measurements on thin films of a conductive polymer blend (PEDOT/PSS). This metallized SPM tip is capable of accurately measuring surface topography while enhancing the electric field of light for apertureless near-field optics. We used a Si₃N₄ contact SPM tip coated by 50 nm of silver. The protective Al₂O₃ coating is harder than the metal structure. The coated structure has improved wear resistance and extended service life, while providing optical properties for the protected tip which are about the same as those of an unprotected tip. Figure 1 shows a sketch of a SERS substrate and a protected tip under the laser in a TERS apparatus.

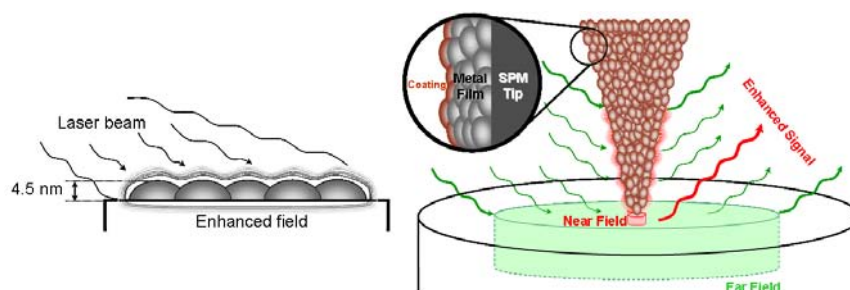


Figure 1. Schematic of an unprotected SERS substrate (left) and a protected tip (right) under the laser illumination showing the location of the enhanced field.

2. EXPERIMENTAL DETAILS

2.1. Protection of SERS Substrates

Coatings envisioned for protecting TERS tips were studied first on SERS substrates to evaluate their effectiveness. The first attempts included the deposition of SiO_x thin layers prepared by the sol-gel process on top of 50nm thick silver films. Acid (HCl) and basic (NH_4OH) catalysts were used during the formation of thin silica layers from a tetraethoxysilane (TEOS) precursor. Films prepared by dip coating, spin coating and solution casting did not cover uniformly the plasmonic structure and the use of a strong catalyst for the sol-gel process seemed to alter the stability of the silver film. Application of the coating procedures to SPM tips was more challenging (data not shown here). In addition, deposition of dodecyl thiol self-assembled monolayers (SAMs) was explored, but the protective layer appeared to reorganize under the laser illumination during the Raman measurements. Finally, physical vapor deposition (PVD) allowed a strict control over the thickness and deposition rates and was easily applied to SPM metallized tips for TERS. The successful results obtained using PVD are summarized in this report.

In order to test the behavior of PVD deposited protective coatings, the plasmonic structure was deposited on a 100nm thick polystyrene film. This film was made by spin coating a 2.5% wt. toluene solution at 2000 RPM for 2 minutes on a silicon wafer from which the native oxide had been etched. Etching improves the spreading of the polymer film on the substrate. After annealing the sample in a high vacuum oven to remove residual solvent and any stress from the coating step (approx. 10^{-7} Torr at 180°C for 2 days), two different types of SERS substrates were fabricated. In one case, the plasmonic structure was in direct contact with the polystyrene film. In the other, an ultrathin dielectric layer was placed between the polymer film and the plasmonic structure to yield a $\text{SiO}_x/\text{Ag}/\text{SiO}_x/\text{polymer}$ multilayer. In both cases, the surface of the metal structure in contact with air was protected by a 5nm SiO_x layer. All of these layers were deposited by physical vapor deposition (PVD) and in all cases the plasmon-active structure was deposited as a 4.5nm thick silver layer. All silicon oxide coatings (SiO_x) were deposited by evaporation of silicon monoxide (SiO).

2.2. Protection of Tip for TERS

Protected metallized tips were prepared by sequential physical vapor deposition (PVD) at 10^{-6} Torr pressure of 50nm silver and then 3nm SiO_x or 1nm, 2nm or 3nm of Al on Sharp MicroleversTM silicon nitride SPM tips. Also unprotected tips (with Ag only) were prepared for comparison. Thickness was monitored with a Sycon (STM-100) quartz-crystal microbalance. Silver, silicon monoxide and aluminum were evaporated from

separate tungsten boats. A deposition rate of 0.2 Å/s was used for deposition of the silver to minimize distortion of the cantilever. Silicon monoxide was deposited at a typical rate of 0.6 Å/s, higher than that of silver, to minimize exposure of the cantilever and the silver structure to the high temperatures required for this evaporation. However, this rate was low enough to ensure a complete and uniform deposition. The adhered Al layer easily generates a passivating Al₂O₃ coating due to the high reactivity of Al with environmental O₂ under normal conditions¹⁹. Alumina is transparent, is harder than silica, and has a very low porosity and high chemical stability.

2.3. Instrument for SERS and TERS

The instrument for TERS used in this work includes a Horiba Jobin Yvon Labram HR-800 Raman spectrometer optically coupled with a Quesant (QScope 250) atomic force microscope (AFM) using a long-working distance Mitutoyo (APO SL50) objective (50X, 0.42 NA). A detailed description of the instrument is presented elsewhere^{3,20}. To measure the optical properties of the tips we used a trapezoidal quartz prism under the AFM head and a white light beam to illuminate the top surface of the prism and create an evanescent field above the prism that could excite emission from a tip brought in contact with that surface. The complete set-up and procedure to measure the optical properties is presented in our previous work²⁰. Optical resonance spectra were measured for both metalized tips and protected metallized tips. The same instrumentation, without the atomic force microscope, was used to measure the enhancements from SERS substrates. Detailed descriptions of the experimental setups for TERS measurements and measurements of the tips' optical properties have been presented elsewhere^{3,20}. TERS contrasts provided by the tips have been estimated using a 50nm thick poly(3,4-thylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) film spin coated on an aluminum mirror.

