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Studies of Branched Dialkyldithiophosphinic Acids on Gold and Stretchable Gold Films Using Silica Nanoparticles

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By

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Abstract

This first half of the thesis reports the synthesis of new branched symmetric dithiophosphinic acids (DTPAs), and the formation and characterization of DTPA SAMs on As-Dep and TS gold. Chapter 1 introduces the definition of self-assembled monolayers (SAMs) and SAMs with multidentate adsorbates. The binding of DTPA SAMs on gold depends on the roughness of gold: on as-deposited (As-Dep) gold, DTPA adsorbates bind in a mixture of bidentate (60%) and monodentate (40%), while on templated-stripped (TS) gold, the SAMs chelated to the gold surface. Chapter 3 investigates packing density, organization of alkyl chain and chain crystallinity of $(C_6C_2)_2$DTPA and $(C_5C_1)_2$DTPA SAMs on As-Dep and TS gold.

The second half of the thesis focused on the research area of stretchable electronics. Chapter 2 presents the background and application of stretchable electronics and different ways that have been used to increase the stretchability and conductivity of stretchable electronics, such as conductive materials, soft substrates and topographies of substrates. Chapter 4 reports the using of E-Beam evaporation to deposit Au thin film onto polydimethyl siloxane (PDMS) elastomeric substrates, by inducing micro-structured modified fumed silica interlayer to enhance the stretchability and conductivity of the thin metal films. Also, by simply altering the weight ratio of modified silica:PDMS interlayer, the resistance change can be tuned, which leads to different functional samples.

Dedication

This thesis is dedicated to my parents abroad, who always cheer me up and give me motivation every time I feel stressful. They provide me the chance to study and live in Canada with endless support for these many years.

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I really appreciate my supervisor, Dr. Tricia B. Carmichael who supervised me for the last two years at University of Windsor. I thank you for making me believe in myself, and know the meaning of responsibility. Also, I would like to thank Steve Carmichael for cooking delicious food, great BBQ, sharing wines and everything in our group parties.

I should thank all my colleagues in my lab for providing help and support, especially Michael-Anthony who supervised me when I firstly worked in the lab, and Akhil who always makes me spend money and talks about gossip after hard working in the lab. I would also thank for all the friends in the departments for motivating me in a "different" way, and also Beini who are always by my side wherever I go and whatever I do.

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List of Abbreviations

AFM	Atomic force microscopy
As-Dep Au	As-deposited gold
BEs	Binding energies
CNTs	Carbon nanotubes
°C	Degree Celcius
cm	Centimeter
DTCs	Dithiocarbamates
DIBAL	Diisobutylaluminium hydride
DTPA	Dithiophosphinic acid
EDTA	Ethylene diamine tetraacetic acid
EGaIn	Gallium-indium eutectic
hrs	Hours
HR-XPS	High-resolution XPS
Hz	Hertz
kcal	Kilocalorie
MCT	Mercury cadmium telluride
MPTMS	3-Mercaptopropyl trimethoxysilane
mM	Millimolar concentration
mL	Milliliter
mm	Millimeter
nm	Nanometer
NMR	Nuclear magnetic resonance
PDMS	Polydimethylsiloxane
PU	Polyurethane

PVAc	Polyvinyl acetate
RAIRS	Reflection-adsorption infrared spectroscopy
R	Alkyl chains
RSHs	n-alkanethiols
RS-SRs	Dialkyldisulfides
RSRs	Dialkylsulfides
RMS	Root-mean-square
R_s	Sheet resistance
SAM	Self-assembled monolayer
SEM	Scanning electron microscope
S_{dr}	Surface area ratio
THF	Tetrahydrofuran
TPDTC	Terphenyldithiocarbamate
TGA	Thermogravimetric analysis
TS Au	Template-stripped gold
UV	Ultraviolate
XPS	X-ray photoelectron spectroscopy
μm	Micrometer
υ_{as}	Asymmetric stretch
υ_s	Symmetric stretch

Chapter 1

Introduction of Self-Assembled Monolayers (SAMs)

1.1 Background

Self-assembled monolayers (SAMs) are highly ordered, single layer molecular films formed from the adsorption of organic molecules, with three specific features, onto a solid or liquid surface as shown in Figure 1.1. The head group has a highly affinity to the metal substrate, the adsorption between the molecule and the metal surface happens with the formation of a covalent bond. This exothermic process is called chemisorption.[1] In the middle of the molecule, alkane chains are most common, facilitating ordering during assembling process through van der Waals interactions. Longer alkyl chains have more van der Waals interactions, producing more ordered SAMs than those formed from shorter alkyl chains.[2,3] Although the self-assembly process is driven by the chemisorption of the head group and van der Waals interactions between neighbouring molecules, the interfacial properties (wettability by water, which can affect its adhesion, friction and lubrication[4]) of the SAM are dictated by the terminal group that is present at the surface of the monolayer. Self-assembled monolayers can be formed on a wide range of substrate including metal oxides, and coinage metals (Au, Ag, Cu, Pt, Pd).[5-8] SAMs with a siloxane headgroup have been shown to form on glass, however, this class of molecular adsorbates require more difficult conditions during assembling, including synthesize, purify, soak and anneal steps.[9] Another type of SAMs are phosphonic acids on metal oxides and silicon. To produce ordered SAMs, high-temperature annealing and substrate pre-treating might be used, which is too complicated to prepare.[10]

