MPTMS self-assembled monolayer deposition for ultra-thin gold films for plasmonics

Pushkar K Gothe, Dhruv Gaur and Venu Gopal Achanta
Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400005 India
E-mail: achanta@tifr.res.in

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Abstract
(3-mercaptopropyl) trimethoxysilane (MPTMS) as an adhesive layer helps realize plasmon compatible few monolayer uniform gold films. We present, significantly faster, thermally assisted vaporization and immersion methods for MPTMS monolayer deposition. Presence and properties of MPTMS monolayers are established by fourier transform infrared spectra, ellipsometry and atomic force microscopy. Sub-nanometer rough, 0.7 nm thick MPTMS monolayers are used to fabricate large area gold gratings by electron beam lithography followed by either lift-off or reactive ion etching. In addition to retaining the plasmonic response over broadband, MPTMS layer helps realize 5 nm thin gold films of uniform coverage.

1. Introduction

Self-assembled monolayers (SAMs) are of great importance for molecular electronics, chemically active interfaces, adhesive layers, interface barrier layers to inhibit metal diffusion, sensors and other devices [1–7]. Deposition and device fabrication processes are critical for successful use of SAMs for different applications [1]. Early work in the field focused on the deposition of SAMs on uniform, thin metal films like gold and silver and their applications [1–10]. However, a relatively more recent challenge is to achieve uniform few monolayer metal films to study the properties in the quantum regime as well as for plasmonic applications. Gold being inert, compared to other metals like Silver and Aluminum, is the often used material for plasmonic studies in the visible to near-infrared wavelength regions [11]. However, gold adhesion is poor on most of the surfaces and the conventional adhesive layers like Chromium, Titanium or Nickel are not suitable for plasmonics. There are several studies to understand the role of adhesion layer on the optical response of gold structures. Theoretical as well as experimental studies found that the adhesion layers weaken, shift as well as broaden the plasmon resonance [12–17]. In addition, the patterning of the adhesion layer modifies the plasmon response. Compared to metallic adhesion layers, dielectric metal–oxide adhesion layers like titanium oxide (TiO₂) and Chromium oxide (Cr₂O₃) were shown to be better [12, 13]. Among all the reported dielectric adhesion layers that are suitable for plasmonics, a monolayer of (3-mercaptopropyl) trimethoxysilane (MPTMS) that has functional groups present at both terminals of the molecule is the best so far [18–20]. Shen et al reported the first use of MPTMS as an adhesion layer for nanostructures [18]. The silanol group (Si-OCH₃) at one terminal reacts with the SiO₂ surface silanols [19] (Si-OH groups form the modified substrate surface) to form hydrogen bonded intermediates. This is followed by the elimination of H₂O and CH₃OH to form stable Si-O-Si bonds on the SiO₂—MPTMS interface (Figure 1). The thiol group (–SH) at the other terminal of the MPTMS molecules acts as a good anchor for Au atoms. In addition to improving the adhesion, the SAMs also help in achieving highly smooth gold films [21]. Earlier reports on vapour- and liquid- phase deposition of MPTMS monolayer involved a process time that was a few hours to 1 week long [18–26]. For practical applications, one needs to have faster deposition methods that help the adhesion of gold to substrates as well as smooth, uniformly covered few monolayer gold films. In addition to faster processes for depositing the adhesion layer, it is challenging to establish the presence of monolayer. In this paper, we address the three critical issues governing the adhesion
layer for gold. One is to achieve fast deposition techniques that are compatible with lithographic processes. Secondly, is there a way to establish the presence of monolayer and thirdly, is the adhesion layer compatible for low loss, broadband studies. We present two fast deposition methods for MPTMS monolayer deposition. We studied different characterization techniques and found the presence of alkyl groups of the monolayer in the Fourier Transform Infrared (FTIR) spectrum. We present results showing compatibility of MPTMS monolayers to reactive ion etching (RIE) and lift-off processes. For plasmonic applications, we show that the MPTMS monolayer is suitable for broadband plasmonics covering visible to near-infrared wavelengths.

In the following, experimental details of thermally assisted evaporation (vapour phase) and immersion deposition (solution phase) methods are described. After presenting characterization results to establish the presence of MPTMS and its properties, grating fabrication and plasmonic response of structures with and

Figure 1. The gold deposition procedure with MPTMS adhesive layer. (a) Si substrate with native oxide layer. (b) Si substrate with modified SiO₂ layer after plasma etching in oxygen. (c) SiO₂ surface partially hydroxylated after cleaning with piranha solution. (d) Surface after hydroxylation. (e) Self-assembled monolayer of MPTMS is deposited with –SH groups on top followed by (f) Au deposition by sputtering.
without MPTMS films are presented. Continuous gold thin films with thickness of 5 nm and above are achieved with MPTMS layer on top of the substrate.