2.4. Aging Conditions and measurements

Protected and unprotected substrates and tips were removed from the deposition chamber and placed inside a desiccator to minimize contact with humidity. Others were stored under ambient conditions to evaluate the effect of commonly used storage conditions on the optical properties and protective layers. In the case of the SERS substrates, the results presented here are representative of three different locations at the surface. In the case of the tips, at least three different tips were scanned at three different positions on a sample. The error in the determination of the contrast was estimated to be $\pm 10\%$. Laboratory temperature and humidity were monitored at the time of each measurement using a digital VWR hydrometer.

A Park Scientific Autoprobe ® CP atomic force microscope operated in tapping mode with Veeco rectangular silicon cantilevers (manufacturer's specifications: $k=16\text{N/nm}$ and $r_{\text{curvature}} < 10\text{nm}$) were used to characterize the surface morphology and thickness of SERS substrates. A FEI Tecnai 12 Transmission Electron Microscope (TEM) and a JEOL JSM 7501 Scanning Electron Microscope (SEM) were used for imaging selected tips. Qualitative elemental analyses of the tips were obtained using an energy dispersive X-ray spectrometer (EDX) coupled to the SEM to check for degradation and contamination of the tips.

Enhancement factors were obtained on a 50nm thick poly(3,4-thylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) film spin coated from an aqueous dispersion (Baytron® P from HC Starck) on an aluminum mirror. In some cases enhancement factors were also checked using a 20nm CdS thin film.

3. RESULTS AND DISCUSSION

3.1. SERS substrates

Figure 2 shows one 100nm polystyrene film, the silver structure on that polymer film, and the SiO_x protected silver structure, respectively. Height of the films (h) and root mean square roughness (r_{RMS}) values were obtained from the images. The initial spun coated polystyrene film was very smooth ($h=100\text{nm}$; $r_{\text{RMS}}=0.3\text{nm}$). After the 4.5nm thick silver islands were deposited, a very rough and highly structured surface was seen ($h=4.5\text{nm}$; $r_{\text{RMS}}=0.96\text{nm}$). Finally, the 5nm thin SiO_x coating conformally covered the silver islands, filling some of the interstices between the islands ($h=5.0\text{nm}$; $r_{\text{RMS}}=0.94\text{nm}$).

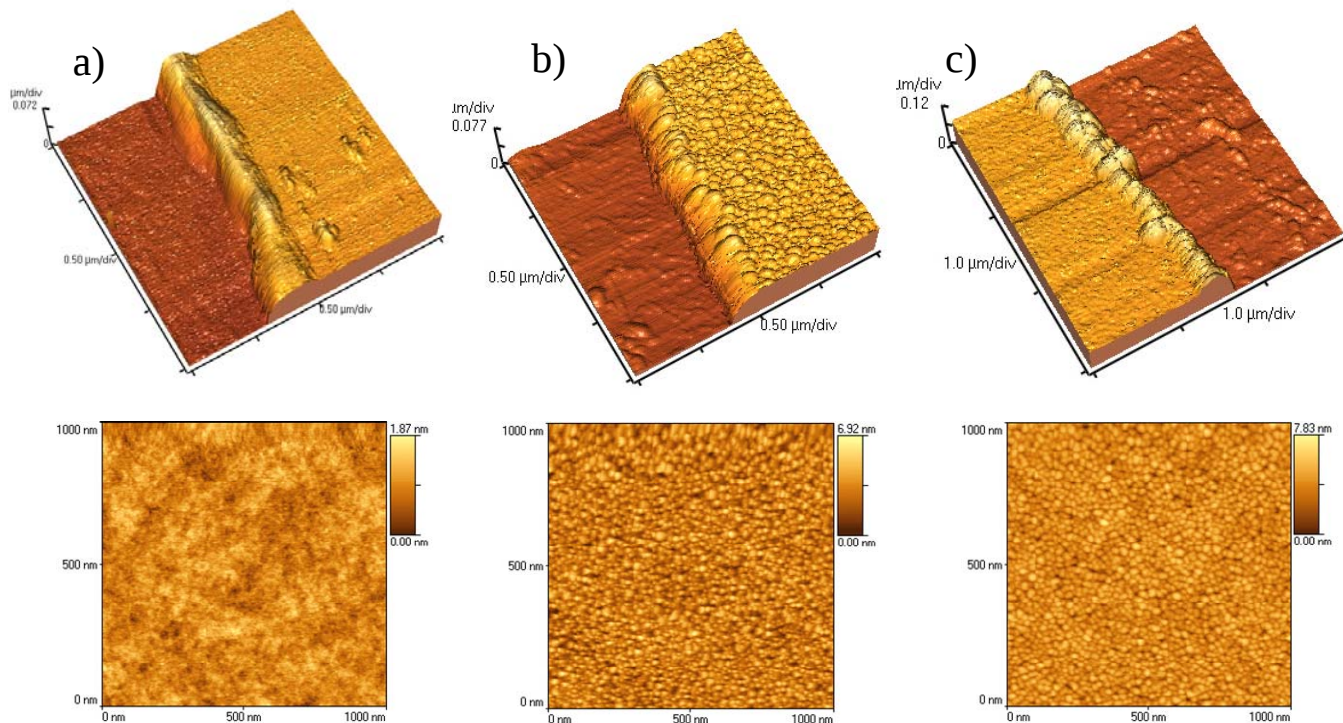


Figure 2. Morphology of test sample of 100nm polystyrene film (a) before deposition of any overlayer, (b) after PVD of 4.5nm layer of silver, and (c) after additional PVD of 5nm layer of SiO_x. The top images in each case show the edge of a scratch so that one can see the height of the film. The images in the bottom row were taken on the higher part of the sample in each case, away from the accumulated debris at the edge of the scratch.

The intensity of the benzene ring breathing mode ($\sim 1000\text{ cm}^{-1}$) in the Raman spectrum of the polystyrene film was followed over time for protected and unprotected films. The samples were not exposed to the 1mW laser light for more than 1h during the experiment. The variations in Raman intensity with time for these samples over a period of 15 days (360 hours) are shown in Figure 3.