The most well-studied SAMs are thiol-functionalized molecules on coinage metals. Of all the metals, gold has been most studied because chemisorption of the organosulfur compound to gold is highly favourable (~30 kcal/mol[11,12,13]). Additionally, gold is inert; it

does not oxidize in ambient conditions like copper or silver[14] and does not react with most chemicals.
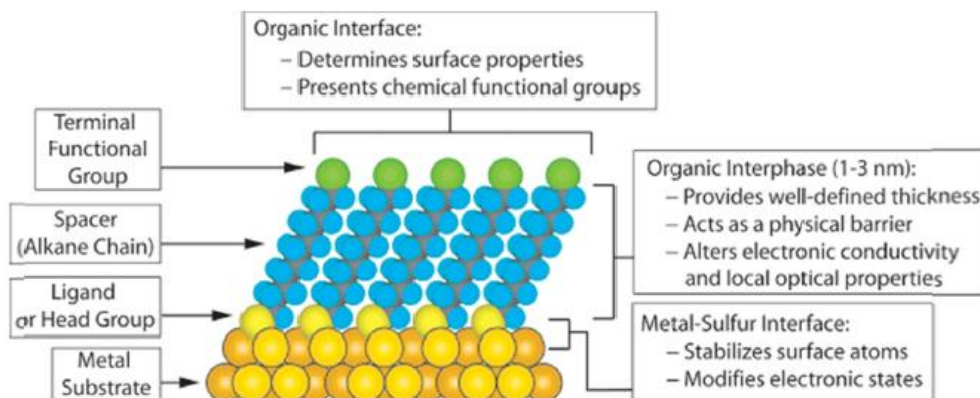
Figure 1.1. Schematic diagram of an ideal n-alkanethiol SAM on gold with the anatomy and characteristics.[1]

1.2. Structure of alkanethiolate SAMs

The organosulfur adsorbates are widely used in SAM formation, includes organic alkanethiols, aromatic thiols, sulfides, disulfide, thiocarbamates and dithiolcarbinates.[15,16] The organosulfur compounds are known to coordinate to surfaces of gold, which can be achieved form solution immersion. The simplest structure organosulfur compound (alkanethiols, RSHs) can produce robust and well-defined SAMs, when the alkanethiol, in solution, is brought in contact with a clean gold surface, a highly favorable Au-S bond will form.[17,18,19] Besides, alkanethiols have a superior solubility, which enables the formation of alkanethiolate SAMs on gold of varying chain lengths.[1,20]

The preparation of SAMs by adsorption of alkanethiols on gold is very easy, by immersing a clean gold substrate, into a dilute solution of the adsorbate (~1 mM). The typical immersion time ranges from 12-18 hours at room temperature (25°C). During the process, the alkanethiols adsorb on the gold and lose the hydrogen, which is not been proved.[16,21,22] The most common surface structure of SAMs of on an Au (111) surface is generally believed to be trans-extended and tilted approximately 30° from normal, and the spacing of sulfur atoms on the surface is 4.99 Å, $n > 11$ (for $n < 10$, the SAMs are less ordered);[23,24] alkanethiolates has a similar structure with dialkyldisulfides, the S-S bond is cleaved at the gold surface.[25,26] Chain orientation in alkanethiol SAMs have a tilt angle on the linear backbone away from the surface normal (α), and the angle of rotation about the long axis of the molecule (β).[1,8,16] These two angles change (depending strongly on the substrate) to maximize both the packing density and the number of van der Waals interactions between neighboring molecules.

1.3. Chelating SAMs with multidentate adsorbates

Alkanethiolate SAMs provide a simple, ordered system for many applications, such as molecular junctions and etch resists.[27-33] However, the low energy barrier to molecular diffusion and desorption causes poor thermal or electrical stability and packing density of the SAM, which may limit the life time of a real device and prevent their use in real electronic devices.[34] A paper by Chinwangso *et al.* describes a variety of multidentate (bidentates and tridentates) adsorbate structures that have been used to generate well-defined SAMs with multiple attachment points to the underlying substrate. This bonding arrangement allows the formation of SAMs with enhanced stability through the entropy-driven "chelate effect" (Figure 1.2).[35]
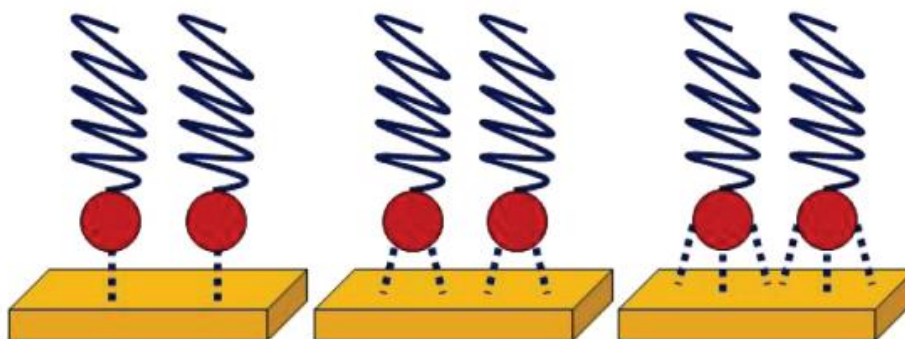
Figure 1.2. Illustration of components of SAMs monodentate, bidentate, and tridentate bonding modes between adsorbate and substrate.[35]
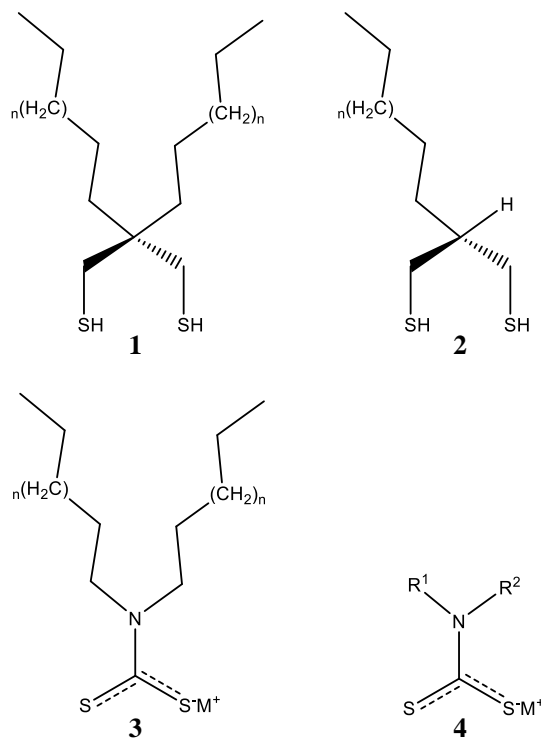
Figure 1.3. Structures of chelating adsorbates for SAM formation.
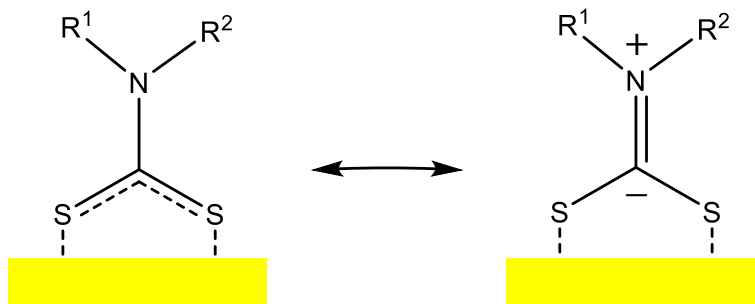
Figure 1.4. Mesomeric forms of the DTC headgroup chelates on gold.

