Alkanephosphonates on Hafnium-Modified Gold: A New Class of Self-Assembled Organic Monolayers

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Abstract: A new method for assembling organic monolayers on gold is reported that employs hafnium ions as linkers between a phosphonate headgroup and the gold surface. Monolayers of octadecylphosphonic acid (ODPA) formed on gold substrates that had been pretreated with hafnium oxychloride are representative of this new class of organic thin films. The monolayers are dense enough to completely block assembly of alkanethiols and resist displacement by alkanethiols. The composition and structure of the monolayers were investigated by contact angle goniometry, XPS, PM-IRRAS, and TOF-SIMS. From these studies, it was determined that this assembly strategy leads to the formation of ODPA monolayers similar in quality to those typically formed on metal oxide substrates. The assembly method allows for the ready generation of patterned surfaces that can be easily prepared by first patterning hafnium on the gold surface followed by alkanephosphonate assembly. Using the bifunctional (thiol–phosphonate) 2-mercaptoethylphosphonic acid (2-MEPA), we show that this new assembly chemistry is compatible with gold–thiol chemistry and use TOF-SIMS to show that the molecule attaches through the phosphonate functionality in the patterned region and through the thiol in the bare gold regions. These results demonstrate the possibility of functionalizing metal substrates with monolayers typically formed on metal oxide surfaces and show that hafnium–gold chemistry is complementary and orthogonal to well-established gold–thiol assembly strategies.

Introduction

Control over the surface and interfacial properties of materials is essential to their integration into a wide range of applications, and a variety of surface functionalities are required to meet the needs of current and future materials modification.[1–6] Self-assembled monolayers (SAMs) are particularly attractive candidates for materials modification because they produce well-defined surfaces that can incorporate a wide range of functionalities without significantly modifying the bulk properties of the underlying material. While thiol monolayers have been extensively studied for the surface modification of coinage metals,[1,2,7] it is desirable to discover and develop new surface chemistries that offer enhanced or orthogonal functions to those of the thiols.

Alkylphosphonate monolayers have been widely investigated for use in the functionalization of metal oxides,[8–10] as well as

hafnium-modified silicon dioxide.[11,12] For example, silicon dioxide modified with hafnium(IV) has been used to create patterned, two-dimensional gold nanoparticle arrays.[13] However, the modification of gold substrates with an alkylphosphonate using a hafnium linker has not been previously described. Here we report how hafnium oxychloride or hafnium(IV) chloride can be used to modify gold surfaces and how the resulting film can be employed as a substrate for alkanephosphonate monolayer assembly.

Development of a class of molecular films based upon phosphonate monolayers on gold offers a number of potential benefits that complement the attributes of alkanethiol monolayers on gold. Alkylphosphonate adsorbates assembled on hafnium-modified gold may exhibit enhanced stability. The gold/hafnium/alkylphosphonate chemistry can be used to modify metal and metal oxide surfaces concurrently, such as gold electrodes patterned on a silicon substrate. This makes it ideal for use in the homogeneous functionalization of electrode arrays

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for numerous electronics applications. The phosphonate chemistry may offer the possibility of patterning gold surfaces with stable domains. Previous work by Imbayashi et al. has shown that when two different thiols are phase separated on a gold substrate, they interdiffuse over time and blur the boundaries between the two functionalities.[14] As long as diffusion does not occur between thiol and alkylphosphonate/hafnium domains, the hafnium/phosphonate chemistry should allow the creation of well-defined boundaries between two different surface functionalities. For example, it could be used as a barrier to prevent diffusion between adjacent patterned thiol regions on a surface or to pattern a region on a gold surface before subsequent modification with a thiol adsorbate. Finally, it may be possible to use this assembly chemistry to create monolayers with thiol reactive terminal functionality, such as maleimide groups, which are used for biochip applications.[15,16]