Although the data for both samples display some scatter, the overall trend for the sample with the protective coating is a somewhat slower rate of decay of the Raman signal than for the sample with the unprotected silver film. However, even though an improvement was observed with this thin protective coating, the signal still decayed in time and humidity seemed to play an important role - a fact that became more evident after measurements were made during the winter. These winter measurements will be presented below. It was anticipated that a thicker protective coating would provide better protection and therefore the thickness was increased. A 10nm thick SiO_x coating was tested next. The normalized intensity data in Figure 4 demonstrate clearly that the 10nm thick coating completely stops degradation of the Raman signal enhancement over a period of 19 days (456 hours). This result is very interesting for SERS substrates, but such a thick protective coating would not be as useful for TERS. In order for a signal to be obtained from beneath the tip in TERS, it must be possible to bring the plasmonic structure quite close to the sample.

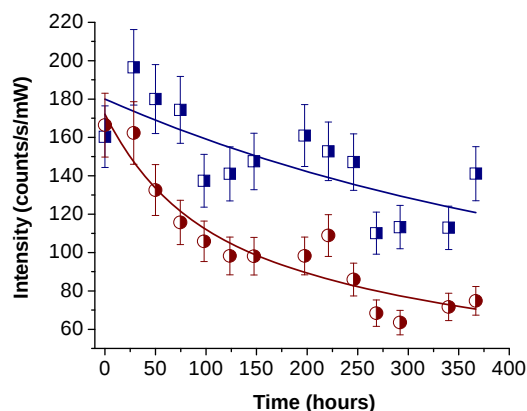


Figure 3. SERS intensity of the benzene ring breathing mode ($\sim 1000 \text{ cm}^{-1}$) for a 100nm PS film covered by a 4.5nm silver film and protected by 5nm of SiO_x (squares), and a 100nm PS film covered by a 4.5nm unprotected silver film (circles) measured during the summer ($40\% < \text{Relative Humidity (RH)} < 60\%$).

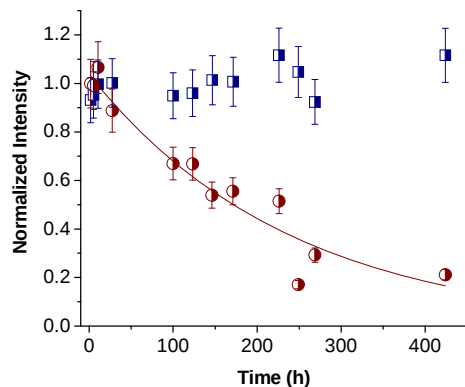


Figure 4. Normalized surface enhanced Raman intensity of the benzene ring breathing mode ($\sim 1000 \text{ cm}^{-1}$) for a 100nm PS film covered by a 4.5nm silver film protected by thick 10nm of SiO_x (squares), and a 100nm PS film covered by a 4.5nm unprotected silver film (circles), measured during the summer ($40\% < \text{RH} < 60\%$). The curve is a guide for the eye.

In the general case one may wish to use a layer of silver as a plasmonic structure in another geometry. That is, one might wish to deposit a silver film, protect it with a thin layer of SiO_x and then deposit the analyte atop the protected silver structure. For this reason, protection of the silver structure with SiO_x was also tested in another geometry in which the surface of the silver is everywhere in direct contact with the protective SiO_x layer. The polystyrene contacts the SiO_x layer. This was achieved by depositing the PS film first, then depositing a SiO_x film atop it by PVD. This deposition was followed by deposition of Ag and finally by deposition of SiO_x again.

Figure 5 shows spectra for three samples. The top (blue) is a spectrum from a sample of the previous section for which there was no SiO_x layer between the PS and the silver. The middle spectrum corresponds to the case in which a 2.5nm thick SiO_x layer has been placed between the PS and the silver structure. The bottom spectrum is for a sample with a 5nm thick intervening SiO_x layer. The intensity of the peak for the benzene ring breathing mode decreases sharply with the imposition of the 2.5nm film between the analyte and the plasmonic structure. With an increase of the thickness of the layer between the PS and silver to 5nm the decrease of the signal is even worse. Although using a thickness of 2.5nm carries a large price in intensity, we were able to consistently create contiguous films at this thickness and we are confident that a film of this thickness provides significant protection.

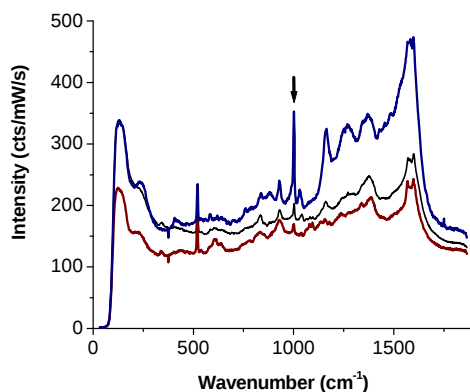


Figure 5. Surface enhanced Raman spectra showing the benzene ring breathing mode (arrow) for three 100nm PS films coated in different ways. The top curve corresponds to a sample with a 4.5nm silver film directly in contact with the PS and protected at the air interface by a 5nm thick layer of SiO_x (top). The middle curve corresponds to a sample in which the 4.5nm thick silver film is separated from the PS by a 2.5 nm thick film of silica. The bottom curve is for a sample with the same geometry as for the middle curve, but with a thicker intervening silica layer of 5nm thickness.

3.2 Morphology and Optical Spectra of Tips for TERS

Silver is attacked by sulfur compounds present in the atmosphere under ambient conditions to form silver sulfide in a process known as tarnishing. Figure 6 shows an energy dispersive X-ray spectroscopy (EDX) spectrum from a tip coated with a 50nm thick silver film left unattended under ambient conditions for 1 week during the summer (higher humidity). The EDX spectrum indicates the presence of sulfur, consistent with the contention that the silver coating on the tip chemically degrades under ambient conditions.

