Characterization of Self-Assembled Monolayers on a Ruthenium Surface

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ABSTRACT: We have modified and stabilized the ruthenium surface by depositing a self-assembled monolayer (SAM) of 1-hexadecanethiol on a polycrystalline ruthenium thin film. The growth mechanism, dynamics, and stability of these monolayers were studied. SAMs, deposited under ambient conditions, on piranha-cleaned and piranha + H2SO4 cleaned substrates were compared to monolayers formed on H-radical-cleaned Ru surfaces. We found that alkanethiols on H-radical-cleaned Ru formed densely packed monolayers that remained stable when kept in a nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) shows a distinct sulfur peak (BE = 162.3 eV), corresponding to metal–sulfur bonding. When exposed to ambient conditions, the SAM decayed over a period of hours.

INTRODUCTION

Chemisorbed organic monolayers, formed by self-assembly, provide a convenient and flexible method to tailor the physical and chemical properties of the surfaces of metals, metal oxides, and semiconductors.1,2 Self-assembled monolayers (SAMs) have attracted considerable attention in the past decade due to their potential applications as photoresists in lithography,3,4 protective layers to prevent oxidation,5 to aid or prevent wetting,6–8 to enhance adhesion,9–11 to speed electron transfer,12,13 and to prevent X-ray-induced damage.14,15 Better surface passivation using SAMs is of interest to protect ultrathin membranes from chemical degradation.16,17 SAMs are also used as active and passive molecular lubricants to increase the lifetime and efficiency of microelectromechanical systems devices.18,19

The adsorption of self-assembled monolayers of alkanethiols on gold, silver,20,21 and copper5,22,23 has been extensively studied. The high affinity of thiols on the surfaces of noble and coinage metals allows the growth of well-defined organic surfaces with practical and highly alterable chemical functionalities at the interface. Recently, the structure and stability of self-assembled organic monolayers on the platinum group family, notably on Pt4,24 and Pd,25 have been investigated. It has been observed that SAMs on oxidizing metals (e.g., Pt and Pd) exhibit a strongly bound metal–sulfur interface, making them well suited for the fabrication of semiconductor-based microelectronics and nanoelectronics. Compared to gold, SAMs of alkanethiolates on palladium and platinum are more compatible with standard silicon fabrication processing techniques (e.g., CMOS). It is easier to achieve lower surface roughness with Pt and Pd, while their small grain size results in better etch characteristics and lower defect densities in etched structures.26

Ruthenium is an effective hardener for platinum and palladium and is alloyed with these metals to make electrical contacts for severe wear resistance.26 Ruthenium is used in the electronics industry for chip resistors, and as a catalyst for ammonia, and acetic acid production. Ruthenium compounds can be used in solar cells to convert light energy into electrical energy.27 Ru thin films are used as the bottom electrode in VLSI capacitors based on high dielectric materials, and as a capping layer for optics compatible with extreme ultraviolet lithography (EUVL).28 SAMs on ruthenium, like those on Pt and Pd, have potential advantages over gold and silver; they have less roughness and smaller grain size, compared to Au and Ag, so etched structures have fewer defects and better stability against wet chemical etchants. Furthermore, Ru, Pd, and Pt are CMOS compatible. However, SAMs on oxidizing metals have some challenges associated with the deposition of SAMs on oxygen-free surfaces. For the efficient deposition of high density and stable SAMs, cleaning strategies, handling of samples in an inert environment, and the use of deoxygenating solvents are the critical parameters.20,21

In this article, we characterize SAMs on ruthenium, which to the best of our knowledge have never been reported. We study the preparation and characterization of self-assembled monolayers, formed by the chemisorption of n-alkanethiols (1-hexadecanethiol, CH3(CH2)15SH) on thin polycrystalline films of ruthenium. The formation, chemical stability, and elastic modulus of alkanethiol-based SAMs on Ru are investigated and compared with similar SAMs on Au. We also compare SAMs grown on Ru surfaces that have been cleaned by piranha,
sulfuric acid and piranha, and by exposure to atomic hydrogen. An important factor in the chemical stability of thiol-based SAMs is the bonding strength of the metal–sulfur interface; therefore, we focus on the evolution of the sulfur peaks (S 2p) of the X-ray photoelectron spectroscopy (XPS) over time.

