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Aminopropylsilatrane Linkers for Easy and Fast Fabrication of High-Quality 10 nm Thick Gold Films on SiO₂ Substrates

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Fabricating smooth and contamination-free sub-10 nm thick gold layers on dielectric substrates is of interest for a number of applications, including plasmonics, metamaterials and nanoelectronics. Metallic adhesion layers are often used to facilitate good adhesion between gold and substrates but at the cost of interfacial alloying and subsequent deterioration of the optical and electrical properties of the thin films. Another approach for promoting adhesion between gold and SiO₂ substrates is the use of self-assembled organosilane monolayer linkers, such as (3-aminopropyl)-trimethoxysilane (APTMS). APTMS, however, is a corrosive chemical and its monolayer preparation is highly sensitive to ambient conditions. Here, we introduce an easy and fast immersion process using (3-aminopropyl)-silatrane (APS) for achieving smooth and high-purity gold films and compare its performance to APTMS. Our APS recipe is water based, does not require environmental considerations, and has approximately 6 times faster deposition time than APTMS (30min vs. 3hr). The results demonstrate that both organic molecules promote the formation of continuous and smooth 10 nm thick gold films, without leading to considerable chemical intermixing at the interface. Monitoring the growth evolution of the gold layer indicates a threshold thickness of 6-7 nm for obtaining continuous films. Overall, the ease of use, faster processing time and low toxicity of APS make it an attractive choice for fabricating high-quality ultrathin gold films on SiO₂ substrates.

KEYWORDS: adhesion layer, APS, APTMS, Au thin film, organosilane, microstructure

1. Introduction

Ultrathin, smooth and chemically pure gold films are relevant for a variety of applications in nanophotonics, such as plasmonic waveguides^{1,2}, metamaterials³ and biological and biomedical sensing^{4,5}, as well as applications in nanoelectronics^{6–8}. This is due to the superior optical properties of Au in the visible to near-infrared wavelength range, its chemical stability and high electrical conductivity. At the same time, the low chemical reactivity of Au and its inability to form stable metal-oxide bonds mean that typically an intermediate adhesion layer to create sufficiently strong bonding with a dielectric substrate, such as silica, is needed. Often the sole purpose of an adhesion layer is ensuring device integrity, and other possible effects are ignored. However, with increasing demands for thinner films, the influence of adhesion promoters on the nanometer and even the atomic scale must be studied. In micro- and nanofabrication, Ti and Cr are almost exclusively used for this purpose. Nonetheless, they are known to degrade the optical and electrical properties of the thin films resulting, from interfacial chemical intermixing and diffusion of the metallic adhesion layer into the Au thin film⁹. Studies have shown that Ti and Cr adhesion layers reduce the intensity, broaden the bandwidth and shift the plasmon resonance spectral peak, which in turn deteriorate the performance and sensitivity of plasmonic devices.^{10–13} This has motivated the introduction of alternative adhesion enhancing materials and methods, including silk protein¹⁴, monolayer MoS₂¹⁵, organosilane monolayers^{16,17} and cooling substrates to cryogenic temperatures¹⁸.

Amino-organosilane monolayers containing silanol groups react with SiO₂ to form siloxane bonds at one end, and their amino group at the other end allow for covalent bonding with Au. These organic adhesion layers have been shown to improve detection in surface-enhanced Raman spectroscopy based biosensors^{4,19,20} and in cancer diagnostics.¹³ Furthermore, they are used to fabricate Au electrodes for organic photovoltaics¹⁷ and to adhere gold nanoparticles for spectroscopic purposes^{21–23}, including in DNA detection²⁴. 3-aminopropyl-trimethoxysilane (APTMS) is the most popular amino-organosilane linking agent and its advantages in the fabrication of sub-10 nm thick smooth Au films has already been demonstrated^{17,25}. APTMS, however, is a harmful chemical due to its corrosive nature, its solution-phase deposition is time-consuming (typically a few hours^{26–29}) and demands reduced humidity environments^{26,29}. The aim of this study is to evaluate the potential of 3-aminopropyl-silatrane (APS) for the fabrication of Au films of thickness in the 10 nm range, with an easy, fast, environmentally friendly and stable