Spiroalkanedithiols (**1**, **2**) and dithiocarbamates (DTC, **3**, **4**) (Figure 1.3) are two well studied SAMs where the headgroups can chelate to the gold surface leading to stronger metal-molecule coupling and improve thermal stability compared to the thiol analogue. The structure of spiroalkanedithiols are dominant to the alkyl chain packing density and also influence the frictional properties of the formed SAMs.[36,37] SAMs generated from long chain dialkanedithiols **1** are highly oriented and well packed, while the SAMs formed from monoalkanedithiols **2** are less crystalline than those of analogous from dialkanedithiol.[38] The DTC head group chelates to the gold surface so that even short chain DTC SAMs are stable up to 12 hrs at 85 °C (Figure 1.4).[39] Incorporating aromatic groups in the DTC structures allows for the formation of SAMs that are robust with high thermal stability and conductivity, which is good for the DTC-based molecular junctions. von Wrochem *et al.* studied forming terphenyldithiocarbamate (TPDTC) SAMs on gold, which has a conductance that is two orders of magnitude higher than the SAM of analogous terphenylthiol. [40]

1.4. Dithiophosphinic Acids

One potentially interesting molecule that can chelate to the substrate is the dithiophosphinic acid (DTPA), which consists of a tetrahedral phosphorus center that binds to two sulfur atoms to give a P(S)SH headgroup and also attaches to two pendant groups (Figure 1.5), similar to spiroalkanedithiols. Dialkyl-DTPA molecules have previously been used in industrial applications such as selective separation of precious metals from sulfide ores.[41,42]
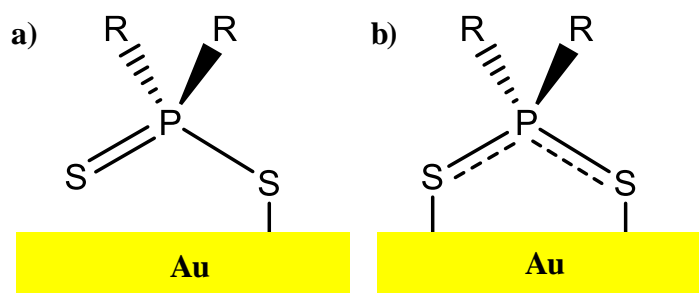
Figure 1.5. Dialkyldithiophosphinic Acid bond to gold surface: a) monodentate and b) bidentate binding.

In recent years, our research group studied more on the self-assembly of phosphorus-containing adsorbates on coinage metals (mostly gold), the potential to investigate the nature of chelating between two sulfur atoms makes DTPA molecules interesting. San Juan and Miller *et al*. examined the nature of binding of the P(S)SH headgroup, the alkyl chain organization and packing density, and the electrochemical properties as a function of varying the R groups. They investigated the van der Waals interactions between the

symmetric and asymmetric, short and long alkyl chains, the resulting packing density and organization in comparison to those of analogous RSH SAMs. They also introduce a phenyl moiety as a pendant group in the DTPAs and form SAMs from a series of PhRDTPAs while varying the alkyl chain length.[43-37] From the studies that we know, DTPA SAMs formed from adsorbates with short alkyl chain (n=5) are disordered and liquid-like, and the alkyl groups become more crystalline and ordered as the alkyl chain length is increased. While on ultrasmooth gold, an opposite trend can be exhibited in which the alkyl layer becomes more disordered and liquid-like as the methylene units is increased.[48]

1.5. Roughness of gold

From Figure 1.5a, monodentate DTPAs have one bounded sulfur to the underlying gold substrate, while the other sulfur does not interact with gold and retains the double bond to phosphorus. Bidentate DTPAs have both sulfur atoms bounded to the gold and have resonance associated with chelation (Figure 1.5b). The chelating structure of the adsorbates depends on the morphology and roughness of the gold substrates. There are two types of gold substrates with different roughness, As-Dep and TS gold, and the way these DTPA SAMs bind to surface depends on the gold substrates. Gold films deposited by electron-beam evaporation (As-Dep gold) are composed of a layer of small grains of ~50 nm, separated by deep grain boundaries of ~10 nm (Figure 1.6), lead to a large root-mean-square (RMS) roughness value of 3 - 5 nm[44,50,51,52] which inhibit the DTPA adsorbates to chelate, provide a mixture of bidentate (60%) and monodentate (40%) in the SAM. The monodentate DTPA molecules have the freedom of rotation about the Au-S bond, resulting in flexible Au-S-P bond angles, which allows dense packing of the

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chain. As the van der Waals interactions between alkyl groups increase with increasing chain length, SAMs that formed are more crystalline.[43,44] In contrast, gold substrates produced by a process known as template-stripped (TS)[49] provide an ultrasmooth surface, which consists of large but flat grains of ~200-500 nm, separated by shallow grain boundaries of ~1.5 nm, lead to a RMS roughness value of ~5Å.[44,50,51,52] In the SAMs that formed on TS gold, all the adsorbates chelate to the gold surface, the bidentate DTPA molecules prevent rotation about the Au-S bond and fix the Au-S-P bond angles. As the length of alkyl chains increases, steric demands of the chains limit the van der Waals interactions, making the alkyl layer disordered and loosely packed.[44,48]
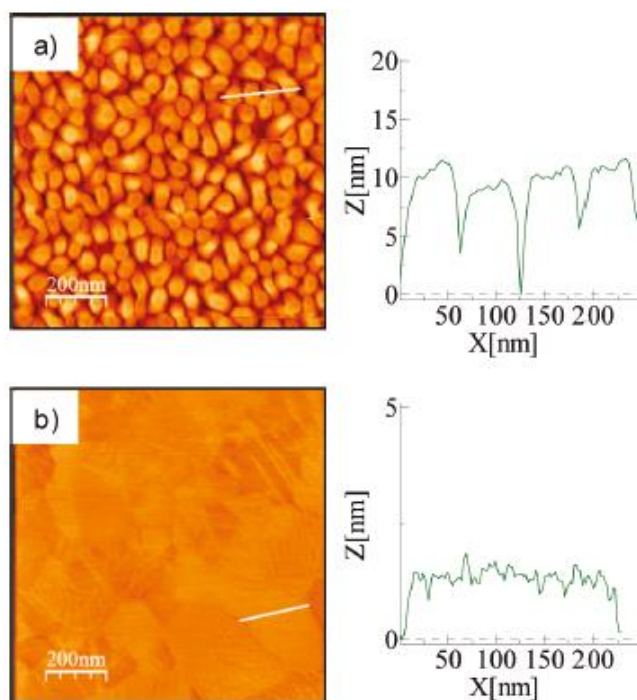
Figure 1.6. Contact mode AFM topographic images of (a) As-Dep and (b) TS gold films.[44]

