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Extending nanoscale spectroscopy with titanium nitride probes

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We present a means of controlling the stoichiometry of titanium nitride (TiN) coatings on probes for tip-enhanced Raman spectroscopy measurements made using sputtering so that outstanding enhancements can be obtained. This provides a more robust alternative to gold-coated tips that also has potential for tuning the plasmon resonance and working in new environments. Proof of concept measurements on poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) thin films demonstrate increases in the observed intensity with contrast values up to 3.1. TiN is mechanically, chemically, and thermally robust. When deposited under appropriate conditions it has optical properties, including a plasmon resonance, very similar to those of gold. However, the spontaneous formation of a surface TiN_xO_y layer with relatively high values of y has prevented attaining enhancements in tip-enhanced Raman spectroscopy beyond that provided by the lightning rod effect. Depositing a thin layer of aluminum to form a passivating Al₂O₃ layer over the TiN plasmonic structure allows the stoichiometry achieved in the vacuum deposition to be maintained. Copyright © 2016 John Wiley & Sons, Ltd.

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Introduction

Tip-enhanced Raman spectroscopy (TERS) is a powerful analytical tool that combines the surface mapping capabilities of scanning probe microscopies and the fingerprint chemical identification of Raman spectroscopy. In TERS, the diffraction limit on the lateral resolution of light is overcome using the enhancement to the Raman signal created near a metalized tip, allowing for resolutions on the order of the tip diameter or smaller.^[1,2] This high resolution, coupled with strong enhancement to the usually weak Raman signal, has made TERS an important technique for providing insight into a variety of systems including graphene and carbon nanotubes,^[3,4] biological systems,^[5–7] co-polymer and polymer blend systems,^[8,9] and even artwork and historical documents.^[10] The primary source of this enhancement is the excitation of surface plasmons in the metal or metallic coating on the tip. When excited by the appropriate wavelength of light (in this case visible) these surface plasmons will oscillate, and when confined by a small gap or point in the plasmonic structure, create a strong, localized electric field (E). This electric field increases the intensity of both the incoming light and the light inelastically scattered by the sample near the tip, leading to an increase in Raman signal intensity proportional to $E^{4,[11]}$ Their strong plasmonic response at visible wavelengths of light has led to gold and silver being the materials of choice for making TERS tips. However, there are two major drawbacks to using gold or silver as TERS tips. First, these metals are soft, and any plasmonic structure made from them is easily degraded through mechanical, thermal, and, in the case of silver, chemical processes. Second, the cost of these materials can be very high, especially in the case of gold; although the small amount of material used for each tip makes this factor less important. The first drawback can be largely overcome in ambient and high-vacuum conditions through the use of a thin protective layer of Al_2O_3 .^[12]

TiN is a robust material with applications in both drill bit coatings^[13] and orthopedics used in joint replacement.^[14] It is mechanically strong, thermally resilient, and chemically stable.^[15] When deposited under the appropriate conditions it manifests optical properties very similar to those of gold.^[16] This has made it a cheaper alternative to gold as a decorative coating for a number of products. TiN also has plasmonic properties similar to those of aold.^[17] Studies performed to elucidate the plasmonic properties of TiN have experimentally measured the real and imaginary dielectric constants of well controlled TiN films and used these measurements to solve Maxwell's equations under well-defined boundary conditions to obtain surface plasmon information.[16,17] These calculations show that the plasmonic properties are similar, but not identical to those of gold, and that these properties can likely be varied with the nitrogen content of the films. Work by Naik et al.^[17] quantifies some of the differences in relevant parameters at a specific nitrogen content, comparing the properties of TiN to those of both smooth gold and nano-patterned gold, a material likely closer to those that would be used in enhanced Raman applications. The most important differences, as far as TERS is concerned, are how electric field enhancement varies with wavelength. It is found that the predicted optimal excitation wavelength for TiN is slightly red shifted from that of gold and that the theoretically predicted optimal field enhancement for TiN is slightly lower than that for gold.