synthesis process. In comparison to APTMS, APS is not harmful, its solution-phase deposition is faster (~ 30 min^{29,30}) and can be performed under ambient conditions^{24,29,30}. It is currently used primarily to enhance the adhesion of nanoparticles^{29,30}. We have investigated and compared the performance of APS in promoting the growth of ultrathin and smooth Au films on SiO₂ to that of APTMS. The deposition of the two organosilanes here is carried out in an immersion step, resulting in an interfacial self-assembling monolayer process²⁶. Self-assembled monolayers have been used to tailor the surface properties of solid materials, in order to generate attractive electrostatic interactions between molecules/ions in the solution and the reactive OH- groups on the SiO₂ surface with the use of appropriate functional groups. These silanol groups perform spontaneous selective bonding with solid substrates through chemisorption at room temperature.³¹ After the deposition of the organic monolayer, gold is sputtered on the modified SiO₂ surface by physical vapor deposition to generate a continuous and smooth metal film (see Scheme 1).

Scheme 1. Schematic illustration of fabrication process of ultrathin gold films on silicon dioxide substrate with APS and APTMS as adhesion layers.

We have studied and compared 10 nm thick Au films deposited on SiO₂ substrates functionalized with APTMS and APS, as well as untreated substrates (details summarized in Table 1). The effect of the surface preparation in each case is examined using contact angle measurements and X-ray photoelectron spectroscopy (XPS). Two key parameters adversely influencing the optical and electrical performance of the Au thin films are surface roughness and chemical contamination from the adhesion layer into the Au films. They are investigated here using atomic force microscopy (AFM) and electron energy-loss spectroscopy (EELS) combined with scanning transmission electron microscopy (STEM), respectively. To gain insight on the effect of the organosilanes on the growth of the Au layers, the microstructure of the polycrystalline Au films are studied using transmission Kikuchi diffraction (TKD) in a scanning electron microscope (SEM). Moreover, the growth evolution of 2 – 8 nm thick gold layers is inspected by

TKD and the coverage of the substrate by the Au layer at different thicknesses is estimated from SEM images. Collectively, the results provide a comprehensive structural characterization of Au thin films fabricated on APTMS and APS-functionalized SiO₂ substrates and demonstrate that high quality 10 nm thick Au films can be fabricated using an easy, fast and environmentally friendly APS recipe.

Table 1: Details of the samples studied here and their labels.

Sample	Substrate	Label
10 nm Au	1 μm SiO ₂ 20 nm SiO ₂	Au/SiO ₂
10 nm Au	1 μm SiO ₂ functionalized with APTMS 20 nm SiO ₂ functionalized with APTMS	Au/APTMS/ SiO ₂
10 nm Au	1 μm SiO ₂ functionalized with APS 20 nm SiO ₂ functionalized with APS	Au/APS/SiO ₂

2. Experimental Methods

Thin film fabrication. The substrates used are single-side-polished 4-inch diameter, and 500 ± 25 μm thick Si wafers of (100) crystal orientation. A 1 μm thick SiO₂ layer is then grown thermally on top by wet oxidation in an anneal-oxide furnace. In the first step, the silicon wafers are cleaned in a Piranha solution (80% H₂SO₄ and 20% H₂O₂) for 15 min, followed by rinsing with deionized water (DI water) and drying with nitrogen to remove organic residuals and to hydroxylate the surface. Immediately after, 3-aminopropyl-trimethoxysilane (APTMS) and 3-aminopropylsilatrane (APS) are deposited by an immersion process to attach a monolayer of the organosilanes to the SiO₂ substrate. Functionalization with APTMS, requires a 3 h immersion of the cleaned wafer in a solution of 2.5 vol% APTMS, 2.5 vol% DI water and 95 vol% isopropanol (IPA). A 97% solution of APTMS, H₂N(CH₂)₃Si(OCH₃)₃, was purchased from Sigma-Aldrich/Merck. The bonding process of APS to the wafer in an aqueous solution takes 30 min.^{24,29} APS, purchased from Enamine, is dissolved to a 50mMol solution, which was further diluted to 1:300 in deionized water. The surface treatment is performed under a fumehood in a class 1000 cleanroom at temperature $22^\circ\text{C} \pm 2^\circ\text{C}$ and humidity $44\% \pm 2\%$. After surface modification, a DC sputtering system (LESKER) is used to deposit 10nm thick Au films on top of the organic layer. The Au thin film was sputtered from a high-purity (99.99%) Au target onto the sample surface with a deposition rate of 10 Å/s and under 3-4 mTorr process pressure.