### EXPERIMENTAL SECTION

**Materials.** 1-Hexadecanethiol (CH₃(CH₂)₁₅SH) was obtained from Sigma-Aldrich and used without further purification. Ethanolic (99.99%) was obtained from Pharmco (Brookfield, CT). Polycrystalline ruthenium (Ru) thin films with thicknesses of 12 and 47 nm were deposited on Si(100) wafers by physical vapor deposition (PVD) using dc magnetron sputtering. The silicon wafers' native oxide (SiO₂), which promotes the adhesion of the Ru substrate, has a thickness of 0.7 nm. The RMS surface roughness of the Ru thin films was measured to be 0.23 and 0.28 nm for the 12 and 47 nm thick films, respectively.

**Ruthenium Surface Cleaning and SAM Deposition.** Ruthenium is very sensitive to oxidation; the outermost surface chemisorbs oxygen rather strongly due to high Ru=O bond dissociation energy (528 kJ/mol).31 Once the oxide is removed, exposure to ambient environment was performed using primary He⁺ ions (energy: 3 keV). The ions are determined from the average of these measurements. To seven measurements were performed and the contact angle was measured to be 1 h and 7 days.

**Ethanol and water, followed by drying in a stream of dry nitrogen.** To submerge in 8.2 mM solution of thiol in ethanol for 96 h at room temperature. To remove other surface contaminants, but neither is expected to remove surface oxide. For this purpose, we treated the ruthenium surface with atomic hydrogen. Atomic H from an MPS-ECR plasma source (Specs GmbH, Berlin, Germany) was used to clean the Ru surface. The samples were exposed to H radicals from a remote plasma (flux of 1 × 10¹⁵ cm⁻² s⁻¹) for 10 min and immersed into ethanolic solution (protected N₂ environment) immediately after taking the samples out of the chamber to slow oxidation. Oxidation was also slowed by flushing the head space of the flask with nitrogen.

For comparison purposes, ruthenium samples were also cleaned by immersing in piranha solution, consisting of 70% H₂SO₄ and 30% H₂O₂. After immersion, the substrate was immediately and thoroughly rinsed with high-resistivity Milli-Q water to remove any debris from cleaning, followed by immersion in ethanol. A second, more aggressive solution-based treatment was also tried. The Ru samples were cleaned in piranha solution for 10 min and then immersed in H₂SO₄ for 10 min, followed by rinsing in high Milli-Q water and, afterward, immersed in ethanol. Both treatments remove atmospheric carbon and other surface contaminants, but neither is expected to remove surface oxide.

To deposit monolayers, the cleaned ruthenium substrates were submerged in 8.2 mM solution of thiol in ethanol for 96 h at room temperature. After deposition, each sample was rinsed thoroughly with ethanol and water, followed by drying in a stream of dry nitrogen. To measure the stability of the deposited monolayers, the samples were exposed to ambient laboratory conditions for a period varying between 1 h and 7 days.

**SAM Characterization.**

**Contact Angle Measurements.** The static and dynamic contact angles were determined at room temperature, using a sessile drop contact angle goniometer (Krüss G10) at a relative humidity of 60%. Ultrapure Milli-Q water, with the resistivity of 18 MΩ cm, was dropped onto the sample surface from a syringe needle, and the droplet image was recorded immediately. For each sample, five to seven measurements were performed and the contact angle was determined from the average of these measurements.

**Low-Energy Ion Scattering (LEIS).** LEIS (Qac100, ION-TOF) was performed using primary He⁺ ions (energy: 3 keV). The ions are raster scanned over a 1 × 1 mm² analysis area at normal incidence while scattered ions are collected at a scattering angle of 145° and integrated over the full azimuth with an electrostatic analyzer. Typical ion doses for analysis are in the order of 2 × 10¹⁰ ions/cm², which is at or below the quasi-static limit. This means that surface sites with possible sputter damage from the analysis do not contribute significantly to the measured ion signal.