1.6. Scope of thesis

The focus of first half of this thesis is to use a new R_2DTPA to form SAMs on both As-Dep and TS gold films. We use branched symmetric short chain DTPA adsorbates, $(C_6C_2)_2$DTPA and $(C_5C_1)_2$DTPA, which have a similar molecular structure to $(C_6)_2$DTPA, and exam the packing density, organization of the alkyl chains and chain crystallinity of the SAMs on gold. This work is presented in Chapter 3.

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Chapter 2

Introduction of Stretchable Electronics

2.1. Background

During the past decade, electronic devices are becoming more and more important in our daily life. These devices are rigid because the electronic components are made of brittle and stiff conductive materials. As the development the material science, it is a trend to enable the transistors or circuitries in the electronic devices to be stretchable and flexible to provide convenience for us. So flexible and stretchable electronics have the potential to outperform the traditional rigid devices in terms of flexibility, stretchability and weight.

2.2. Applications of Stretchable Electronics

Electronics have the potential to enrich our daily lives with soft, bendable and even wearable devices that can monitor body conditions, sensors that can accommodate the human body's curvilinear shape, rollable and foldable paper-like displays, wearable smart surgical gloves, and skin-like prosthesis.[1-5] A paper-like display/screen is so thin and flexible that it can be rolled into small volumes, it is expected to be used for various applications from big screen TVs, to car displays which can bend around the contours inside of the vehicle (Figure 2.1 a). Similar to paper-like screen, flexible solar panel can also be rolled into a tube and conform to various shapes (Figure 2.1 b).[6]
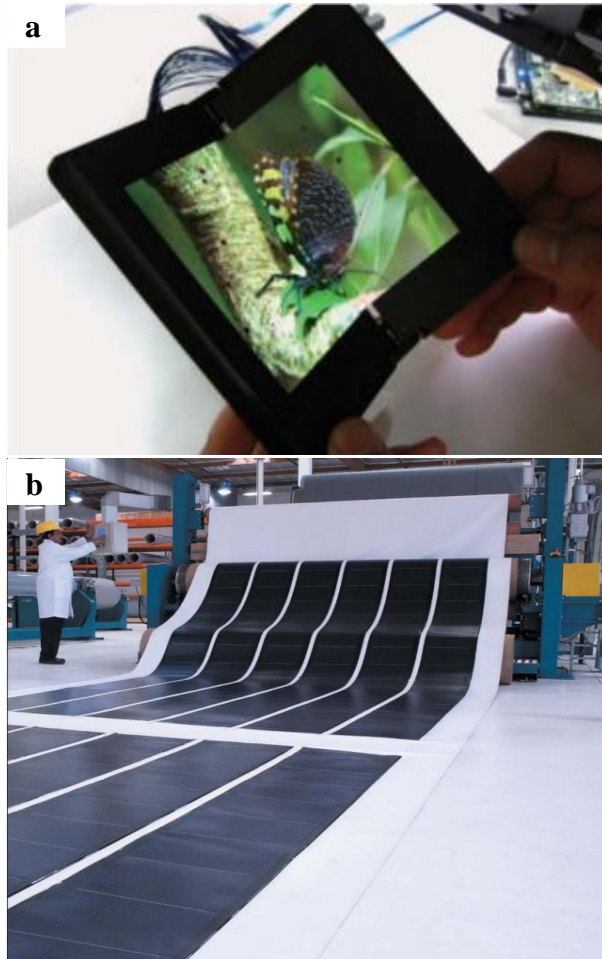
Figure 2.1. Applications of flexible electronics: (a) paper-like flexible screen,[7] (b) flexible solar cell panel.[6]

However, ability to be bent and flex is not enough to satisfy every daily need, to overcome the restriction, stretchable electronics is extended. It is now well studied in materials science, which can maintain the functionality and conductivity when a large strain is applied and restore back. Stretchable electronics represent a much more challenging class of research for applications where circuits must be wrapped conformally around complex curvilinear shaped surfaces, or integrated with soft biological tissues that are impossible using devices that offer only flexibility.[8] Rogers'