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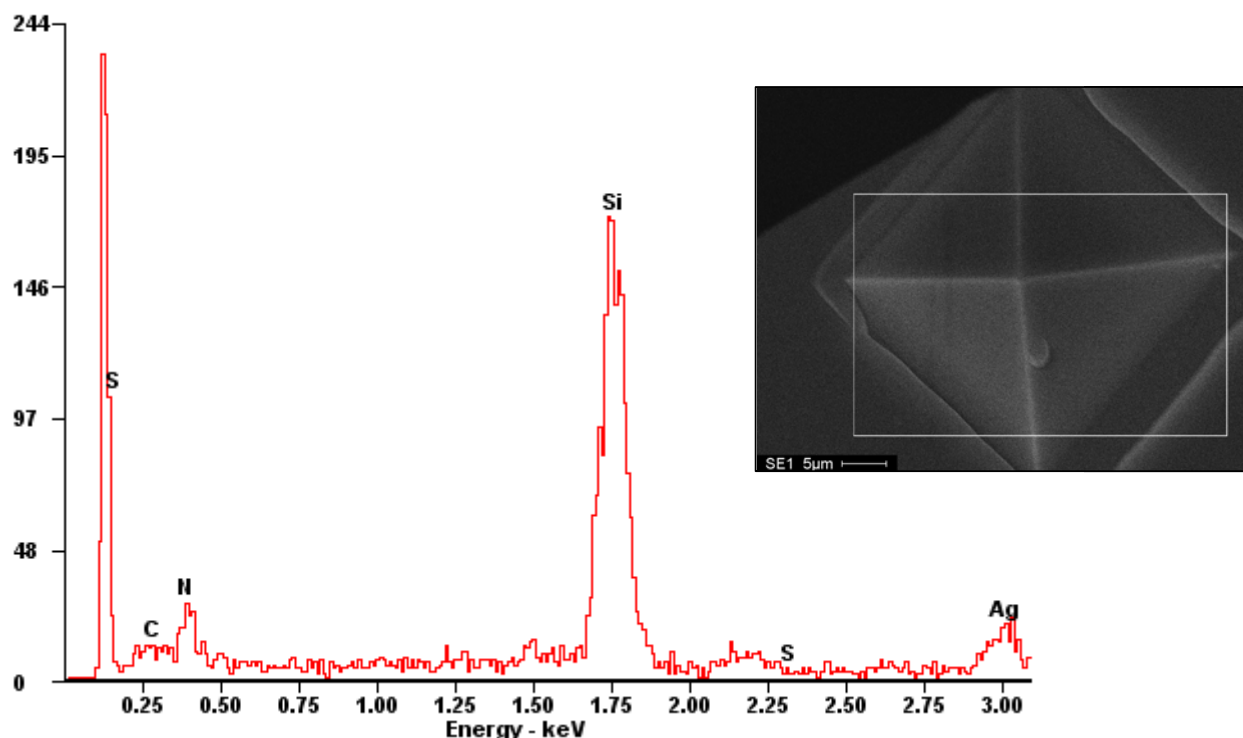


Figure 6. EDX spectra of a silver-coated Si_3N_4 SPM tip showing traces of S that evidence tarnishing. The SEM image in the inset shows the area of the tip from which the spectrum was obtained.

3.2.1 Tips Protected by SiO_x

An adequate thin protective coating must conformally follow the surface topography of the silver structure and cover completely the entire metal structure to reduce attack from environmental agents. A transmission electron microscopy (TEM) image of one tip, shown in Figure 7, reveals the morphology of the 3 nm SiO_x layer fabricated by PVD on the 50nm Ag plasmonic structure already present on the tip. It is known that the evaporation of silicon monoxide (SiO) results in a film of amorphous silicon oxide (SiO_x) at residual pressures higher than 10^{-6} Torr²¹. From TEM images of several representative tips the radii of the protected, metallized tips were determined to be 20-25 nm.

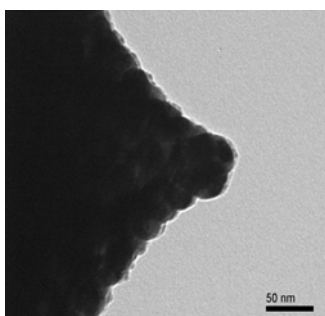


Figure 7. TEM image of a metallized silicon nitride tip with a 50nm Ag film protected by 3nm of SiO_x .

After seeing that the protective coating did not significantly affect the morphology of the plasmonic structure, it was important to compare the optical properties of unprotected and protected tips. Optical spectra for an unprotected silver tip and a SiO_x protected silver tip are shown in Figure 8. Silicon nitride uncoated tips showed an optically flat spectrum with a very low signal intensity (data shown in ref. 17). The spectra from the unprotected and protected metallized tips both show wavelength dependence with a maximum between 650 nm and 700nm. However, details of the shapes of the resonance spectra and maxima positions for the tips with protected and unprotected films differed. The spectrum from the SiO_x protected tip showed two local maxima. One peak was located between 550nm and 600nm and the other peak between 680 and 730nm. Two peaks were seen for multiple tips from two different batches of tips. It may be that multiple resonances result from the presence of more than one particle or cluster of particles at the tip apex.

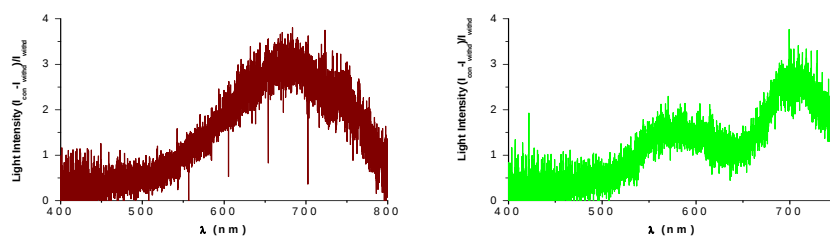


Figure 8. Optical spectra for an (a) unprotected silver-coated Si_3N_4 tip, and a (b) silicon oxide protected silver-coated Si_3N_4 tip.