**X-ray Photoelectron Spectroscopy.** Angle-resolved XPS (Thermo Scientific Theta Probes) data were analyzed employing Semicell sensitivity factors32 and inelastic electron mean free path values calculated according to the method of Cumpson and Seah.33 High-resolution spectra of the C(1s) (overlaps with Ru(3d)), S(2p), O(1s), and Ru(3d) core levels were collected at a pass energy of 50 eV. The curve fitting of the S(2p) core levels was performed using Gaussian–Lorentzian (70%:30%) line shapes while the spin–orbit doublet separation was kept constant at 1.2 eV with a fixed area ratio of 2:1. Curve fitting was carried out by starting at the low binding energy side of the S(2p) envelope and systematically adding component core levels toward higher binding energies as required.

**Atomic Force Microscopy (AFM).** We used an AFM (Bruker Dimension Edge) to quantify the surface roughness. All images were taken in tapping mode in air and at room temperature. A Si cantilever with a spring constant of 40 N/m was used to acquire images. Image processing was performed using the WSXM software package.34 The AFM was also used to perform nanointerference tests to measure the elastic modulus of the ultrathin organic monolayers. For this, a force modulation cantilever (HQ2NSC36/CR−Au BS, NanoAndMore) that had a tip radius of <8 nm, and stiffness of 2.5 N/m was used. Force−deformation (F−d) data were obtained from the raw force−displacement (F−d) curves by subtracting the cantilever deflection and using the Derjaguin−Muller−Toporov (DMT) model for the elastic modulus. All measurements were acquired in an ambient atmosphere at a temperature of 23 °C and a relative humidity of approximately 19%.

### RESULTS AND DISCUSSION

**Wettability of the Ru Surface.** Ruthenium chemisorbs oxygen quickly; therefore, it is mandatory to remove the surface oxide and other contaminants from the Ru substrate before SAM deposition. The contact angle measurements are summarized in Table 1. The data show that SAMs deposited on piranha-treated samples have achieved insufficient contact angles which indicates that the cleaning methods commonly used for gold form a low-density hydrophilic monolayer on Ru substrates. However, SAMs grown on atomic H treated Ru form a hydrophobic self-assembled monolayer, indicating that the SAM layer is relatively dense.

| Table 1. Wetting Properties of Milli-Q Water on SAMs of 1-Hexadecanethiol (CH₃(CH₂)₁₅SH) Deposited on a Ruthenium Surface |
|------------------|------------------|
| system           | cleaning method  | contact angle (deg) |
| (C₁₆-SAM)-Ru (12 nm) Atomic-H | piranha         | 33.59 ± 0.67         |
| (C₁₆-SAM)-Ru (12 nm) Atomic-H | piranha         | 62.60 ± 0.69         |
| (C₁₆-SAM)-Ru (5 nm) Atomic-H | piranha + H₂SO₄ | 65.68 ± 0.15         |
| (C₁₆-SAM)-Ru (12 nm) Atomic-H | static          | 103.77 ± 0.05        |
| (C₁₆-SAM)-Ru (47 nm) Atomic-H | dynamic         | 104.4 = 92.5 = 11.9  |
|                  | static           | 101.72 ± 0.17        |
|                  | dynamic          | 100.1 ± 30 = 10.1    |

The wetting properties of the SAMs of 1-hexadecanethiol on atomic H cleaned ruthenium are similar to analogous SAMs on gold, silver, copper,20,21 and palladium.26 Li et al. measured the contact angle of hydrophobic methyl-terminated SAMs of C₁₆SH and C₁₈SH on Pt as 91° and 104°, respectively,24 which is comparable to the results reported here. The results of the contact angle on nonoxidized Ru are consistent with those reported for alkanethiolate SAMs deposited on gold surfaces. The high contact angle indicates that the SAMs are densely packed and have more crystalline-like ordering, probably due to increased intermolecular van der Waals interactions.