In addition to deposition on wafers, gold films are deposited on TEM grids (TEMwindows.com) with 20 nm thick SiO₂-windows to allow electron transparent analysis of the Au thin films for TEM and TKD. The fabrication was carried out under the same conditions as the wafer pieces. An in-house built sample holder was used to fixate the 3 mm TEM grids inside the LESKER sputtering system chamber, in order to allow concurrent deposition on wafer pieces and TEM grids.

Contact angle measurements. The contact angles between water and the sample surfaces were measured by Krüss Drop Shape Analyzer DSA100 to determine the hydrophilic properties of the modified surfaces. 5 different droplets with 4-5 μ l volumes were analyzed, with 10 different measurements taken from each and the results were averaged in each case.

XPS. The XPS instrument is a ThermoScientific K-alpha X-ray photoelectron spectrometer by Thermo Fischer Scientific, equipped with an Al K α 1486.7 eV X-ray source and a 3 kV Ar ion gun. High resolution spectra were averaged over 20 scans, which were performed with a spot size of 400 μ m and an energy steps of 0.05 eV. The elemental composition analysis of the XPS data was carried out using the Thermo Advantage v5.9914 software from ThermoScientific.

AFM. AFM measurements were performed on a Dimension Icon-PT system by Bruker using a peak force modulation. 1 μ m² areas were scanned with a scan rate of 0.977 Hz and 512 measurements per line. The AFM probe of the cantilever has a nominal tip radius of 8nm, 70 kHz resonant frequency, and a 0.4 N/m spring constant.

SEM and TKD. Secondary electron images were recorded using a Zeiss Supra 40VP SEM operated at 15kV. The high resolution secondary electron images were acquired with an Inlens detector with a working distance of 4.5 – 5.0 mm at a pressure of 10⁻⁶mbar (HV-mode). Bright-field STEM images and TKD maps were acquired using a Thermo Fisher Nova 600 NanoSEM equipped with an Optimus TKD detector from Bruker. Orientation maps were processed using the Esprit 2.2 software from Bruker and the TSL OIM analysis program. The microscope was operated at 30 kV electron acceleration voltage, 1.7 nA beam current and 3nm beam step size. The working distance was 5.1mm and the aperture size 30 μ m.

STEM and EELS. High-angle annular dark-field (HAADF) STEM imaging and EEL spectroscopy were carried out on a Thermo Fisher Titan 80-300 (S)TEM instrument fitted with a field emission electron gun and a Gatan GIF Tridium spectrometer and operated at 300 kV. The

probe convergence semi-angle was 17 mrad and the probe size ~ 1.5 Å. The EELS spectrometer collection semi-angle was 18 mrad and energy resolution ~ 0.8 eV. Core-loss EEL spectra were analyzed after fitting a power law model to the background signal and removing its contribution. Thin lamellae for cross-sectional viewing and analysis with TEM were prepared by focused ion beam (FIB) milling using a dual beam Thermo Fisher Helios NanoLab 600 FIB-SEM system. Protective layers of C and Pt were deposited on sample surfaces prior to ion milling. The FIB was operated at 30 kV. Lamellae were cut out, lifted and attached to TEM Cu half-grids, on which the final thinning to electron transparency (50 – 100 nm) was performed.

3. Results

3.1 SiO₂ surface functionalization with organosilanes

The SiO₂ surface before any treatment, after treatment with piranha and after bonding with the organosilanes were examined for their hydrophilicity using contact angle measurements. The measurements were obtained with a CCD camera at room temperature and were averaged over 5 DI water droplets in each case. The results are presented in Table 2. The initial SiO₂ surface prior to treatment has a contact angle of 25°. After the cleaning and hydroxylation step with a Piranha solution (4:1, H₂SO₄:H₂O₂) for 15 min, the angle decreases, which represents a hydrophilic change, due to the high coverage of –OH groups onto the silicon dioxide surface. Upon the APS and APTMS grafting, the contact angles change to 48° and 56°. These values are in agreement with the literature values.^{19,21,32} The higher hydrophobicity of the surface after the silanization process indicates a successful grafting of APS and APTMS with their amino terminated end-groups on the silicon dioxide surface.