2. Experimental methods

Figure 1 shows schematic of the deposition process for gold layer on MPTMS. The substrates were cleaned before deposition of MPTMS to enable the formation of a self-assembled monolayer. The substrate to be coated is cleaned by rinsing in IPA solution and then blow drying with nitrogen followed by oxygen plasma cleaning at 80 W power and 1 Pa pressure for 10 min. The substrate is treated in a freshly prepared Piranha solution (a 1:1 mixture of sulphuric acid, H₂SO₄ and hydrogen peroxide, H₂O₂) for 10 min at room temperature followed by rinsing in DI water and blow drying with dry nitrogen gas. The residual H₂O, if any, on the substrate is removed by heating the substrate to 110 °C for about 15 min. The substrate is then immersed for 10 min in a hydroxylation solution with a 6:1:1 composition of DI water, HCl and H₂O₂ heated to 85 °C. The substrate is further rinsed in DI water and blow dried with nitrogen. This causes the Si-O-Si bonds to be replaced with Si-OH bonds on the surface. These hydroxyl (–OH) groups are suitable anchors for the deposition of MPTMS. The substrate is heated to 110 °C for about 15 min to remove residual H₂O₂, if any, on the substrate.

The MPTMS layer deposition by thermally assisted evaporation and immersion deposition are detailed below. The basic vapour phase deposition process reported earlier is a time consuming process to deposit a monolayer of MPTMS on a substrate [12]. In this, the substrate is kept exposed to an open vial of MPTMS in an evacuated chamber or glove box. The vapours from the MPTMS reach the substrate and react with the hydroxyl bonds on the surface thereby starting the deposition process.

In order to achieve faster deposition, the substrate and a stainless steel dish containing 1 ml of MPTMS are placed in a specially designed chamber maintained at a higher temperature and a negative pressure. The substrate is placed upside down next to the evacuation port on a sample holder. The chamber is evacuated continuously to maintain a pressure of the order of 10⁻² mbar while heated to a temperature of 90 °C. After exposure to MPTMS vapours, substrate is taken out and rinsed with isopropyl alcohol, blow dried with nitrogen and heated to 85 °C for 10 min to remove any unattached MPTMS. The parameters were varied to study their effect on the deposited MPTMS layer. The optimal conditions for the thermally assisted evaporation to achieve monolayers of MPTMS were found to be, chamber temperature is 90 °C, chamber vacuum is ~10⁻² mbar and deposition time of 1 h. The optimum temperature was initially obtained by depositing MPTMS layers on a substrate loaded inside a hydrothermal reactor.

Earlier reported immersion deposition methods were carried out in 0.005 M solution of MPTMS in Toluene for 30 min [6] and 0.01–0.04 M solution of MPTMS in Benzene for 30 min [7]. We carried out the immersion deposition method by studying a wide range of concentrations of MPTMS in Benzene and immersion times. The hydroxylated Si or quartz substrate is immersed in a 0.005 M to 0.04 M solution of MPTMS in 10 ml Benzene in a petri-dish for 15 to 30 min to allow uniform deposition of the MPTMS layer. Benzene is a volatile solvent, so the petri-dish is covered with an Aluminium foil to reduce evaporation. The substrate was taken out and rinsed with Benzene and then with Chloroform, Methanol and DI water to remove the dangling (un-bonded) MPTMS molecules from the substrate before blow drying with dry nitrogen. The optimum conditions found for immersion deposition are, 0.01 M concentration of MPTMS in Benzene for 30 min at room temperature.

3. Results and discussions

MPTMS layer deposited on Silicon substrates were tested with various methods to establish the presence of monolayer.

Fourier transform infrared (FTIR) spectroscopy in reflectance (ATR) mode showed two distinct signature peaks in the region 2800 cm⁻¹ to 3000 cm⁻¹ indicating the presence of Alkyl (C–H) groups [27]. Figure 2(a) shows the FTIR spectra of both the samples with respect to bare substrate. The blue arrows indicate the additional alkyl group resonances.

For the thermally assisted evaporation process (figure 2(a)), the MPTMS deposited at 90 °C for 1 h at 10⁻² mbar had distinct peaks at 2885 and 2928 cm⁻¹ confirming the presence of Alkyl (C–H) groups and thus the presence of MPTMS. For immersion deposition process (figure 2(a)), the MPTMS deposited using 0.01 M of MPTMS shows distinct peaks at 2871 and 2918 cm⁻¹ corresponding to the alkyl (C–H) groups. It may be noted that, the functional group signal from monolayers is very weak and the alkyl peaks were used for verification earlier as well [28].