The static contact angle for C₁₆SH on Ru is similar to that observed for C₁₈SH on platinum.28 In general, the contact angle of C₁₆SH on Ru is 11° lower than that observed for gold.
and silver and 16° lower than copper and palladium for C18SH. These differences are most likely due to residual oxidation on the Ru surface (see below). The dynamic contact angle hysteresis for C16SH SAM on Ru (θ_{advancing} = θ_{receding} = 11.9°) is larger than that for C18SH SAMs on gold but lower than on silver, copper, and palladium. The dynamic contact angle is related to chemical heterogeneities, roughness, and conformational disorders. AFM imaging (see below) suggests that the surface roughness is rather low, which may account for the low contact angle hysteresis compared to Pt and Pd.

**LEIS Studies.** Figure 1 shows the LEIS spectrum for a SAM (1-hexadecanethiol)-covered ruthenium surface and a clean ruthenium surface. The spectrum for a clean Ru surface after H-radical treatment shows an oxygen peak at (1200 eV), indicating that the surface is partially oxidized. The atomic hydrogen treatment removes the native oxide of the Ru surface, but it does not protect the Ru against reoxidation. Since the outermost surface of Ru chemisorbs oxygen rather strongly, the surface is rapidly covered with oxygen after hydrogen treatment.

Only atoms in the outermost surface layer give rise to LEIS surface peaks. Because of effective shielding of the carbon chain of the thiol by hydrogen atoms, no surface C signal was observed in the LEIS spectra. Furthermore, the SAM-coated Ru shows neither a Ru peak nor an oxide peak; however, it is not possible to conclude that the SAM forms a closed layer from the LEIS spectrum alone. Unlike the surface oxide in the clean Ru example, the SAM is expected to have a thickness on the order of 2 nm. From purely geometrical considerations, LEIS can only detect holes larger than 1.4 nm. However, from the AR-XPS (see below), we estimate that the surface density is 3.8 × 10^{14} cm^{-2}, giving an average separation between molecules that is on the order of ~0.3 nm. Thus, the high contact angle, the suppressed Ru LEIS peak, and the AR-XPS data all suggest that the layer is closed.

**SAM Layer Thickness.** The SAM on Ru thickness was determined to be 2.2 ± 0.2 nm using AR-XPS, indicating that the 1-hexadecanethiol is not tilted with respect to the surface. To determine the thickness, the alkane chain was modeled as a CH₂ layer with the bulk density of dodecane (0.75 g cm^{-3}), yielding an attenuation length of 3.8 nm for Ru 3d photoelectrons. This attenuation length is in perfect agreement

![Figure 1](image1.png)

**Figure 1.** LEIS spectra He⁺ ions scattered by SAM (1-hexadecanethiol)-capped and clean ruthenium surfaces. The scattering angle is 145°.

![Figure 2](image2.png)

**Figure 2.** AFM images with scanning size of (1 μm × 1 μm) of thin Ru film. (a) Atomic-H cleaned Ru substrate, (b) H-plasma cleaned Ru substrate kept in ethanol, (c) Ru substrate covered with SAM of 1-hexadecanethiol, and (d) the height profile.
with the value of 4.2 nm reported by Mendoza et al. for alkanethiols on Au, \(^{35}\) when that attenuation length is scaled by the \((KE(Ru)/KE(Au))^{0.6}\), with \(KE(x)\) the kinetic energy of Ru 3d and Au 4f photoelectrons from the respective substrates.

**SAM Topography.** Figure 2 shows AFM images with scanning size of \((1 \mu\text{m} \times 1 \mu\text{m})\). The RMS roughness of the Ru surface (atomic-H cleaned) was measured to be \(0.23 \pm 0.05\) nm, which is the same as that of the as-deposited Ru layer. Apart from contamination, the AFM images show no evidence of aggregates, and, importantly, no holes are observed at the resolution limit of the AFM (\(\sim 10\) nm), which is in agreement with the contact angle and LEIS results. The RMS roughness of the SAM capped surface in Figure 2c is measured to be \(0.84 \pm 0.05\) nm, which includes the effects of the contaminants. However, for the highlighted rectangular subarea, the surface appears to be densely packed with a measured RMS roughness of \(0.33 \pm 0.05\) nm, as shown in Figure 2c.