Table 2. Contact angle measurements during thin film fabrication

Substrate	Treatment	Contact angle of DI water θ°	
SiO ₂	Without treatment	$25^\circ \pm 2^\circ$	
SiO ₂ -OH	Piranha sol.	$9^\circ \pm 2^\circ$	
SiO ₂ -organosilane	Silanization process	APTMS	$56^\circ \pm 3^\circ$
		APS	$48^\circ \pm 2^\circ$

XPS was employed to analyze the chemistry of the functionalized sample surfaces, in order to further verify the presence of the organosilanes on SiO₂. XPS spectra containing the silicon, carbon and nitrogen signals are presented in Figure 1. The high-resolution spectra in Figure 1 show the Si 2p peak of the SiO₂ surface, the C 1s peak, from the carbon content of the organosilanes, as well as possible hydrocarbon contamination, and finally the N 1s peak, confirming overall the presence of the amino groups of APS and APTMS.

The Si 2p peaks in Figure 1(a) and (d) show contributions at 103 eV, 104 eV, both of which are attributed to Si⁴⁺. The higher binding energy of Si, compared to 99 eV for Si⁰ (bulk silicon), indicates oxidized Si in SiO₂ and in the siloxane bonds (Si-O-Si) of the organic adhesion layers.^{20,33} The C 1s peaks in Figure 1(b) and (e) are difficult to interpret, due to contribution from hydrocarbon contaminants (285 eV). Nevertheless, the C peak positions at 285.0 eV indicate C-C bonding and those at 286.2 eV at 286.5 eV C-N bonds.^{33,34} The N peaks in Figure 1(c) and (f) confirm the surface attachment of the organosilanes, with peak positions at 400.0 eV for APS and two peaks at 399.4 eV and 400.7 eV for APTMS. Amine groups at 400 eV are defined as non-protonated or “free NH₂”, while the additional peaks of at 400.7 eV (APTMS) and the minor signal at 402.8 eV (APS) indicate the presence of hydrolyzed amine groups, which correlate well with the literature values.^{21,33,35,36,37}

Figure 1: High-resolution XPS spectra of the APTMS (a-c) and APS (d-f) modified Si wafers. (a, d) show the Si 2p peak, spectra (b,e) the C 1s peak and (c, f) the N 1s peak.

3.2 The morphology and microstructure of the Au thin films

AFM was used to measure the surface roughness of the fabricated Au thin films. $1 \times 1 \mu\text{m}^2$ areas were scanned using an automated Peak Force Tapping mode, with a scan rate of 0.977Hz, 512 probes/line and a height range limit of $2.0 \mu\text{m}$. AFM maps of Au/SiO₂, Au/APTMS/SiO₂ and Au/APS/SiO₂ along with their corresponding root-mean-square (RMS) surface roughness values are displayed in Figure 2. The RMS values are averaged over five independent sample areas with a Z sensor noise level of $< 30 \text{ pm RMS}$. We measure RMS values of 0.4 nm for the Au/APTMS/SiO₂, 0.5 nm for the Au/APS/SiO₂ and 1.6 nm for the Au/SiO₂ sample. For comparison, the silicon substrate RMS value is 0.2 nm. These measurements are consistent with previous studies.^{9,28} The AFM analysis demonstrates that both adhesion layers improve the smoothness of the Au film.

Figure 2. AFM maps ($1\times1\mu\text{m}^2$) of the (a) Au/ SiO₂, (b) Au/APTMS/SiO₂ and (c) Au/APS/SiO₂ samples.

Plan-view secondary electron SEM images of the Au/SiO₂, Au/APTMS/SiO₂ and Au/APS/SiO₂ samples are shown in Figure 3. The Au layer without any adhesion layer is clearly not continuous, with cracks visible across the sample surface in Figure 3(a). In comparison, the Au films deposited with APS and APTMS adhesion layers appear continuous in Figure 3(b) and (c). Both samples with organic adhesion layers show very fine grain sizes distributed over the sample surface.

Figure 3: SEM images of (a) Au/SiO₂ (b) Au/APTMS/SiO₂ and (c) Au/APS/SiO₂ samples on Si wafers (1 μ m thick SiO₂ layer), and STEM images of (d) Au/SiO₂, (e) Au/APTMS/SiO₂ (f) Au/APS/SiO₂ on TEM membranes (20 nm thick SiO₂ layer). The length of the scale bar in all the images is 200 nm.