group introduced an electronic eye by using stretchable electronics (Figure 2.2 a).[9,10] Intrinsically stretchable polymer light-emitting devices were created as shown in Figure 2.2 b.[11] The stretchable sensors can be made on very thin elastic substrates that fabricated on a catheter has also delivered into the other human organs, such as blood vessel (Figure 2.2 c).[12] Figure 2.2 d shows prosthetic skin which can bend and stretch like normal skin and allow the wearer to feel pressure, temperature and moisture.[4]
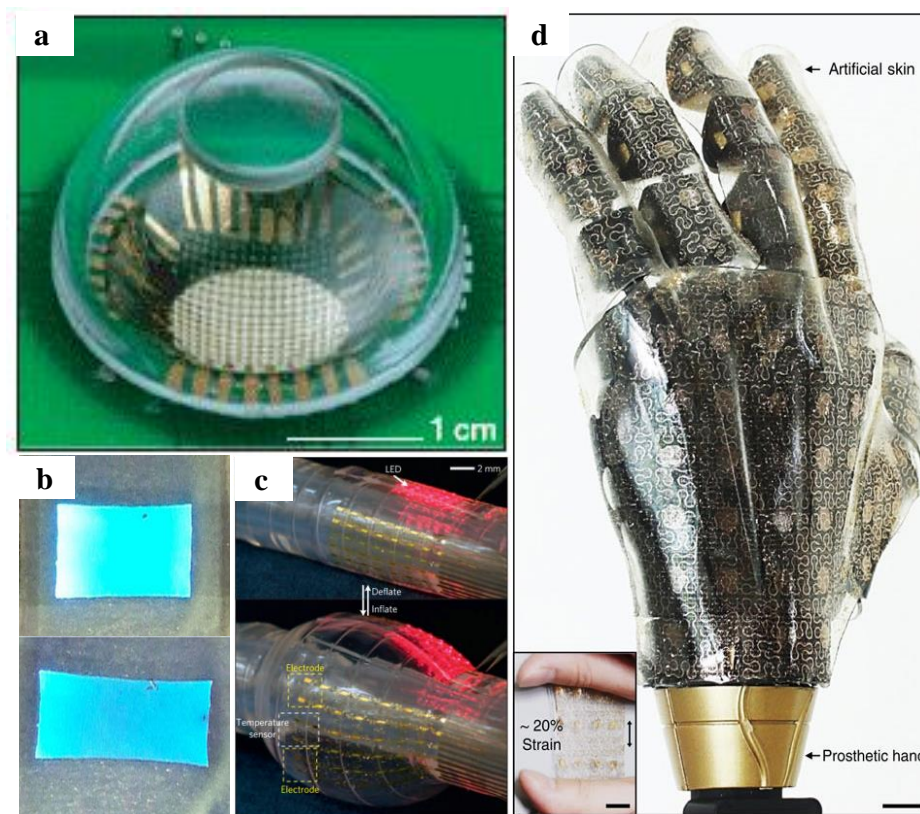
Figure 2.2. Applications of stretchable electronics: (a) a hemispherical electronic eye camera,[10] (b) an intrinsically stretchable polymer light-emitting device,[12] (c) a stretchable sensor on an expandable catheter,[13] (d) smart artificial skin covering a prosthetic hand.[4]

Stretchable electronics is a modern technology to fabricate stretchable electronic devices by depositing electronic onto soft substrates. The key to make functional, stretchable electronics is good electrical performance and mechanical robustness. Organic semiconductors and conducting polymers were appealing materials for stretchable electronics attributing to their intrinsic stretchability, light weight, and low cost.[13,14] These stretchable electronics prototypes have the potential to enrich our lives.

2.3. Conductive materials on stretchable substrates

Soft materials, such as polydimethyl siloxane (PDMS), polyurethane (PU), butyl rubber and Ecoflex,[15,16,17] show excellent mechanical deformability while having unsatisfactory electrical properties (not conductive). Among all these materials, PDMS has become the most popular soft substrate due to its high stretchability, biocompatibility, transparency, commercially availability, and its ability to be molded.[18] The PDMS elastomer and cross-linker mixture are prepared and casted on the patterned Si mould or simply poured into a petri dish, then after degassing in vacuum and thermal curing, a PDMS thin film can be peeled off. The geometry and shape of the micro-features are well-controlled by the patterns on Si mould, which is made with photolithography. However, the ability to stretch is not enough to fabricate the stretchable electronic device.

Some strategies to thin film fabrication is develop materials that can withstand high strain because of their physical properties. Carbon based materials such as carbon nanotubes (CNTs) and graphene have the desirable mechanical and electrical properties. The CNT/PDMS composite films show very little variation in resistance under multiple stretching-and-releasing cycles up to a strain level of 40%.[19] Lee *et al.* presented

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stretchable, printable, and transparent transistors composed of monolithically patterned graphene film, which can maintain stable operation at stretching up to 5% after 1000 or more cycles.[20] Besides, metal nanowires, conductive polymer, and nanoparticles[21,22] have been identified as attractive materials for stretchable devices due to excellent electrical properties, high transparency, and mechanical flexibility, stretchability and stability.[23,24] A highly conductive and stretchable conductor with silver nanowires (AgNWs) embedded just below PDMS can achieve a large range of tensile strain (0 – 50%) after a few cycles of stretching/releasing of substrate.[25] Lipomi *et al.* demonstrated a transparent conducting polymer (PEDOT : PSS) with a fluorosurfactant onto stretchable PDMS substrates, where no significant cracking (~2 cracks mm^{-1}) occurs before 30% uniaxial strain.[26] Although these nano materials were developed in the past decade, metal is still the best conductor in terms of conductivity, stability, compatibility, and cost.[27]

2.4. Metal films on stretchable substrates

Another approach to achieve stretchable electronics include the use of naturally flexible and stretchable polymeric substrates in combination with metal thin films.[28] Most conductive rigid materials like metals may exhibit good electrical performance and stability, but freestanding metal films fracture at tensile strains below ~1%,[29] even for gold, which is the most malleable and ductile of all known metals. It has been observed that when free-standing metal films are expanded during the deformation of a substrate they fracture at strains of a few percent.[30,31] Bulk metals are normally considered rigid materials, however, any material in sufficiently thin form is flexible and become stretchable when structured into proper shapes, which have been demonstrated by the work from the groups of Suo, Someya and Rogers.[32,33,34] Thus, metal films which are

well-attached on elastomeric substrates must show excellent stretchability. Thin metal films attached on soft elastomeric substrates can sustain much larger tensile strain (by tens of percent) compared to free-standing metal film, because strain can be delocalized over the whole surface, the metal film only experience small strains, without suffering fatigue.[35,36]