**XPS Characterization.** High-resolution S 2p spectra for alkylthiolates on gold and copper clearly exhibit a single doublet with binding energy (BE) of \(\approx 162.0\) eV.\(^{22,23,36}\) In comparison with gold, the high-resolution S 2p core level spectra for SAMs on Ru in Figure 3a have two distinct components. The two components are labeled as S1 and S2 with increasing binding energies. The S1 is the dominant component of S 2p spectra with the BE between 162.3 and 162.4 eV. On the basis of the BE, we assign the S1 component as alkylthiolates bound to the Ru substrate (metal–sulfur bond). This assignment is in good agreement with the reported S 2p values for alkylthiolates on Au,\(^{27}\) Ag,\(^{27}\) Cu,\(^{22}\) Pt,\(^{19,24}\) and Pd.\(^{26}\)

The S2 peak (S2P\(_{3/2,3/2}\)O) is associated with sulfur bound to oxygen (sulfites and sulfates) and has the BE of 166 eV. The S2 component with BE of about 166 eV and the higher BE components are generally the outcome of the increasingly higher oxidation states of sulfur. The S 2p doublets at 166 eV correspond to sulfite S\(^{4+}\) and those about 169 eV as sulfates. Similar results have been found for SAMs on Pt and oxidized Pt surfaces,\(^{25}\) and eventually, it was concluded that the oxidation of thiol groups is mediated by the metallic surface oxide.\(^{24}\)

Given the similarities between Ru and Pt, it is likely that a similar process occurs for Ru. Finally, the nature of the S2 component at 166 eV is not completely understood, and due to low intensity and the complex line shape, significant uncertainty is associated with the assignment of this S 2p\(_{3/2}\) core level component.

The S 2p spectra shown in Figure 3 can all be fit with two doublets, each with a ratio of 2:1 and a separation of 1 eV. As described above, these peaks correspond to metal-bound thiols and oxidized sulfur. The absence of a doublet at a binding energy \(\sim 1\) eV higher than for metal-bound thiolate indicates that no physisorbed thiol is present. Our findings are comparable to those obtained from SAMs deposited on template-stripped Pt films.\(^{24}\)

**SAMs Stability in Air.** The XPS spectra in Figure 3 show the changes to the oxidation state of the SAM of 1-hexadecanethiol on Ru surface and are summarized in Table 2. The layer passivation is examined for samples that were stored in dry nitrogen (N\(_2\)) for a period of 45 days and for samples exposed to air for varying amounts of time. After 45 days in dry nitrogen, there is no change in the binding energy of the S2 component (166 eV) of the S 2p spectra. Over 45 days, the total sulfur on the surface contribution drops from 5.4 to 4.3 at. %, which is within the measurement uncertainty, and indicates that the SAM is not desorbing from the substrate.

The total O 1s intensity increases both with time, and exposure to air, indicating that the amount of oxygen in the
sample increases from 4 to 9 at.% over 45 days. Since the O 1s signal can be both related to oxidation of the thiol and the Ru, it is difficult to perform a stoichiometric composition analysis. Peak fitting suggests that the ruthenium oxide concentration increases from 3.4 to 6.7 at.% which is a change that is about the same as the fit uncertainty. Similarly for alkanethiol SAMs on copper, the O 1s XPS scan of the 530−536 eV region reveals that the oxygen content is below the detection limits.22 However, the lack of carbonate and carboxyl contributions to the C 1s spectra suggest that the majority of oxidation is due to ruthenium oxide formation. The C 1s spectra in all cases is dominated by the main carbon peak (C1) with BE between 284.5 and 284.94 eV, corresponding to the hydrocarbon chains. It is difficult to determine the C 1s peak because of overlap with Ru 3d3/2; however, the noticeable trend is that the C 1s peak intensity decreases slightly, from 41 to 38 at. % over 45 days. These data indicate that the SAM is slowly changing from a SAM bound to a metal surface to one bound to an oxide surface.