We initially investigated the use of hafnium/alkanephosphonate chemistry to generate a hydrophobic surface between the fingers of interdigitated gold electrode arrays on a silicon dioxide substrate.[11,12] It was thought that this could be accomplished by first selectively modifying the silicon dioxide portion of the substrate with hafnium/*n*-octadecylphosphonic acid (ODPA), followed by modification of the gold with an alkanethiol. After treating the substrate with only hafnium/ODPA, the entire surface, including the patterned gold region, exhibited uniform hydrophobicity. Subsequent X-ray photoelectron spectroscopic analysis showed the presence of hafnium and phosphorus on the entire surface, including silicon dioxide and gold regions, indicating that the hafnium/ODPA binds to both the glass and gold surfaces. Moreover, the hafnium/ODPA layer was able to block thiol adsorption to the gold upon exposure of the substrate to a solution of allyl mercaptan (see Supporting Information).

Following these initial investigations, we explored and characterized these alkanephosphonate monolayer assemblies on hafnium-modified gold. We found that the approach forms alkanephosphonate monolayers that are sufficiently well-ordered and dense to resist displacement by thiols in subsequent treatment steps. The approach allows easy preparation of patterned substrates. In addition, the hafnium−gold chemistry is compatible with and orthogonal to gold−thiol assembly strategies. We demonstrate this capability by using hafnium-patterned gold surfaces in tandem with the bifunctional molecule 2-mercaptoethylphosphonic acid (2-MEPA) to create a unique patterned surface.

Experimental Section

Materials. Hafnium dichloride oxide octahydrate (Alfa Aesar; 99.998%), hafnium(IV) chloride (STREM; 99.9+%), *n*-octadecylphosphonic acid [$CH_3(CH_2)_{17}P(O)(OH)_2$] (Alfa Aesar), allyl mercaptan (Avocado Research Chemicals, Ltd.; 70%), zirconium dichloride oxide octahydrate (Alfa Aesar; 99.9%), Shipley 1818 Photoresist (Shipley Company, Marlborough, MA), and Microposit 351 Developer (Shipley Company) were used as received. 2-Mercaptoethylphosphonic acid [$HS-(CH_2)_2P(O)(OH)_2$] was synthesized as previously reported.[13] Methyl alcohol (J.T. Baker; 100.0%) was distilled over magnesium. Deionized water (18.2 MΩ-cm) was purified with a Barnstead Nanopure Diamond system. Absolute ethyl alcohol (Aaper Alcohol and Chemical Company) was sparged with nitrogen for approximately 20 min prior to use.
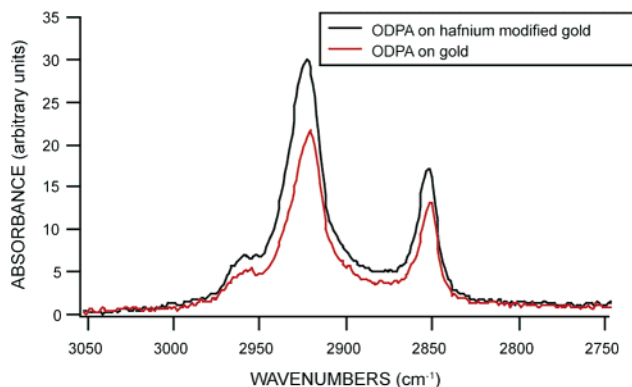
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Figure 1. PM-IRRAS spectra for octadecylphosphonic acid monolayers formed directly on gold (red line) and on gold modified with a hafnium linker (black line). The spectra are baseline normalized, and although the relative intensities within each spectrum are correct, the absolute spectral intensities cannot be compared between the two spectra.

Preparation of Substrates. The Si substrates used in this study were cut from n-type ⟨100⟩ wafers with 10−20 Ω-cm resistivity (University Wafer, Boston, MA). The Si and glass substrates used in this research were cleaned in a piranha solution (7:3 concd H_2SO_4/30% H_2O_2) for 15 min, rinsed with copious amounts of deionized water, and dried under a stream of argon prior to any assembly chemistry. Gold substrates on both glass and Si were prepared by evaporating 10 nm of chromium to promote adhesion of the gold layer, followed by 100 nm of gold. The gold-coated substrates were exposed to ozone for 10 min in a UV/ozone cleaner supplied with laboratory air at room temperature prior to further modification. Unpatterned monolayers of ODPA on Hf-modified gold were prepared by soaking gold-coated glass slides in either a 5 mM aqueous solution of $HfOCl_2$ for 3 days at 50 °C or a 5 mM solution of $HfCl_4$ in methanol for 30 min at room temperature. Upon removal from the soaking solution, the substrates were rinsed with deionized water or methanol, dried under a stream of argon, and soaked in a 1 mM ethanolic solution of ODPA for 24 h.