The only previous successful use of TiN for an enhanced Raman application that the authors are aware of is that of a discontinuous TiN film as a surface-enhanced Raman spectroscopy (SERS) active substrate.^[18] In that work, a discontinuous, 'island' morphology

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was achieved when deposited on a silicon wafer. It is in the small gaps between 'islands' that plasmon confinement could occur, and enhancement could take place. This discontinuous SERS film was able to provide a modest contrast of 0.4, enough to provide evidence that TiN can be used for enhanced Raman applications.

Presented here for the first time are TiN-coated atomic force microscopy (AFM) tips for use in TERS. These are a valuable addition to the TERS toolbox, providing an alternative to gold tips that is robust. In addition, some of the unique properties of TiN could provide further advantages in the future. Its thermodynamic stability of bulk properties over a range of stoichiometries^[19] could open the door for tips with a tunable excitation wavelength, without sacrificing resolution, based on deposition conditions. There are also indications, including its good stability and use as an adhesive layer in semiconductors^[20] and sensor chips,^[21] that TiN-coated tips could help extend TERS into use in aqueous environments. However, the key to realizing this potential is a means to maintain the stoichiometry of the outermost surface of the TiN coating after the tip is removed from the vacuum in which it has been deposited.

Methods

Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) films

Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/ PSS) in the form of a Baytron P solution was obtained from H.C. Starck (see related disclaimer in the Acknowledgements section). Thin films were made by spin casting a 2:1 ethanol (EtOH) to PEDOT/PSS solution volume ratio mixture at 33.3 Hz onto aluminum mirrors. The EtOH was filtered three times through a pore size of 0.45 μ m before being added to the solution to minimize defects in the film.

TiN/Al deposition

TiN thin films, nominally 40-nm thick, were deposited onto silicon nitride AFM tips (Bruker Model: MLCT; see related disclaimer in the Acknowledgements section) as well as a 1×2 cm silicon wafer via DC reactive magnetron sputtering (Denton Vacuum Discovery 18, Moorestown, NJ). All samples were pre-cleaned using a 30-s RF bias immediately before deposition. Prior to deposition, a base pressure of 2.5×10^{-6} Torr(mmHg) was observed, and deposition was performed at a pressure of 2×10^{-3} Torr (mmHg). High-purity (99.999%) Ar and N₂ were used as the sputtering and reactive gases, respectively. A Ti target (99.9%) was used as the sputter source. A deposition power of 250 W was used. Protected tips were produced by sputtering a thin aluminum layer, nominally 2-3-nm thick, onto the TiN-coated tips without removing them from the system or exposing them to atmosphere. For the aluminum deposition, highpurity (99.999%) Ar was used as the sputtering gas, and an aluminum target (99.99%) was used as the sputter source. The deposition power was 250 W. Because of the reactivity of aluminum with environmental O₂, a passivating Al₂O₃ layer is formed upon exposure to atmospheric oxygen.[22-27]

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were performed on metalized silicon wafers using a PHI Versaprobe II Scanning XPS Microprobe and the accompanying SmartSoft control package. All measurements were taken using a 25 W, 15 kV source with measurements taken over a $100 \,\mu\text{m}^2$ area. Survey scans were taken with a pass of $117.4 \,\text{eV}$ and a step of $0.5 \,\text{eV}$, and high-resolution scans were taken with a pass of $11.75 \,\text{eV}$ and a step of 0.1 eV. The number of sweeps was adjusted for each measurement range to ensure a good signal to noise ratio. All spectra were analyzed using the MultiPak Data Reduction Software.

Microscopy

A JEOL JSM 7501 scanning electron microscope (SEM) was used to image coatings on AFM tips. More specific parameters are noted with the images provided.