The microstructure of the Au thin films were examined using TKD and the obtained crystal orientation maps are presented in Figure 4. TKD's working principles are similar to those of electron back scatter diffraction (EBSD), but in TKD Kikuchi maps are acquired in transmission mode from electron transparent specimens, leading to its improved lateral spatial resolution (down to ~ 10 nm).^{38,39} As shown in the supporting information, the black regions in the Au film without adhesion layer arise from discontinuity in the Au layer since the diffraction signal from these regions only has signal from the amorphous SiO₂ substrate. In contrast, the black regions in Figure 4(b) and (c) do contain Kikuchi bands from the Au film (*i.e.* the film is continuous), but are not indexed due to the spatial resolution limitations of TKD.^{38,39}

Figure 4: TKD maps of (a) Au/SiO₂ (b) Au/APTMS/SiO₂ and (c) Au/APS/SiO₂ samples on electron transparent membranes (20 nm thick SiO₂ layer). (d – f) Histograms showing the size distribution of the {001}, {101} and {111} grains and the overall size distribution of the grains in each sample.

The grain size distribution for each of the samples are plotted in Figure 4 (d)-(f). The Au grains in the sample without an adhesion layer agglomerate without forming a complete metal layer, and are on average 45 ± 34 nm in diameter. The majority of the large grains in this samples have a {111} orientation, while the smaller ones have a {001} orientation. The APTMS/Au and APS/Au samples have much finer grain sizes, with average diameters of 16 ± 7 nm and 15 ± 7 nm, respectively. Moreover, the grains in these two samples have slightly more random orientations.

3.3 SiO₂ /Au interface

Figure 5 shows HAADF STEM images of the cross-sections of the three samples studied. The non-uniform intensity of the Au region in the sample without an adhesion layer in Figure 5(a) confirms the discontinuity of the Au film. No such contrast is seen in the Au region in the images of the Au/APTMS/SiO₂ and Au/APS/SiO₂ samples in Figures 5(b) and (c), confirming the

continuity and the smooth surface of the Au films in these samples. A closer examination of the SiO₂/Au interface is made in Figure 5(d)-(f). The intensity in HAADF STEM images is primarily related to the atomic number of the atomic species present in the sample⁴⁰, and the images can be used directly to (qualitatively) assess local variations in the chemical composition. The laterally summed intensity profiles in Figure 5(d)-(f) show ~ 1.0 nm thick interfacial region between SiO₂ and Au in the sample without an adhesion promoter and up to 2.0 nm thick interface region in the Au/APTMS/SiO₂ and Au/APS/SiO₂ samples. The difference between these two measurements is consistent with the length of a monolayer of the organosilane molecules (~ 0.8 nm).

Figure 5: HAADF STEM images of the cross-sections of (a) and (d) Au/SiO₂, (b) and (e) Au/APTMS/SiO₂ and (c) and (f) Au/APS/SiO₂ samples. The intensity profile of each image summed along the length of the structures is plotted in yellow in (d) – (f) and the width of the SiO₂ – Au interface in each sample is marked by the dashed lines.

EELS was used to probe the chemistry of the interface in the Au/APTMS/SiO₂ and Au/APS/SiO₂ samples. EEL spectra recorded from different positions along the interface in the samples are presented in Figure 6. On average, ~ 1.5 – 2.0 nm of interfacial region containing signals from Si, O and Au is detected (points (iii) – (v) in Figure 6). Signal from the N atoms of the APTMS and APS molecules could not be detected. This is most likely due to imperfect vertical alignment of these molecules when bonded to the SiO₂ substrate, resulting in the poor alignment of their N-terminated ends and thus, poor detection efficiency when viewed along the interface here. The

carbon C K-edge signal is not included in Figure 6, as an amorphous carbon signal could be detected everywhere on the sample (most likely due to redeposition from the C protection layer during the FIB milling). A decrease in the onset energy of the Si L_{2,3} edge in the interfacial region (positions (iii) – (v)) compared to the signal acquired from the SiO₂ substrate (position (i)) can be observed in Figure 6(c) and (f). As the energy of the first peak in the Si L_{2,3} edge is related to the oxidation number and the bonding state of the Si atoms^{41–43}, this change represents the Si atoms bonded to C in the APTMS and APS linker molecules, instead of those bonded to the more electronegative O in the substrate. No clear change in the O K-edge can be determined in Figure 6(d) and (g). It should be noted that the N_{2,3} edge of Au occurring at 545eV overlaps with the O K-edge⁴⁴ and is present in the spectra acquired at positions (iv) and (v).