Layering the rigid conductive metal film with stretchable elastomers to achieve a combination of desirable properties for stretchable electronics/devices is more appealing than the other conductive materials on elastomers. As we mentioned above, even ductile metal, like freestanding gold film, fractures at tensile strains below ~ 1%, despite of the film thickness.[30] Various technologies have emerged for depositing thin metal film on soft substrates such as sputter deposition,[35] physical vapor deposition,[29] chemical vapor deposition,[37] ink-jet printing,[38] and electroless deposition.[39] In this thesis, we choose electron beam evaporation, which is a physical vapor deposition technique, for the appeal of non-contact and programmable control to ensure precise metal thickness. By depositing metal film on soft substrates, such as PDMS, can suppress the strain localization, makes it stretchable on the conductors. The challenge is that as the stretchability is increasing, the conductivity of the metal film is decreasing rapidly, due to the cracks that propagate across the metal film as it is elongated and interrupt the conductive pathway.
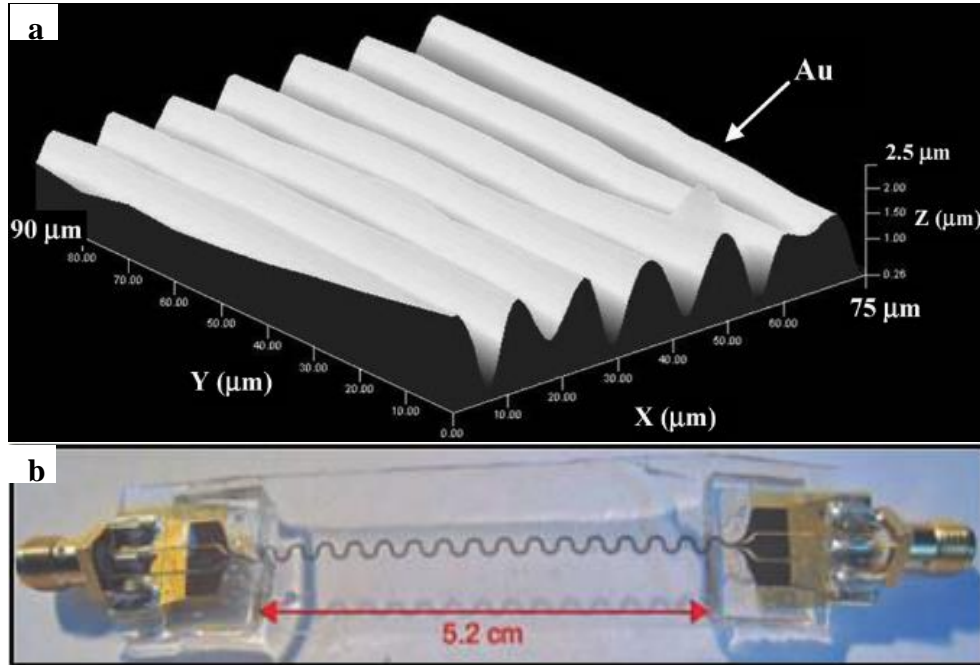
Figure 2.3. a) buckled gold surface structure after release from 15% pre-stretch,[41] b) serpentine structured metal embedded in PDMS.[33]

One possible way to realize stretchability is by incorporating wavy structures in thin metal films through nonlinear buckling, or wrinkling on soft substrates.[40] The design ideas of strain-relief patterns of conductive film structures also include serpentine, and interlocking (Figure 2.3).[41,42,43] Wavy, serpentine and interlocking structures reduce the actual strain on the film by converting external tensile motion into bending motion. As the strain experienced by the metal films is reduced by the deposition pattern of the metal, the component can be successfully incorporated in stretchable electronic devices. By inducing a buckled topography PDMS surface, increased stretchability of a few tenths of percent can be obtained, by comparing to metal on flat PDMS, but the resistance increases linearly when a critical strain is reached.[29] The PDMS substrate with mogul-patterned surface can be multi-directionally stretchable and versatile for various thin

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metal films, also the valleys and bumps structures enable the stability. The applied strain can be efficiently absorbed by the valley regions, resulting in minimal interference with motion-induce stress to remain conductive after 1000 stretching cycles at 50% stain.[44] Lacour *et al.* showed metal films on micropillar array PDMS substrate exhibit high electrical conductivity and can stretch reversibly to 20% without failing electrically. In which cracks are allowed and the cracks seem to start or stop at the closest pillar base at site of local strain maxima, the cracks widen but do not propagate at higher strain, and additional narrower cracks appear in between the pillars.[45]

Our group used spin-coating to deposit an aqueous emulsion of poly(vinyl acetate) (PVAc) onto an oxidized PDMS surface to achieve a microstructured PDMS substrate surface. When coated with gold, these structure remains conducive up to 65% elongation.[46] Because the microstructured surface provides numerous defect sites that localize strain when stretching, prevents long crack propagation and preserve the conductive pathways. Au is used for the highly conductivity, and will not be oxidized which makes gold a desirable metal in the stretchable electronics filed, compared to Cu and Ag.

2.5. Scope of thesis

In the second half of the thesis, we focused on using E-Beam evaporation to deposit Au thin films onto PDMS substrates, which is oxidized and spin coated with modified-silica, to induce a micro-structured PDMS substrate by using agglomerated silica nanoparticles to enhance the stretchability and conductivity. These structures can maintain a similar stretchable electrical behavior to the PVAc glue structures. By altering the weight ratio of modified-silica:PDMS interlayer, the resistance change can be tuned, which can lead to different functional stretchable devices. This work is presented in Chapter 4.

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Chapter 3

Branched Dialkyldithiophosphinic Acid Self-Assembled

Monolayers on Gold

3.1. Introduction

Forming densely-packing, well-ordered self-assembled monolayers (SAMs) on gold is one of the well-studied methods to research the surface properties, which are determined by the terminal tail group of the adsorbates. Since the introduction of SAMs, researcher have been motivated to create SAMs with a range of interfacial properties, such as wettabilities and frictional coefficient. Dialkyldithiophosphinic Acid (DTPA) molecules have two potential binding modes to gold surface: one is anchored by a single Au-S bond (monodentate), whereas the second is anchored by two Au-S bonds (bidentate) (Scheme 3.1). Srisombat *et al.* studied about the stability of mono, bis-, and trischelating alkanethiol SAMs, it showed that SAM thermal stability correlates to the degree of chelation (i.e., tridentate > bidentate > monodentate).[1]