Photolithographic patterning of the Si substrates was achieved using Shipley 1818 Photoresist. The resist was applied using a dropper and spin-coated onto each gold-coated wafer at a speed of 3000 rpm for 60 s. Solvent was driven off by heating the wafer on an aluminum block at 110 °C for 60 s. The substrate was then placed under a prefabricated emulsion mask using an OAI Model 200 Contact Mask Aligner and exposed to UV light for 11 s (125 W/cm^2). The photoresist patterns were developed by agitating in a mixture of 3.5:1 deionized water/Microposit 351 Developer for 60 s. The substrates were rinsed again in deionized water and dried under a stream of nitrogen. The patterned substrates were heated at 120 °C for 1 h to improve the adhesion of the photoresist to the substrate. Any photoresist residue remaining within the exposed gold regions was removed by an oxygen plasma treatment (300 W, 5 s, 400 mT).

Following the oxygen plasma treatment, the substrates were rinsed with deionized water and immediately transferred to a 5 mM aqueous solution of $HfOCl_2$ at 50 °C for 3 days. The substrates were then sonicated in water for 5 min to remove any physisorbed material, rinsed with water, and dried with a stream of argon. Photoresist was removed by sonicating the substrates in acetone, followed by a short oxygen plasma treatment as described above. The patterned substrates were then soaked for 1 h in a 1 mM ethanolic solution of 2-MEPA. The substrates were finally soaked in a 5 mM aqueous solution of $ZrOCl_2$, sonicated for 5 min in water to remove physisorbed material, and rinsed with water before drying the finished substrates with a stream of argon.

Analysis Techniques. Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) studies were performed on a Nicolet Magna-IR 550 spectrometer with dual channel input and equipped with a photoelastic modulation (PEM) accessory (ThermoNi-
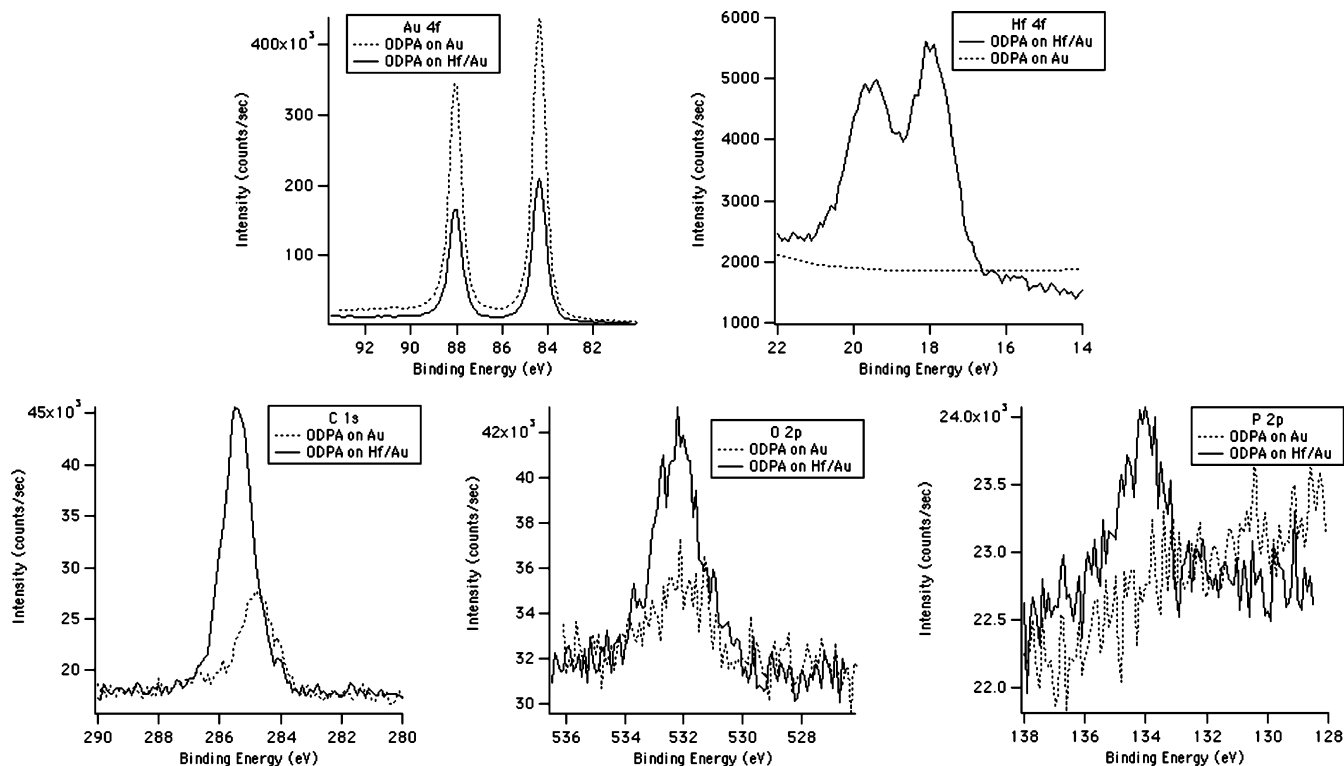
Figure 2. XPS spectra for octadecylphosphonic acid (ODPA) monolayers formed directly on gold (dashed line) and on gold modified with a hafnium linker (solid line). The data indicate that the monolayer coverage on the Hf/Au surface is significantly higher.