Enhancement of Raman signals of tips protected by SiO_x and stability of the enhancement over time

The appropriate coating for optical applications must not diminish the plasmon activity of the metal structure. The objectives of protecting plasmonic structures for optical applications are achieving corrosion protection and improved wear resistance without compromising enhancement. That we have achieved these objectives has been proven by measurements on thin films of a conductive polymer blend (PEDOT/PSS) and an inorganic material (CdS). The results were similar for the two films, though the intensity of the signal was higher for the inorganic layer. Most of the results presented here are for the CdS film. Comparison of signals from protected and unprotected tips and quantification of the phenomena central to defining the behavior of such structures requires definition of the terms "enhancement factor" (EF) and "contrast".

Contrast and enhancement factor are based on comparison of "withdraw" and "contact" signals. The withdraw signal is measured with the tip pulled far from the sample so that there is no enhancement from the tip. The signal observed is the far-field signal ("far") collected from the entire area illuminated by the incident beam with diameter of about 1 micron. This is an unenhanced signal and is not localized. The contact signal is measured with the tip in contact with the sample. In this case, there is strong enhancement in a nanoscale region about the contact with the tip^{3,4}. The near-field signal ("near") from this very small region is strongly enhanced. The collected signal, however, contains both the far-field and near-field signals ($I_{\text{far}} + I_{\text{near}}$), so the overall increase in signal seems modest. In order to calculate the actual enhancement of signal one must account for the large difference in the volume of the region from which the far-field signal comes and the volume of the region from which the near-field signal comes. The enhancement factor is given by³:

$$EF = \frac{I_{\text{near}}}{I_{\text{far}}} \frac{V_{\text{far}}}{V_{\text{near}}} = \left(\frac{I_{\text{total}}}{I_{\text{far}}} - 1 \right) \frac{V_{\text{far}}}{V_{\text{near}}} \quad (1)$$

where V_{near} and V_{far} are the sampling volumes from which the near-field and far-field signals come. There is also another important characteristic, contrast, that is the ratio of the total signal measured when the tip in contact to the signal measured when the tip is withdrawn:

$$\text{Contrast} = \frac{I_{\text{near}}}{I_{\text{far}}} = \left(\frac{I_{\text{total}}}{I_{\text{far}}} - 1 \right). \quad (2)$$

Contrasts of tips coated with 50nm silver films were similar whether measured on the PEDOT/PSS film or on the CdS film, though the intensity of the signal was higher from the inorganic layer. When a tip coated with a 50nm silver film was used in TERS, a contrast factor of 2.0 was achieved on a CdS film. In Figure 9 the contact (solid lines) and withdraw (dotted lines) signals from a 20 nm thick CdS film on an aluminum mirror are shown. Measurements were made with unprotected tips (left plot) and tips protected by a 3nm SiO_x coating (right plot). The measured contrast factors were 2.0 and 1.8, respectively. The contrast is reduced by only 10% when the 3nm thick protective coating is added to the tip. The thickness of the protective coating and the material characteristics make it a suitable protective coating for optical applications.

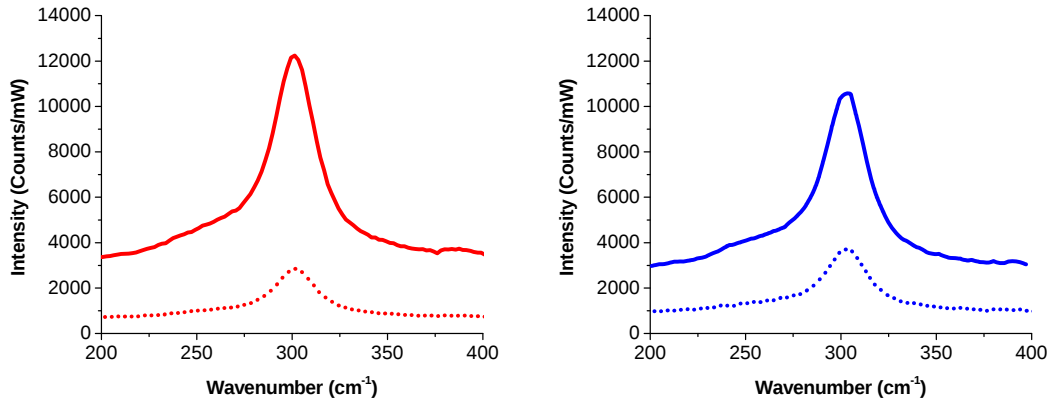


Figure 9. Contact (solid lines) and withdraw (dotted lines) signals from a 20 nm thick CdS film on an aluminum mirror. Contact signals were collected using a metallized silicon nitride tip with 50nm of silver: unprotected (left) and protected by 3 nm of SiO_x (right). The measured contrast factors are 2.0 and 1.8, respectively.

One of the main problems of unprotected silver plasmonic structures upon exposure to environmental conditions is a decay of the enhanced signal over time due to silver degradation. The rate at which the signal decayed was reduced by addition of the protective coating for a first set of tips, as shown in Figure 10. The rate of decay was documented over 30 days. For this particular set of data, the initial contrast for the unprotected tip was about 10% higher than the contrast for the protected tip but we believe this difference is due to the unprotected tip having a better plasmonic structure rather than the coating on the protected tip causing a loss of intensity. Data for a tip from the second batch are shown in Figure 11, which presents the contact and withdraw signals from a 20 nm CdS film on an aluminum mirror. We used a metallized silicon nitride tip coated by silver

without protection or protected by SiO_x for multiple measurements made over a period of three weeks, with the tips having been stored under dry conditions between uses, but the measurements made at the high humidity characteristic of the summer. After the three weeks period, contrasts were 0.4 and 0.7, respectively.