TERS measurements

This TERS system set-up has been detailed elsewhere.^[28] The current experiments were performed in a side-illumination geometry, through a Mitutoyo (APO SL50) objective (×50, 0.42 NA) at a 65° tilt with respect to the sample surface normal, using a krypton ion laser (647 nm). A polarizer and spatial filter were placed in the incident beam path before the objective, and a Horiba Jobin Yvon Labram HR-800 Raman spectrometer was used to collect the data. Measurements were performed at 0.84 mW with 60 s acquisition times. Enhancement was measured by directly comparing the intensities measured at a spot with a tip engaged with the surface and with the tip withdrawn far from the surface. The withdraw distance is several millimeters to ensure no contribution to the withdrawn signal is the result of the tip. This withdraw distance is more than sufficient considering that enhancement should drop off over the distance of a few tens of nanometers. The degree of enhancement provided by a tip is characterized by its contrast, defined as $(I_{eng}/I_{wit}) - 1$, where I_{eng} is the signal intensity with the tip engaged and I_{wit} is the signal intensity with the tip withdrawn. All peak fitting was performed using OriginPro 9.1 software.

Results and discussion

Unlike the case of a SERS active substrate, for which very rough, discontinuous films are not only acceptable, but desired in order to create small gaps for plasmon confinement, a TERS tip must have intact, conformal coatings covering the entirety of the tip apex, or a well-defined structure or particle localized at the tip apex. This is because in a TERS system, the plasmon confinement occurs at the geometric discontinuity caused by the sharp point of the tip, allowing the strong, localized electric field to occur. It is just as important that any protective layers be conformal to the underlying plasmonic structure, both to ensure the proper protection and to prevent signal from being blocked by shadowing effects that may occur in the course of the deposition. To ensure that the desired coatings were achieved, newly coated tips were examined using SEM. As can be seen in Fig. 1, a conformal coating was achieved for both protected and unprotected (without an Al₂O₃ coating) tips. Initial measurements using the TiN coated tips were unable to demonstrate contrast greater than 0.8.

This enhancement is in good agreement with lightning rod effect calculations performed for the tips using the equations derived by Liao and Wokaun^[29]:

$$\gamma = 3/2(a/b)^2(1-A_a)$$

where γ is the lightning rod factor, *a* is the length of the long axis, *b* is the length of the short axis, and A_a is a depolarization factor. For



Figure 1. (a) An SEM image of an AFM tip conformally coated with TiN. (b) An AFM tip conformally coated with both TiN and Al₂O₃.

high aspect ratio systems, such as an AFM tip, A_a approaches 0, b is taken to be ~100 nm as determined by SEM, and a is taken to be the tip length as reported by the manufacturer. Using this lightning rod factor and assuming the enhanced signal comes from the entire area under the tip apex, the expected enhancement can be calculated. The agreement between this calculation and the 0.8 contrast achieved between the enhanced and unenhanced signal by the unprotected TiN tips indicates that the enhancement is the result of a lightning rod effect, a topological effect that results from the strengthening of electric fields at a sharp point, rather than plasmonic enhancement by the TiN. The lightning rod effect can occur without localized plasmon excitation if the incident light has an electric field component parallel to the long axis of the tip. The lack of plasmonic enhancement from the TiN can be explained as resulting from the large amounts of oxygen in the TiN coatings observed with XPS. These measurements show that the surface of the film is made up primarily of $\rm TiO_2$ and $\rm TiN_xO_v$ with relatively high values of y, which results in the blocking of enhancement from



Figure 2. Layer compositions of the elements measured with XPS. Those at times less than 25 min reflect the composition at a depth reached after that sputtering time. The points at 25 min represent a final measurement after 15 min exposure to atmosphere.

surface plasmon resonance. As shown in Fig. 2, depth profiling with XPS reveals that the majority of the oxygen is limited to the top 20 nm of the film with smaller amounts of TiN_xO_y in the bulk. This result is in agreement with compositions of layers observed by Guillot et al.^[30] However, while Guillot et al. attributed the presence of oxygen to residual gas in the deposition chamber, we propose that the oxygen-rich surface layer forms once the film is exposed to the atmosphere. To test this hypothesis, after sputtering in the XPS chamber, the TiN-coated test piece was removed from the XPS chamber and allowed to sit in atmosphere for 15 min. When the sample was returned to exactly the same measurement position, a high surface oxygen content was measured at the location where the sample had earlier been sputtered. The XPS compositions after exposure to atmosphere are denoted by the points at 25 min in Fig. 2.