Table 1. Quantification of XPS Data for ODPA Monolayers Formed on Gold with and without a Hafnium Linker[a]

monolayer	Au (4f)	P (2p)	C (1s)	O (1s)	Hf (4f)
ODPA on gold	59	0	33	5	--
ODPA on Hf-modified gold	22	6	58	10	2

[a] Values given are relative atomic concentration. In the absence of phosphorus signals for ODPA on gold, we conclude that carbon and oxygen signals recorded for this sample are adventitious.

colet, Madison, WI) using 1024 signal-averaged scans with a mirror velocity of 0.9494 cm/s and a resolution of 2 cm^{-1}. The PEM module consists of beam steering and focusing optics, a wire grid polarizer, a PEM head and controller assembly (Hinds Instruments, Hillsboro, OR), an MCT-A liquid nitrogen cooled detector (ThermoNicolet, Madison, WI), and an SSD Demodulator (GWC Instruments, Madison, WI). For PM-IRRAS, no background spectrum collection is necessary.[17] Baseline normalization[18] was performed using Igor Pro software (Wavemetrics, Lake Oswego, OR).

X-ray photoelectron spectroscopy measurements were conducted using a Kratos Axis HSi spectrometer (Kratos Analytical, Chestnut Ridge, NY) with a monochromated Al Kα X-ray source. Contact angle measurements were conducted using a microscope equipped with a goniometer, utilizing the sessile drop method.[19] TOF-SIMS imaging experiments were carried out using an ION-TOF Model IV spectrometer (ION-TOF, Münster, Germany) with a bismuth liquid metal ion gun as the primary ion beam.

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Results and Discussion

Building on the intriguing results from our initial XPS studies (see Supporting Information), we performed a series of experiments to explore the surfaces resulting from the hafnium/ODPA treatments and to understand why these treatments prevent thiols from binding to the gold surface. By characterizing gold surfaces modified with hafnium followed by ODPA using contact angle goniometry, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), and XPS, we found that the hafnium linker chemistry allows for self-assembly of high quality alkanephosphonate monolayers on gold. We also used gold substrates patterned with hafnium to generate unique surfaces in tandem with gold−thiol assembly methods.