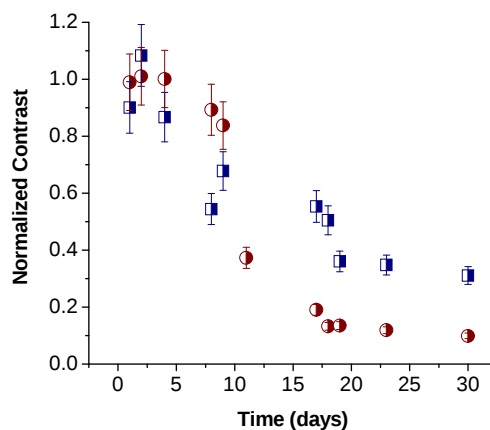


Figure 10. Normalized tip enhanced Raman contrasts for an unprotected silver-coated Si_3N_4 tip (circles) and a silver-coated Si_3N_4 tip protected by a SiO_x 3nm thin layer (squares) on a 20nm thick CdS film (wavenumber 250 cm^{-1}) of over a period of 30 days.

Addition of the protective coating clearly slows the degradation of the signal over a 30 day period. An even slower rate of decay of the contrast with time was observed under conditions of lower humidity (data not shown). The contrast was tracked during the winter time using a protected and an unprotected tip with a 50nm thick PEDOT/PSS film with an average lab temperature of 68°F and a relative humidity below 15%. Those results highlight the important influence on the degradation of plasmonic structures of water vapor surrounding the tip during the measurement.

The ratios of the contrast factors of the tip with protection and tip without protection were very similar for the different batches, but the initial contrasts in the two experiments were different. Figure 11 compares the signals measured with an unprotected tip and a corrosion protected tip for the batch with higher initial enhancement. Enhancements for unprotected tips have been measured for many tips and this initial contrast of 2.0 for the unprotected tip is consistent with that larger body of measurements. These results show a higher decrease in contrast for the unprotected tip, over a time of 3 weeks, than for the protected tip. After three weeks of use, with storage under dry conditions, the protected metallized tip has an enhancement 75% higher than that of the unprotected tip.

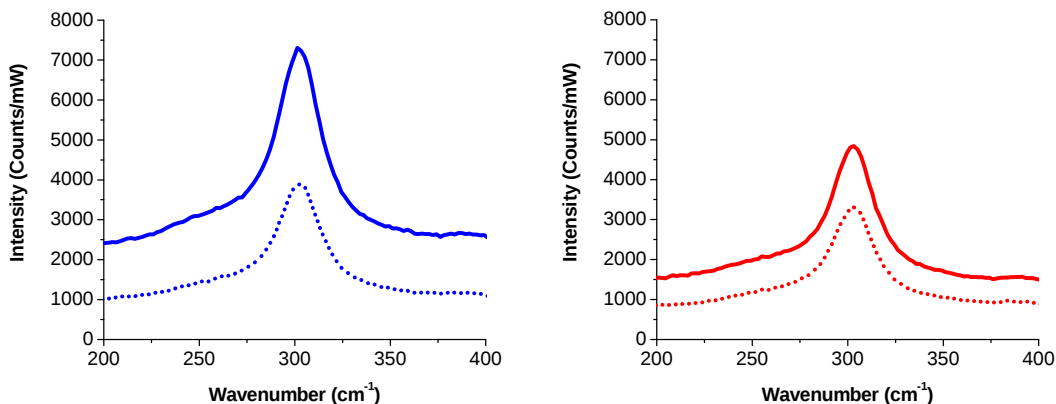


Figure 11. Contact (solid lines) and withdraw (dotted lines) signals from a 20 nm CdS film on an aluminum mirror. Contact signals were collected using a metallized silicon nitride tip with 50nm of silver (left) and protected by 3 nm of SiO_x (right) after multiple measurements made over a period of 3 weeks, with the tips having been stored under dry conditions between uses. Contrast factors are 0.4 and 0.7, respectively.

Wearing resistance of tips protected by SiO_x

During scanning the tip is in contact with the sample and it wears. Wear increases the tip radius, decreasing the resolution of the topography image and making the optical image unstable. It would be desirable for a protective coating to prevent wear of the plasmonic structure tip as well as alleviating degradation of the signal enhancement due to chemical changes. Plasmonic structures protected with SiO_x coatings are expected to show higher wear resistance than their unprotected counterparts as well as prolonged life of effective enhancement. TEM images of three tips, shown in Figure 12, illustrate the changes that occur with wear for an unprotected and protected tip. The image of an unprotected tip fabricated by PVD of 50nm Ag plasmonic structure on a Si₃N₄ SPM tip before it has been used for any scanning shows complete coverage of the tip by the silver coating. After a silver-coated tip without protection has been used to scan a thin polymer film three times, the metallic structure has been removed from the apex and silver has been pushed away from the apex and it has accumulated on the base of the blunted tip (middle image). Traces of what look like silver particles left on the tip are evident in the image. In the case of the SiO_x protected Si₃N₄ tip (right), after scanning the same polymer film three times the apex is not as sharp as it was originally, but the silver layer remains intact.