Gold films deposited by electron-beam evaporation (As-Dep gold) are composed of a layer of continuous small grains of ~25-50 nm, separated by deep grain boundaries of ~10 nm,[2] which inhibit the DTPA adsorbates from chelate binding, provide a mixture of bidentate (60%) and monodentate (40%) in the SAM. In contrast, gold substrates produced by a process known as template-stripping (TS) provide an ultrasmooth surface, which consists of large but flat grains of ~200-500 nm, separated by shallow grain boundaries of ~1.5 nm.[3-6] In the SAMs that formed on TS gold, all the adsorbates chelate to the gold surface, the bidentate DTPA molecules prevent rotation about the Au-S bond and no changes in the Au-S-P bond angles.
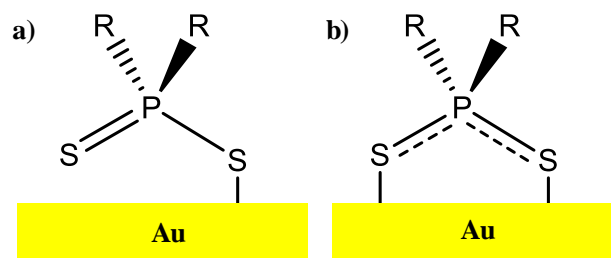
Scheme 3.1. Dialkyldithiophosphinic Acid bond to gold surface: a) monodentate and b) bidentate binding.

Our group has explored the use of chelating dialkyldithiophosphinic acids (R_2DTPA) to expand the understanding the relationship between adsorbate structure and SAM structure, as well as to access SAMs with new structures and interfacial properties.[7,8,9] Miller *et al.* published a study of SAMs formed from $(C_{16})_2$DTPA, which possess headgroups that are capable of either mono- or bidentate binding to a gold surface.[10] As mentioned above, As-Dep gold films consist of small grains and deep grain boundaries, which causes the some of the DTPA adsorbates to adopt monodentate binding. The monodentate binding allows rotation about the Au-S bond and small changes in the Au-S-P bond angle, enables the alkyl groups to pack densely in DTPA on As-Dep gold.[9,10] However, TS gold films consist of large and flat grains, so all the DTPA adsorbates can chelate to the surface. The resulting alkyl layer organization of DTPA SAMs on As-Dep gold DTPA is liquid-like and disordered because of a relative decrease in van der Waals interaction between the chains. As the chain length increases, the alkyl layer becomes more crystalline and ordered. While all the DTPA adsorbates chelate to the TS gold surface, which conflicts with the steric demands of the bulky DTPA headgroups, limits

the packing density as the alkyl chain length is increasing. Shortening the chain length can reduce the steric demand of the alkyl groups, and change the structure and packing density of the adsorbates in the SAM. So SAMs formed from adsorbate with short alkyl chain (n = 5) are ordered and crystalline, and the alkyl groups become increasingly disordered and liquid-like as the number of methylene units is increased. This trend is opposite to the behavior exhibited by DTPA SAMs on As-Dep gold substrates, in which the alkyl layer become more crystalline and ordered as the alkyl chain length is increased, in terms of flexibility of monodentate adsorbates and the increasing of van der Waals interactions between alkyl groups.

We introduce SAMs formed from branched symmetrical DTPA adsorbates, $(C_6C_2)_2DTPA$ and $(C_5C_1)_2DTPA$, which have the similar structure with $(C_6)_2DTPA$ studied in Miller's paper.[17] We study whether the branch alkyl chain can fill the empty space and have a higher packing density SAM on TS gold or the steric demands of the short alkyl chain play a role to result a liquid-like SAM. Using X-ray photoelectron spectroscopy (XPS), we establish that SAMs consist of bidentate adsorbates on TS gold and a mixture of mixture of bidentate (60%) and monodentate (40%) on As-Dep gold. We compare the alkyl chain organization of the DTPA SAMs to similar main chain length without the branched chain DTPA and analogous RSH SAMs on TS and As-Dep gold using reflection-adsorption infrared spectroscopy (RAIRS), contact angle measurements.

3.2. Experimental Section

All chemicals were purchased commercially and used as received. Anhydrous tetrahydrofuran and diethyl ether were obtained from an Innovative Technologies solvent purification system. Nuclear magnetic resonance (NMR) spectroscopic data were obtained and recorded on a Bruker Avance 300 MHz or a Bruker Avance 300 MHz Ultrashield at room temperature, and shifts are reported in parts per million (ppm). $^{31}P\{^1H\}$ NMR spectra were referenced externally to 85 % H_3PO_4 (δ = 0 ppm). ^1H NMR spectra were referenced to residual proton peaks of $CDCl_3$ (δ = 7.27 ppm). $^{13}C\{^1H\}$ NMR spectra were referenced to $CDCl_3$ (δ = 77.0 ppm).

3.2.1. Synthesis of Branched DTPAs

Synthesis of $(C_6C_2)_2P(O)H$ and $(C_5C_1)_2POH$ The Grignard reagent $(BrMgC_6C_2)$ or $(BrMgC_5C_1)$ (generated by refluxing the appropriate alkyl halide with Mg turnings in THF) was added in excess (~4 eq.) to a solution of diethyl phosphite and refluxed in THF for 48 h, described by Müller *et al.*[11] Subsequent quenching, extracting and rinsing were performed according to Guoxin *et al.*[12] to give the symmetrical phosphine oxide $(C_6C_2)_2P(O)H$ as a yellow oil at 20% yield and $(C_5C_1)_2P(O)H$ as a grey-yellow oil at 22% yield.

$(C_6C_2)_2P(O)H$: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz, 298 K): δ 31.09. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ 6.97 (d, $|^1J_{P-H}|$ = 445 Hz, PH), 1.78–1.30 (m, 4H, PCH$_2$), 1.57–1.50 (m, 2H, PCH$_2$CH), 1.40–1.12 (m, 16H, CH$_2$), 0.85–0.74 (m, 12H, CH$_3$).

$(C_5C_1)_2P(O)H$: ^{31}P {^1H} NMR (CDCl$_3$, 121 MHz, 298 K): δ 35.39. ^1H NMR (CDCl$_3$, 300 MHz, 298 K): δ 6.84 (d, |$^1J_{P-H}$| = 445 Hz, PH), 1.85–1.60 (m, 4H, PCH$_2$), 1.57–1.46 (m, 2H, CH), 1.34–1.16 (m, 8H, CH$_2$), 0.89–0.78 (m, 12H, CH$_3$).