In our assembly strategy, gold substrates are first ozone treated and then soaked in a 5 mM solution of HfCl$_4$ in methanol at room temperature for 30 min. After removal from the hafnium solution, the substrates are rinsed with nanopure water for 15 min and then soaked in a 1 mM ethanolic solution of ODPA. Control experiments were also performed where the gold substrate was immediately placed in the ODPA soaking solution after ozone treatment. After soaking in ODPA solutions for 24 h, the resulting substrates were characterized by contact angle goniometry, PM-IRRAS, and XPS.

ODPA monolayers formed directly on gold yielded a static contact angle of 82 ± 3°, whereas the contact angle measured for ODPA monolayers formed on gold with the hafnium linker was 105 ± 2°. This suggests the formation of reasonably dense, well-ordered monolayers of ODPA on the hafnium-modified gold. This measurement is in good agreement with contact

Scheme 1. Processing Steps for Fabrication of Hf/Zr Patterned Substrates
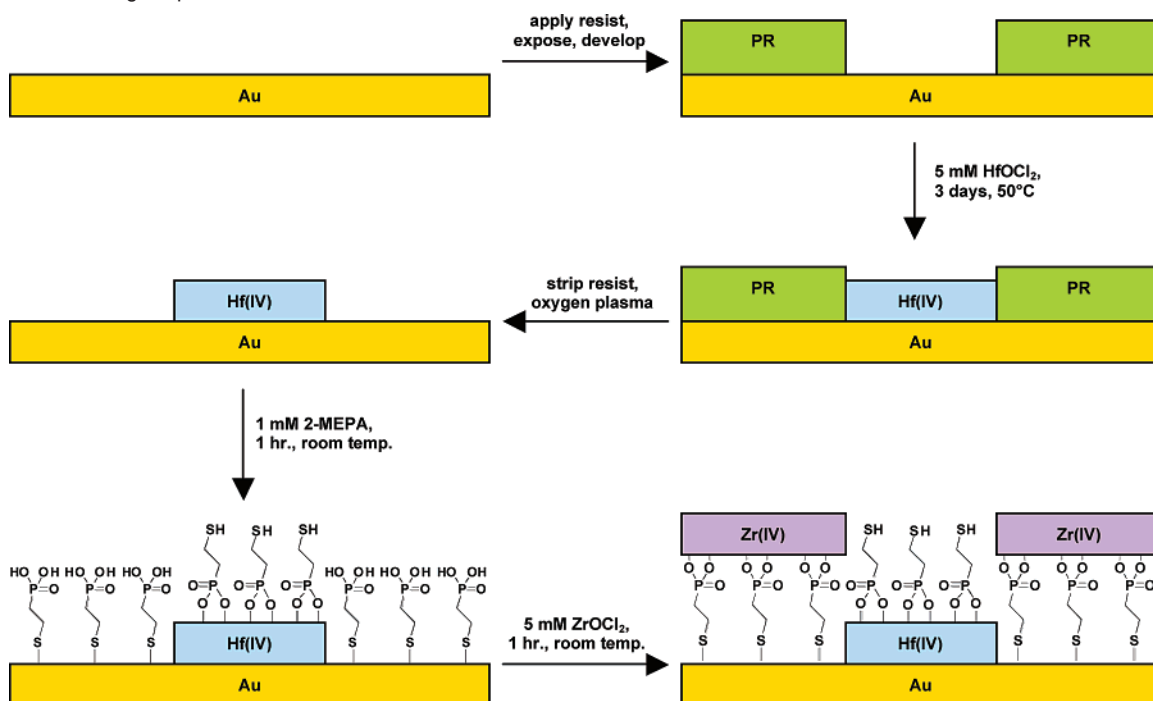
angles measured for ODPA monolayers on other substrates, including TiO_2 and Ta_2O_5.[20–22]