Figure 6: HAADF STEM images of the (a) Au/APTMS/SiO₂ and (b) Au/APS/SiO₂ samples along with the EELS spectra recorded from points i – vi showing the Si L_{2,3} edge (c, f), O K-edge (d, g), Si K-edge and Au M_{4,5} edge (e, h) at these points in each sample.

4. Discussion

Our investigations of Au layers deposited on SiO₂ demonstrate that 10 nm thick continuous and smooth polycrystalline Au films can be grown after functionalization with APTMS and APS molecules. We measure comparable surface roughness values for the Au/APTMS/SiO₂ and Au/APS/SiO₂ samples and the films have very similar microstructures. In contrast, the Au/SiO₂

sample was not continuous and had a significantly rougher surface. Examination of the microstructure of the samples reveal that this difference in morphology is accompanied by clear difference in the lateral size of the grains of different orientations in the polycrystalline Au films. When grown directly on the SiO₂ surface, the Au layer is composed of grains with a wide size distribution: {111} grains with large lateral dimensions, and {001} grains of much smaller diameters. This has been explained in terms of the surface free energy and adatom diffusion rate on different crystal planes in gold^{9,45,46}. In the initial stages of the growth, the Au atoms arriving on the SiO₂ surface are expected to nucleate into small crystallites of varying orientations. Due to the higher surface free energy of the {100} planes in the fcc gold, atoms arriving there are less likely to migrate to the neighboring regions and therefore, {100} grains tend to grow vertically but not laterally. Conversely, {111} planes of the fcc gold possess the lowest surface free energy and thus, the higher diffusion rate of Au atoms arriving on these surfaces makes it likely for them to migrate to the neighboring regions and expand laterally. This anisotropy continues with growth, leading to considerable surface roughness in the gold layer.

In the case of Au films grown on surfaces functionalized with APTMS and APS, we find smooth and continuous polycrystalline gold layers with much smaller average grain sizes, narrower size distributions, and less preferential orientation of the grains. To determine the minimum gold layer thickness for achieving 2D morphology on APTMS and APS functionalized substrates, samples with Au layer thicknesses between 2 – 8 nm were examined (see supporting information). The results indicate a threshold thickness of approximately 6 – 7 nm. Moreover, the narrow size distribution and the relatively random orientation of the grains in the Au layer appear to persist as the gold layer thickness increases from 2 nm to 10 nm. A similar monodisperse grain size of gold films has been shown to occur when using Cr and Ti adhesion layers.⁹ However, the majority of the grains there were found to have {111} orientations. We interpret the finer grain size in the Au/APTMS/SiO₂ and Au/APS/SiO₂ samples relative to Au/SiO₂, in terms of increase in the number of nucleation sites, aided by the covalent bonds forming between Au and the N terminals of the organosilane molecules. After the nucleation, however, insufficient preference for different crystallographic orientations seem to exist, resulting in a broad range of the orientation of the grains. Chatterjee *et al.* studied nanoparticles nucleated on surfaces with different functional groups and observed a similar lack of selectivity in the orientation of Au particles on surfaces functionalized with amine groups.⁴⁷ It was argued that the higher interfacial energy in Au-

amine^{48,49} and the high temperature of single crystal Au formation on amine groups is the driving force for the observed weak orientation selectivity. A schematic representation of the growth evolution of the Au layers on SiO₂ with and without functionalization with APTMS or APS is shown in Figure 7.

Figure 7: Schematic representation of (a) the initial nucleation and (b) further growth of Au crystallites deposited directly on SiO₂ showing the anisotropic growth of grain with different orientations. In comparison, functionalization of SiO₂ with APTMS or APS leads to (c) increased number of nucleation sites at the initial stages and (d) more uniform growth of crystal grains of different orientations further on.