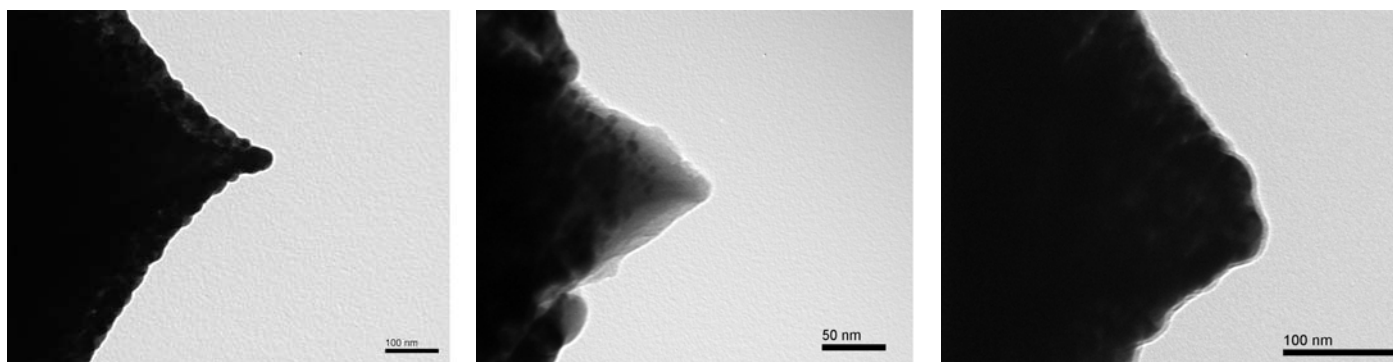


Figure 12. TEM images showing morphologies of an unprotected, silver-coated Si₃N₄ tip before use (left), of another unprotected tip after scanning a PEDOT/PSS thin film three times (middle), and of a third tip, which has a protective coating, after similar use (right). Note that the magnifications differ somewhat from image to image.

3.2.2 Tips Protected by Al₂O₃

After SiO_x coatings for tips were studied, coatings of Al₂O₃ were investigated. An adequate thin protective coating must follow the surface topography of the Ag structure and completely cover the structure to reduce attack from environmental agents. TEM images of one protected tip reveal a smooth morphology of a 3 nm Al₂O₃ layer fabricated on a 50nm Ag structure of the tip (Figure 13a,b). From TEM images of several representative tips the radii of the protected, metallized tips were determined to be 25-30 nm, comparable to the radii of unprotected tips. TEM images also demonstrate that the metallic structure has been removed from the apex and silver accumulated on the base of the blunted unprotected tip after scanning a relatively soft polymer film only three times (Figure 13c), while the silver layer remains almost intact for the Al₂O₃ protected tip after three scans of a hard, patterned silicon substrate (Figure 13d).

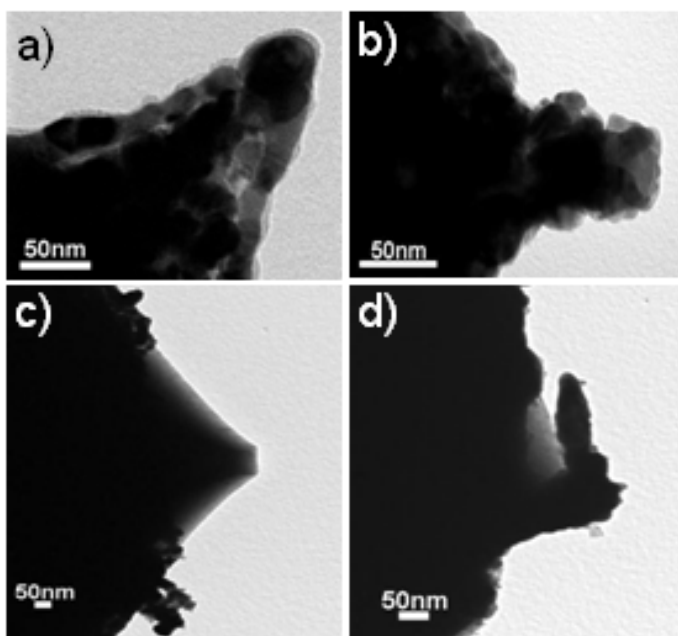


Figure 13. TEM images of a metallized silicon nitride tip with a 50nm Ag film protected by 3nm of Al₂O₃: (a) freshly prepared and (b) after 40 days of measuring enhancement of a polymer film. (c) The morphology of an unprotected, silver-coated Si₃N₄ tip after scanning a PEDOT/PSS thin film three times. (d) A tip which has a 3nm Al₂O₃ protective coating, after scanning a hard silicon substrate. Note that the magnification and orientation of the tip axis differ somewhat from image to image.

No significant difference has been observed between the optical spectra of the unprotected and protected tips (Figure 14): Both show a broad peak at ~650-700 nm, but the protected tip shows a bit sharper resonance. These characteristics were seen for multiple tips from two batches. The most important characteristic of an apertureless tip is its enhancement factor. Comparison of the TERS efficiency of the protected and unprotected tips can be done using the TERS "contrast"^{4, 18}.

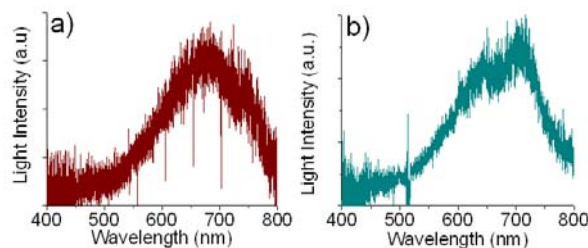


Figure 14. Optical (Plasmon resonance) spectra for (a) an unprotected silver-coated Si_3N_4 tip, and (b) a silver-coated Si_3N_4 tip protected by a 2 nm thick Al_2O_3 ultrathin coating.

The measurements clearly demonstrate that the contrast ($\sim 1.15 \pm 0.10$) remains unaffected when the Al_2O_3 protective coating of thickness up to ~ 3 nm is added (Figure 15). The contrast was monitored over 40 days (Figure 16), during which a tip was stored either in air or in a desiccator. The tips were exposed to 1 mW laser light for less than 1 h during measurement of each point. The contrast of the unprotected tips decayed over 5 to 20 days, even when the tips were not used, the rate of decay depending on the storage conditions (Figure 16). At the same time, the contrast decreased only $\sim 20\%$ for tips protected by 1 nm of Al_2O_3 and remained unaffected for those protected by 2 nm or 3 nm of Al_2O_3 , even after 40 days (Figure 16). Addition of the protective coating stops degradation of tip efficiency over a period longer than a month even in an open air. Even though SiO_x protective coatings slow the rate of contrast decay, they are not able to stop it completely. Thus, Al_2O_3 coatings are more effective.