PM-IRRAS data show two major peaks (Figure 1) for ODPA assemblies deposited directly on gold as well as for monolayers formed on gold with a hafnium linker. ODPA monolayers formed on hafnium-modified gold exhibit significantly larger peaks than those for ODPA monolayers formed on bare gold. This indicates that a monolayer of higher coverage is formed on the hafnium-modified gold, though PM-IRRAS cannot be used to determine the coverages quantitatively. The two peaks at 2922 cm^{-1} and 2851 cm^{-1} correspond to the CH_2 (asym) and CH_2 (sym) peaks, respectively.[23] The shoulder of the CH_2 (asym) peak at 2959 cm^{-1} corresponds to the CH_3 (asym) peak.[23] These peak positions are in good agreement with the IR spectra observed for ODPA monolayers on other substrates.[24] Although the CH_2 (asym) peak position is at a slightly lower frequency than that normally observed for very dense, well-ordered films, this value for ODPA monolayers on hafnium-modified gold is within range for reasonably well-ordered alkylphosphonate monolayers on metal oxide surfaces.

In order to further clarify the PM-IRRAS data, we attempted to determine the difference in the amounts of ODPA on bare gold and hafnium-modified gold surfaces more quantitatively by utilizing XPS. The XPS data for ODPA monolayers formed on gold with and without the hafnium linker are shown in Figure 2. Table 1 summarizes the atomic concentration quantification. No phosphorus is observed for ODPA assemblies formed on

gold without a hafnium linker present, indicating that the amount of ODPA present on these substrates is below the detection limit of the instrument or that the adsorbate readily desorbs under a vacuum. The XPS data for ODPA assemblies formed on hafnium-modified gold show the presence of hafnium, phosphorus, oxygen, and a significant amount of carbon. The gold peak is also significantly attenuated. These data indicate that an ODPA monolayer has formed on the hafnium-modified gold. The Hf $4f_{7/2}$ peak appears between 17 and 18 eV, indicative of the Hf^{4+} chemical state, and no chlorine is observed by XPS, indicating that the surface species formed by hafnium on gold is likely a hafnium oxide.

The contact angle, PM-IRRAS, and XPS data all indicate the presence of a stable ODPA monolayer on hafnium-modified gold. In contrast, XPS and TOF-SIMS data for ODPA deposited on bare gold show nearly undetectable amounts of ODPA on the surface. PM-IRRAS data for ODPA on bare gold indicate the presence of a monolayer structure. Furthermore, contact angle measurements show that the gold substrates exposed only to an ethanolic solution of ODPA are more hydrophobic than bare gold substrates, indicating the presence of some organic material on the surface. It is possible that either weak binding to the gold allows for ready desorption of ODPA from bare gold under a high vacuum in the XPS experiments but not under the ambient conditions of the PM-IRRAS and contact angle studies or the small amount of ODPA present in those samples, coupled with the relatively low atomic sensitivity of phosphorus in XPS, makes it difficult to detect. In either case, taken together, these data suggest that there may be small patches of organized ODPA on the bare gold surface, but the majority of the surface is likely unmodified.

We were initially surprised that hafnium treatment would facilitate alkanephosphonate binding to gold because the binding of a "hard" cation (Hf(IV)) to a "soft" surface like gold seems unlikely: gold generally prefers soft donor atoms such as sulfur.

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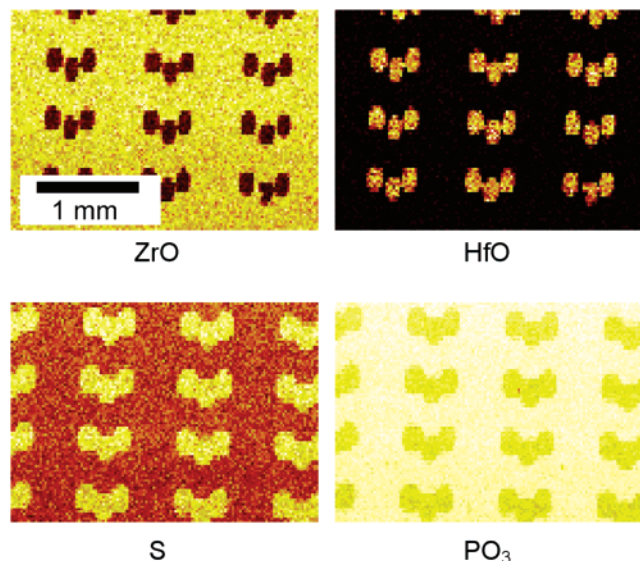
Figure 3. TOF-SIMS imaging data from patterned sample. The bright areas correspond to higher ion yields. In the images for S and PO$_3$, the presence of both fragments is detected over the entire surface; however, the differences in intensity between the patterned regions and the surrounding surface reflect the difference in the orientation of 2-MEPA on those areas of the substrate.