Probing the morphology and chemistry of the Au - SiO₂ interface in the APTMS/Au and APS/Au samples also reveals very similar properties. We observe a maximum 2.0 nm thick interface, accounting for the organosilane monolayer and some interfacial roughness, in these samples. No additional intermixing or alloying with the Au layer was observed, confirming the high chemical purity of the thin films. In the case of metallic adhesion layers, a few nanometer thick interface formed of partially oxidized metallic adhesion layer and an additional ~ 2 nm diffusion and alloying of the adhesion layer into the Au layer has been observed.⁹ These modifications will adversely influence the optical properties and conductivity of the Au thin films^{12,13,25,50,51}, especially when the thickness of the Au layer is comparable to that of the interfacial region. In contrast, negligible influence from APTMS on the surface plasmon polaritons supported on Au

films down to 6 nm in thickness has been reported²⁵ and similar resistivity values to those calculated or measured for continuous pure Au films have been found for Au films on APTMS surfaces^{28,52}. Given the close to identical structural characteristics measured here, we expect the same performance from Au films grown on APTMS and APS, in terms of their optical and electrical properties. An advantage of APS over APTMS, however, is its ease of use. APTMS is a more harmful chemical than APS and requires environmental considerations, due to its corrosive character. Moreover, APTMS is prone to polymerization and agglomeration in the presence of water^{26,28,29} and thus, its preparation typically makes use of solvents such as toluene^{21,32,53,54} or IPA^{25,28}, and requires reduced humidity environments. Indeed variation in APTMS layer thickness at different ambient humidity levels has been observed²⁶. This adversely affects the quality and reproducibility of the Au layers and ideally, vapor-phase deposition instead of solution-based methods are preferred for preparing monolayers of APTMS.^{17,26} Blue tape was employed here to isolate the organic working solution, in order to avoid possible side reactions at the solution/air interface during the bonding process. In comparison, APS has a more stable molecular structure due to its transannular N – Si bonding and is extremely resistant to hydrolysis and polymerization at neutral pH^{24,29}. Subsequently, an aqueous solution of APS was used in this study and it did not require any environmental considerations. Finally, the immersion time for grafting APTMS on SiO₂ substrates was 3h, while 30min immersion time for APS was found to be sufficient for obtaining similar results. Our preparation protocol for APTMS is identical to that listed by Leandro *et al.*²⁸, in which they observed insufficient adhesion and incomplete growth of Au films on SiO₂ substrates for immersion times shorter than 3h. The 30 min immersion time chosen here for APS was guided by previous studies on functionalization of SiO₂^{24,29}, and our results confirm it to be sufficient for promoting adhesion and achieving ultrathin and smooth Au films.

5. Conclusions

We have presented a solution-based protocol to achieve ultrathin, smooth and high-purity Au films on silicon dioxide with the use of APS. The process is simple, faster and significantly less harmful compared to the more commonly used alternative organosilane, APTMS. Our examination of 10 nm thick Au films deposited on substrates functionalized with APTMS and APS show that both molecules facilitate the growth of continuous, smooth and high-purity gold layers. The Au thickness threshold for achieving 2D films using these organosilanes as adhesion layers was found

1
2
3 to be in the range of 6-7 nm. These polycrystalline Au films were found to have very fine
4 microstructures with monodispersed grain sizes and relatively random crystallographic
5 orientations. Little difference was found between the surface roughness and microstructure of Au
6 films deposited on surfaces with APTMS and APS functional groups. This is in contrast to Au
7 films grown directly on SiO₂ substrates, which were found to be rough and discontinuous, had
8 much larger average grain size and were composed mainly of laterally large {111} grains and
9 small {001} grains. In terms of the chemical composition, no evidence of detrimental inter-
10 diffusion or alloying between the organic adhesion promoters and the gold film was observed. This
11 supports the high electrical conductivity and close to ideal optical properties of Au films with
12 APTMS adhesion layer demonstrated in other studies^{25,28,52}, and we expect a similar performance
13 from APS. Overall, the easier, faster and more sustainable synthesis process of APS over APTMS
14 make it an attractive choice for obtaining high quality ultrathin and smooth gold thin films.
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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge.

TKD scans of unidexed regions in Au/SiO₂, Au/APTMS/SiO₂ and Au/APS/SiO₂ samples; SEM images of 2, 5 and 8 nm thick Au films and the estimated substrate coverage for each thickness;

and TKD microstructure maps of 2, 5 and 8 nm thick Au films along with the size distribution of grains with different crystallographic orientations at each film thickness.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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