The thickness of the MPTMS layer was measured using Ellipsometry. Using refractive index of 1.444 (specified by Sigma Aldrich), the thickness of the film was estimated for the films deposited by the two methods. While the thickness of the MPTMS layer deposited by the immersion deposition process using 10 mM MPTMS
solution is 0.94 ± 0.02 nm, the thickness of the MPTMS layer deposited by thermally assisted evaporation process at 90 °C for 1 h is 0.69 ± 0.02 nm. Using the thickness estimated, the dispersion of MPTMS films was estimated by fitting the ellipsometric data to Cauchy model. Figure 2(b) shows the n and k values of the MPTMS film deposited by thermally assisted evaporation. The Cauchy parameters are n = 1.358 ± 0.006, B = 0.043 ± 0.005, C = −0.0007 ± 0.0003 and central wavelength was 632.8 nm. The mean square error of the fit was 1.221.

Gold films of 100 nm thickness are dc-sputter deposited on substrates with the MPTMS layer. Atomic force microscope image of the gold surface is shown in figures 3(a) and (b). The root mean square surface roughness is 0.483 nm for vapour phase (a) and 0.499 nm for immersion deposited (b) substrates with gold film. These results show that vapour phase deposition provides monolayers with lower surface roughness than the immersion deposited monolayers.

There is considerable interest in realizing few monolayer continuous metal films to study their properties in the quantum regime [21]. Gold films of varying thickness ranging from 2 nm to 10 nm were deposited on MPTMS coated Si substrates by dc-magnetron sputtering. Their surface morphology was studied using SEM (figures 3(c)–(f)). Au layers thicker than 5 nm showed smooth surface morphology that is continuous.
In order to check the adhesion and suitability of the MPTMS for lithography to fabricate nanopatterned samples, the following modified lift-off process was performed [22]. After the deposition of MPTMS on Si substrate, the samples were coated with electron beam resist (Poly (methyl methacrylate) (PMMA)) by spin coating at 2000 rpm. A thin layer of Au (5 nm) was coated to make the surface conducting before patterning with electron beam to write a 1-d grating pattern. The grating parameters are, period is 540 nm and width of air groove is 180 nm. The top Au layer was subsequently removed by reactive ion etching in Ar plasma and the pattern was developed in Methyl isobutyl ketone (MIBK) and Propan-2-ol solution to transfer the pattern onto the PMMA layer. A 100 nm Au layer was then deposited on the substrate. The lift-off process was carried out by immersing the substrate in acetone overnight and then ultra-sonicating it. The PMMA strips with gold above it are removed leaving behind the Au grating pattern bonded to the MPTMS layer. Six grating patterns were fabricated with varying electron beam dosages of 100–150 μC cm\(^{-2}\) with 0.03 nA current.

The SEM image of the optimum pattern for dose of 150 μC cm\(^{-2}\) is shown in figure 4(a). Another sample without MPTMS layer was also processed with the modified lift-off process. The PMMA strips as well as the entire gold film were removed during the lift-off process and no gratings could be observed. This shows that MPTMS improves Gold adhesion making it suitable for lift-off process.

We prepared another grating pattern by dc-sputtering 100 nm gold film on clean fused silica substrate. The top gold film was patterned to have 1-d grating after spin coating PMMA, exposing to the e-beam followed by developing the resist and dry etching in a reactive ion chamber with Ar plasma (138W RF power, 0.5 Pa pressure, for 10 min). Successful realization of gratings by dry etching process shows that the MPTMS monolayer is a robust gold adhesive layer suitable for both lift-off and dry etch processes.

The effect of the MPTMS adhesive layer on the plasmonic response over broadband was studied by measuring the transmission enhancement through plasmonic quasi-crystal (PlQC) structure (hole array with 5-fold rotational symmetry) [11, 29]. The PlQC patterns were made in dc sputtered Au films deposited on fused silica substrates with and without MPTMS monolayer. Using electron beam lithography followed by reactive ion etching, PlQCs were prepared on both substrates over 0.6 mm × 0.6 mm regions with a long range period of 600 nm and hole size of 43 nm (inset of figure 4(b)). A halogen lamp having broad wavelength emission range was near collimated to 0.5 mm spot with <0.5° divergence and is used to measure the transmission through the QC patterns by Ocean Optics USB2000 spectrometer. As seen in figure 4(b), the spectral features remain intact with near identical normal incidence transmitted intensity through gold PlQC structures with and without MPTMS adhesion layer.

**4. Conclusion**

To summarize, two faster deposition processes for MPTMS monolayers on different substrates are demonstrated as adhesion layers for gold. The MPTMS monolayers deposited are compatible with nanofabrication processes involving either lift-off or ion beam etching. The presence of MPTMS is identified from the alkyl group peaks in the FTIR spectra. Further ellipsometric measurements confirmed that the thickness of the deposited MPTMS layers are within the reported monolayer thickness of 0.7 nm. AFM studies showed sub-nm roughness for gold films deposited on MPTMS adhesion layers. Presence of MPTMS layer has little influence on the plasmonic response of the PlQCs which show broadband plasmonic response.
MPTMS layer, continuous metal films with thickness greater than 5 nm are realized with sub-nanometer roughness.

ORCID iDs

Venu Gopal Achanta @ https://orcid.org/0000-0002-2554-5475

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