Although we have not yet been able to fully characterize the bonding between the gold surface and the hafnium linker, given the affinity of hafnium(IV) for oxide surfaces, the higher-than-expected concentration of oxygen by XPS, and the absence of a chlorine signal by XPS, a reasonable hypothesis is that Hf-(IV) binds to a gold oxide[25] layer rather than directly binding to the "soft" gold surface. The presence of Au−O−Hf fragments in TOF-SIMS spectral studies of these surfaces also supports this hypothesis (see Supporting Information).

In previous work,[26] it has been shown that two SAMs can be formed independently by simultaneous adsorption of two different adsorbate molecules from a common solution on a substrate consisting of both gold and metal oxide at its surface. Similarly, the attributes of this new surface chemistry make possible a number of sophisticated orthogonal self-assembly schemes, taking advantage of the specificity of phosphonates for Hf/Au and thiols for Au and the relative stability of each interaction. The chemistry shown in Scheme 1 highlights the use of the hafnium/gold chemistry to design unique patterned surfaces. The last segment of Scheme 1 shows an illustration of the target structure, where the bifunctional molecule 2-mer-captoethylphosphonic acid (2-MEPA) is assembled on a gold substrate that has been patterned with hafnium. We chose a

molecule with both thiol and phosphonic acid functionalities to take advantage of the different binding properties of thiols versus phosphonates. We hypothesized that 2-MEPA would bind through the phosphonate functionality on the hafnium-patterned regions of the surface and through the thiol functionality on the bare gold, thus simultaneously forming two different SAMs from a solution containing a single adsorbate molecule. Zirconium is subsequently deposited on the exposed phosphonate groups on the unpatterned portion of the surface for visualization using TOF-SIMS.

In order to test this idea, a clean gold film was patterned by photolithography to expose areas of the surface. The patterned film was briefly treated with oxygen plasma to remove any remaining resist from the exposed areas, and the substrate was subsequently soaked in an aqueous solution of HfOCl$_2$.[27,13] The photoresist was then stripped with acetone, and the substrate was soaked in a solution of 2-MEPA. After rinsing with copious amounts of ethanol the substrate was soaked in an aqueous solution of ZrOCl$_2$ to mark the regions where the phosphonic acid functionality of 2-MEPA was exposed.

The final structures were imaged by time-of-flight secondary ion mass spectrometry (TOF-SIMS). The images in Figure 3 show ion yields of the HfO, ZrO, S, and PO$_3$ fragments. The patterning of hafnium and zirconium is clearly visible, and the ion yields of PO$_3$ and sulfur reflect the difference in orientation of 2-MEPA between the hafnium-functionalized areas and the bare gold.

Conclusions

In summary, we have described a strategy that can be used to easily assemble stable alkanephosphonate monolayers on gold using a hafnium linker molecule, opening up the possibility of functionalizing gold surfaces with a new class of organic monolayers. We have also described how this chemistry can be used to create patterned gold surfaces. In the process, we have shown that the gold-hafnium assembly strategy is compatible with gold−thiol chemistry and that the two strategies can be used in a complementary manner to create uniquely patterned and functionalized surfaces. We are currently exploring the nature of the surface interactions, how this assembly approach can be employed to attach other metal oxide-binding adsorbates to gold surfaces, and whether these monolayers can be used as etch resists.

Supporting Information Available: Details of substrate preparation, experimental procedures, results from initial XPS studies, and additional TOF-SIMS images. This material is available free of charge via the Internet at http://pubs.acs.org.

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