Exposure to air rapidly increases the oxygen contribution to 19 at. %, the majority of which is due to the formation of ruthenium oxide. Notably, the carbon contribution is reduced to 24 at. %, indicating that about half of the SAM has desorbed. However, the total amount of sulfur on the surface remains unchanged at 4.7%. This indicates that the alkanethiol may dissociatively desorb from the surface, leaving the sulfur headgroup bound to the surface. In contrast, alkanethiols, deposited on Cu are reported to be stable in air, most likely because the Cu−S and Cu−O bonds have similar binding energies.22,31

**Mechanical Strength.** AFM nanoindentation experiments were performed with a force−modulation cantilever to measure the elastic properties. The cantilever spring constant was found to be 2.5 N m−1 via thermal tuning. Force−deformation (F−δ) data were obtained from the force−displacement (F−d) data by subtracting the cantilever deflection, as shown in Figure 5. Considering the profile of the sphere as Hertzian, with a contact radius \( a = \delta R^{1/2} \), it can be shown that the pull-off force is given by

\[
F_{\text{pull-off}} = \frac{4}{3} E^{*} \left( \frac{E^{*}}{R} \right)^{1/2} \delta^{3/2}
\]

Table 2. XPS Stability Analysis of SAMs of 1-Hexadecanethiol (CH₃(CH₂)₁₅SH) on Ruthenium (12 nm) Surface

|                  | after deposition | 21 days | 45 days | air exposure |
|------------------|------------------|---------|---------|-------------|
| C 1s at. %       | 40.7             | 37.1    | 37.3    | 23.3        |
| O 1s at. %       | 4.2              | 6.1     | 8.6     | 18.7        |
| RuOₓ at. %       | 3.4              | 7.9     | 6.7     | 17.1        |
| S and sulfur oxide at. % | 5.4            | 5.3     | 43      | 4.7         |
| layer thickness (nm) | 1.94            | 2.11    | 2.05    | 1.41        |
| SAM surface density \( \times 10^{14} \) (cm⁻²) | 3.79            | 4.13    | 4.01    | 2.76        |

"The samples are stored in dry nitrogen environment; an air-exposed sample is added as comparison."
Figure 5. AFM nanoindentation $F$–$\delta$ curves (loading curves). (a) SAM of 1-hexadecanethiol (CH$_3$(CH$_2$)$_{15}$SH) on gold and (b) SAM of 1-hexadecanethiol (CH$_3$(CH$_2$)$_{15}$SH) on ruthenium. The red dots represent the experimental data while the solid black lines represent the theoretical fits.

$$F = \frac{4}{3} E^* R^{1/2} \delta^{3/2} - 2 \pi R \delta$$

(1)

where $R$ is the tip radius ($R \leq 8$ nm), $\delta$ is the work of adhesion, and $E^*$ is the reduced modulus. In our case, the dominant forces are the capillary forces rather than adhesive forces, and we choose to study only the indentation, not the relaxation when the tip is retracted; therefore, we can neglect the pull-off force ($2 \pi R \delta$).

For a film–substrate combined system, $E^*$ is a function of the Young’s moduli and Poisson’s ratios of the film ($E_{\text{film}}$, $\nu_{\text{film}}$) and substrate ($E_{\text{sub}}$, $\nu_{\text{sub}}$). Based on a first-order elastic perturbation method, the analytical solution for $E^*$ of a film–substrate system was developed by Xu and Pharr$^{38}$ and given as

$$\frac{1}{E^*} = \frac{1}{2} \left[ 1 - \nu_{\text{sub}} + (\nu_{\text{sub}} - \nu_{\text{film}}) I_0 \right]$$

(2)

$$= \frac{2(1 + \nu_{\text{sub}})}{E_{\text{sub}}} \left( 1 - I_0 \right) + \frac{2(1 + \nu_{\text{film}})}{E_{\text{film}}} I_0$$