To overcome this obstacle and achieve plasmonic enhancement, a thin layer of aluminum was deposited onto the TiN as a protective layer before exposing the TiN-coated tips to atmosphere. Thin layers of aluminum have been shown to form passivating layers of Al_2O_3 upon exposure to atmospheric oxygen.^[22-27]Such lavers effectively protect silver-coated tips^[12] and were largely able to prevent the tarnish of silver in TERS tips for at least 2 months.[31] The absence of an oxygen-rich surface layer on the protected TiN films is confirmed with high-resolution XPS spectra of the Ti2p doublet from a silicon wafer coated alongside the tips, as shown in Fig. 3. The signal intensity is lower than that typically seen for Ti peaks because it comes from material underneath the protective Al₂O₃ layer. The protective layer was not sputtered away prior to the measurement to avoid artifacts in the measurement that result from cascade mixing. A very good fit to the data was achieved despite the lower intensity. Peaks at 454 and 460 eV correspond to Ti and its doublet, and peaks at 456 and 462 eV correspond to TiN and its doublet, while peaks at 458 and 464 eV, corresponding to TiO₂ and its doublet, are absent.

Good enhancement was observed with these tips. The enhancement of the protected TiN tips was tested by performing measurements in both the engaged and withdrawn positions on the same spot of a PEDOT/PSS film on an aluminum mirror. PEDOT/PSS was chosen for its relatively strong Raman signal. Fig. 4 shows both the engaged and withdrawn spectra for PEDOT/PSS. The signal enhancement from the protected TiN tip at the surface results in an increase in observed intensity corresponding to a contrast of up to 3.1. This was obtained by fitting the peak at 440 cm⁻¹, which is attributed to deformation of the oxyethylene ring. The average increase in intensity observed across several measurements and fitting multiple peaks in each measurement was 2.39 ± 0.44 . The authors point out that this is not an optimized TERS system. Further



Figure 3. High-resolution scan of Ti2p doublet by XPS taken from a protected TiN film. The peak fits from MultiPak, the difference between the fit and measured spectrum (dashed curve), the positions of the de-convoluted peaks, and their assignments and the percentage of the total area under the curve that each represents are also pictured. Note that no TiO₂ peaks are present.



Figure 4. Raman spectra of PEDOT/PSS film with protected TiN-coated AFM tip engaged (top) and withdrawn (bottom).

enhancement should be possible with optimization of the TiN and Al_2O_3 layer thicknesses, TiN stoichiometry, wavelength and polarization of incident light, and the substrate on which the sample rests. Based on the theoretical comparisons of TiN to gold and on previous in-house measurements using gold tips, it is expected that a fully optimized, protected TiN tip could achieve an increase in signal intensity corresponding to a contrast as high as 8. It should also be pointed out that these tips are quite robust. They have been observed to have a storage lifetime of at least 5 months and provide consistent enhancement even after multiple measurements, each including an engage/withdraw cycle which is the process most likely to cause tip damage.

The use of titanium nitride also opens up new possibilities for TERS. For example, the potential to adjust the optimal excitation wavelength through stoichiometry, rather than film thickness, presents the possibility of tips that are tunable based on deposition conditions without sacrificing resolution. The good adhesion between the TiN and the silicon nitride tips also makes TiN an excellent candidate for TERS in aqueous environments without the need for an additional adhesive layer reported previously.^[32]

Conclusions

Reported for the first time are TiN-coated tips for use in TERS measurements. Coating the TiN with Al so that a native Al_2O_3 protective layer can form is key to making TiN available as a plasmonic material for TERS. The TiN-coated tips provide good enhancement with a contrast between enhanced and unenhanced signal of 3.1 with room for improvement with optimization of the tips. Further, these tips are robust, continuing to provide enhancement after at least 5 months storage and after at least 6 engage/withdraw cycles. By way of comparison, an alumina protective coating increases the lifetime of Ag-coated tips to at least 2 months,^[31] Au-coated tips are substantially dulled after only a few engage/withdraw cycles. The potential for tailoring the plasmonic properties through stoichiometry and leveraging the outstanding adhesion of TiN in order to extend TERS to new environments is also exciting.

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