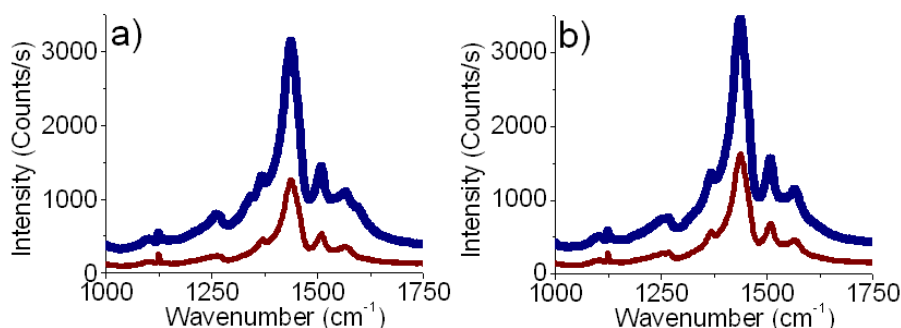


Figure 15. Contact (upper thick lines) and withdraw (lower thin lines) Raman signals from a 50 nm thick PEDOT/PSS film using (a) an unprotected tip and (b) a tip protected with 2 nm thick Al_2O_3 layer at the beginning of the aging experiment ($t=0$). The measured contrast factors were 1.15 ± 0.1 .

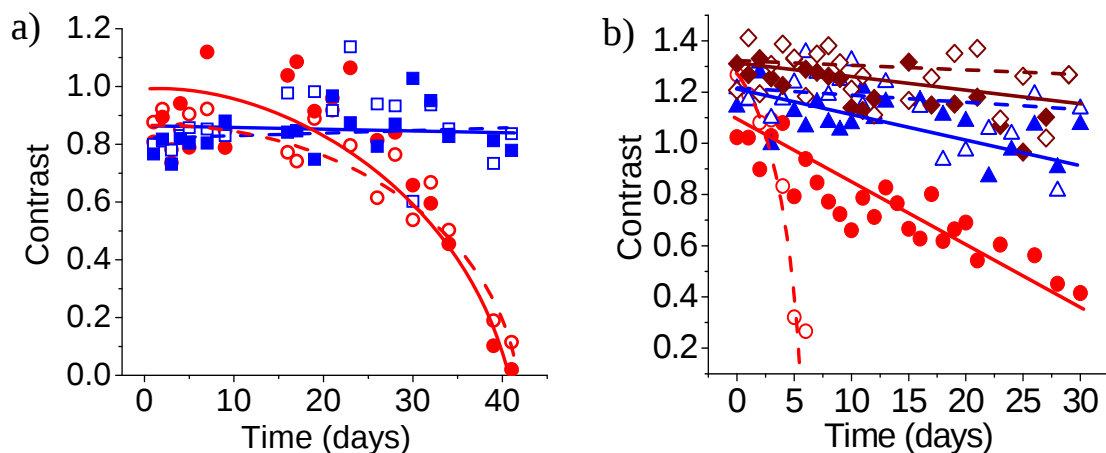


Figure 16. TERS contrast (at wave number 1450 cm^{-1}) as a function of time for a 50nm thick PEDOT/PSS film for unprotected silver-coated Si_3N_4 tips (circles) and a silver-coated Si_3N_4 tips protected by an Al_2O_3 thin layer (triangles, diamonds and squares). (a) The protected tips were coated only by 50nm of silver and 3nm of Al_2O_3 (squares). (b) Data for tips coated with 1nm (triangles) or 2nm (diamonds) of Al_2O_3 . Some tips were stored under ambient conditions (open symbols) and some inside a desiccator (filled symbols). The lines represent guides to the eye. Dashed lines correspond to open symbols.

4. SUMMARY & CONCLUSIONS

We have studied the effect of adding a protective SiO_x layer on the behavior of silver-based SERS substrates and the effect of adding a protective SiO_x layer or Al_2O_3 layer on the behavior of silver-coated SPM tips for TERS. The surface morphology of the silver structure is not altered by the deposition of the protective coating. For SERS substrates, deposition of a 5nm thick protective SiO_x layer slows the rate of decay of the enhanced signal intensity from a polystyrene film. Over a period of 15 days the signal measured on the sample with the protected SERS layer decayed by 20% while that measured on the sample with the unprotected SERS layer decayed by 50%. A 10nm thick SiO_x layer totally stopped degradation of the signal over time. When the SERS layer was separated from the polymer analyte layer by a 2.5nm thick SiO_x protective coating underneath it, the signal intensity was strongly decreased by a factor of 6. This suggests that a protective coating of this type on a TERS tip should have a thickness less than 2.5nm to minimize the impact of the protective coating on intensity.

A SiO_x coating of thickness 3nm nonetheless provides substantial improvement in lifetime for TERS tips made using 50nm thick silver layers and exhibiting an enhancement factor of about 10^4 . For unprotected silver-coated tips, evidence of tarnishing is evident from EDX data after one week when the tips are stored under the normal humid conditions of the summer. Deposition of the protective coating did not alter the morphology of the plasmonic structure. However, the optical spectra of tips protected with a thin SiO_x layer differ substantially from the spectra of the unprotected tips. Protected tips had initial contrasts somewhat lower ($\sim 10\%$) than those of unprotected tips, but after 3 weeks exhibited the contrasts that were 75% higher than for the unprotected tips. The SiO_x coatings also improve the wear characteristics of the tips so that the plasmonic structure is not so rapidly destroyed by using the tip in imaging.

Adding a thin (~2-3 nm) Al₂O₃ protective layer on silver-coated SPM tips for TERS dramatically reduces degradation of the tips with time, without sacrificing initial TERS efficiency (contrast). In addition, the Al₂O₃ protective layer improves markedly the wear resistance of the metal-coated tips. Thus the proposed method of tip coating improves tip resistance to chemical, mechanical and probably laser-induced heating damage. Similar technology can be used for protection of other silver-based structures, including efficient SERS substrates.

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