(3)

where $I_0$ and $I_1$ are weighting functions of the normalized film thickness $\zeta = t/a$ and account for the shear modulus mismatch and Poisson’s ratio effects. $^38$ Here $t$ is the film thickness and $a$ is the contact radius. The weighting functions are defined as

$$I_0(\zeta) = \frac{2}{\pi} \tan^{-1}(\zeta) + \frac{1}{2\pi(1 - \nu_{\text{sub}})} \left[ (1 - 2\nu_{\text{sub}}) \zeta \ln \left( 1 + \frac{\zeta^2}{\zeta^2} - \zeta \right) \right]$$

(4)

$$I_1(\zeta) = \frac{2}{\pi} \tan^{-1}(\zeta) + \frac{\zeta}{\pi} \ln \left( 1 + \frac{\zeta^2}{\zeta^2} \right)$$

(5)

For the Au substrate, the values of $E_{\text{sub}} = 77$ GPa and $\nu_{\text{sub}} = 0.42$ are used, while $E_{\text{film}} = 447$ GPa and $\nu_{\text{film}} = 0.3$.

The sample deformation $\delta_{\text{SAM}}$ can be obtained by subtracting the cantilever deflection from the displacement of the sample stage and given as$^{41}$

$$\delta_{\text{SAM}} = \delta_{\text{piezo}} - \delta_{\text{cantilever}}$$

(6)

where $\delta_{\text{piezo}}$ is the vertical displacement and $\delta_{\text{cantilever}}$ is the deflection of the cantilever. Initially, the indentation tests were performed on a relatively rigid Au film, deposited on a glass substrate, and a Ru film, deposited on a Si wafer. This step is used to calibrate the deflection sensitivity of the cantilever for further analysis. Equation 6 is used to calculate $F$–$\delta$ curves from the $F$–$\delta$ curves. Equation 1 is fit using least-squares to the $F$–$\delta$ data with $E^*$ taken as a free parameter. The uncertainties are obtained from the covariance matrix of the fit. Equation 3 yields the elastic modulus of the SAM, $E_{\text{film}}$, and the outcomes are tabulated in Table 3. Each value of the elastic modulus is an average of six measurements, and the uncertainty is the 95% confidence interval. Our data show that SAMs grown on Ru are substantially stiffer than SAMs grown on Au due to less roughness and higher packing density of Ru.

### Table 3. Experimental Results of Reduced Modulus and Film Modulus for Alkanethiol SAMs on Gold and Ruthenium Substrates

| organic assembly | reduced modulus, $E^*$ (GPa) | film modulus, $E_{\text{film}}$ (GPa) |
|-----------------|-----------------------------|---------------------------------|
| C12-SAM/Au      | 2.63 ± 0.18                 | 2.13 ± 0.19                     |
| C16-SAM/Au      | 5.60 ± 0.50                 | 4.50 ± 0.60                     |
| C16-SAM/Ru      | 10.18 ± 0.14                | 8.23 ± 0.15                     |

### CONCLUSIONS

We have characterized the first, to our knowledge, SAM grown on ruthenium substrate. We have investigated the effectiveness of three cleaning strategies on the formation of SAMs on Ru and studied the growth mechanism, stability, and mechanical properties of these ultrathin organic layers. We found that SAMs grown on H-radical-cleaned ruthenium substrates in an oxygen-poor environment from 8.2 mM ethanolic solution of 1-hexadecanethiol (CH$_3$(CH$_2$)$_{15}$SH) yield stable and densely packed monolayers. These monolayers were found to be chemically stable for a period of one month if kept in the protective environment of dry nitrogen; however, exposure to air leads to the monolayer decaying over a period of 4–7 days. We do not find any evidence of weakly bounded alkyl chains.

XPS analysis shows that the decay of the SAM is due to oxidation of the ruthenium substrate and, consequently, desorption of the thiol from the oxidized substrate. We do not find evidence of thiols binding oxidized sites. The elastic modulus of SAMs/Ru is determined to be about 8.23 GPa, which is nearly a factor of 2 greater than similar SAMs on Au.

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