Synthesis of Nickel Complexed (C$_6$C$_2$)$_2$DTPA and (C$_5$C$_1$)$_2$DTPA The reduction of phosphine oxide precursor (C$_6$C$_2$)$_2$P(O)H or (C$_5$C$_1$)$_2$P(O)H was performed according to Klaehn *et al.*[13] The oxidation with sulfur and the Ni complexation were performed according to Guoxin *et al.*[12] The Ni complex [(C$_6$C$_2$)$_2$P(S)S]$_2$Ni and [(C$_5$C$_1$)$_2$P(S)S]$_2$Ni were synthesized. The Ni complexes were then recrystallized in ethanol.

[(C$_6$C$_2$)$_2$P(S)S]$_2$Ni: ^{31}P {^1H} NMR (CDCl$_3$, 121 MHz, 298 K): δ 97.8.

[(C$_5$C$_1$)$_2$P(S)S]$_2$Ni: ^{31}P{^1H} NMR (CDCl$_3$, 121 MHz, 298 K): δ 97.7.

Synthesis of (C$_6$C$_2$)$_2$DTPA and (C$_5$C$_1$)$_2$DTPA The Ni was uncomplexed according to Guoxin *et al.*[12] by stirring with ethylenediaminetetraacetic acid (EDTA) overnight to yield the DTPA (C$_6$C$_2$)$_2$P(S)SH and (C$_5$C$_1$)$_2$P(S)SH at 6% and 4% overall yield, respectively.

(C$_6$C$_2$)$_2$P(S)SH: ^{31}P {^1H} NMR (CDCl$_3$, 121 MHz, 298 K): δ 70.1. ^1H NMR (CDCl$_3$, 300 MHz, 298 K): δ 2.11–1.97 (m, 4H, PCH$_2$), 1.65–1.50 (m, 2H, PCH$_2$CH), 1.43–1.17 (m, 16H, CH$_2$), 0.90–0.82 (m, 12H, CH$_3$). ^{13}C {^1H} NMR (CDCl$_3$, 75 MHz, 298 K): δ 44.3 (d, |J_{P-C}| = 37.7 Hz, 2C, PCH$_2$), 33.9 (d, |J_{P-C}| = 10.6 Hz, 2C, PCH$_2$CH), 29.3-25.9 (m, 8C, CH$_2$), 14.2 (s, 2C, CH$_3$), 10.5 (s, 2C, CH$_3$).

(C$_5$C$_1$)$_2$P(S)SH: ^{31}P {^1H} NMR (CDCl$_3$, 121 MHz, 298 K): δ 70.8. ^1H NMR (CDCl$_3$, 300 MHz, 298 K): δ 2.20–1.92 (m, 4H, PCH$_2$), 1.70–1.40 (m, 2H, CH), 1.40–1.18 (m, 12H, CH$_2$), 0.93–0.86 (m, 12H, CH$_3$). ^{13}C {^1H} NMR (CDCl$_3$, 75 MHz, 298 K): δ 44.2

(d, $|J_{P-C}|$ = 36.3 Hz, 2C, PCH_2), 33.9 (d, $|J_{P-C}|$ = 9.8 Hz, 2C, PCH_2CH_2), 29.7 (m, 2C, CH_2), 23.2 (s, 2C, CH) 14.5 (s, 2C, CH_3), 10.8 (s, 2C, CH_3).

3.2.2. Gold Substrate Preparation and SAM Formation

Template-stripped (TS) gold films were prepared according to published procedures.[2] 500 nm gold was deposited onto silicon wafers by e-beam evaporation, and then a small drop (10 μL) of Norland Optical Adhesive 83H was applied to the gold surface followed by a 2 cm × 2 cm glass substrate. After curing the adhesive using a UV lamp for 15 min, the glass slide was stripped from the silicon wafer using a scalpel. As deposited (As-Dep) gold films were produced by depositing 2 nm of titanium as an adhesion promoter onto silicon wafers, followed by 200nm of gold, using an electron-beam evaporator. Both As-Dep and TS gold films were used immediately after their fabrication for SAM formation to minimize surface contamination.

Approximately 2 cm × 2 cm TS and As-Dep gold substrates were immersed into a 1 mM SAM solution (**1** and **2**) in anhydrous toluene for 18-24 h. Substrates were then removed from solution, rinsed with anhydrous toluene and dried under a stream of nitrogen.

3.2.3. Characterization

Infrared Spectroscopy Reflection–absorption infrared (RAIR) spectra were collected using a Bruker IFS 66/v spectrometer in single reflection mode equipped with an mercury cadmium telluride (MCT) detector and Harrick Autoseagull accessory. The p-polarized light was incident at 85° from the surface normal, and 1024 scans were collected at a resolution of 2 cm^{-1}.

Contact Angle Measurements Water and hexadecane contact angles were measured using the sessile drop method on a Ramé-Hart contact angle goniometer equipped with a microliters syringe. In each case, contact angle measurements of at least three drops from three different samples were averaged.

X-ray Photoelectron Spectroscopy (XPS) XPS spectra were collected at Surface Science Western (London, Ontario, Canada) using a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromatic Al Kα source. The detection limit of the instrument is 0.1-0.5 atomic percent. Both survey scan and high-resolution analyses were carried out over a 300 μm×700 μm scan area. Survey scan analyses were carried out with a pass energy of 160 eV, and high-resolution analyses were carried out with a pass energy of 20 eV. Samples were analyzed at a 30º takeoff angle (60º tilt). High-resolution sulfur line shapes were fit using one pair of spin-orbit-split components (2 $p_{3/2}$ and 2 $p_{1/2}$) assuming a Gaussian/Lorentzian (70%:30%) line shape and a fixed splitting energy of 1.18 eV with a 2:1 area ratio.

3.3. Results and Discussion

3.3.1. Synthesis of Branched Alkyl DTPAs

For synthesis of **1** $(C_6C_2)_2P(S)SH$ and **2** $(C_5C_1)_2P(S)SH$, we performed a Grignard reaction using 4 equivalents **3** of the reactant with diethyl phosphite to form the phosphine oxide **4**. Reaction with diisobutylaluminium hydride (DIBAL-H) then generated the secondary phosphine, and oxidation with elemental sulfur provided the crude product **5**. We complexed the crude the product with $NiSO_4$, recrystallized the blue

oil **6** in diethyl ether and decomplexed the Ni^{2+} with EDTA in NH_4OH. The organic product was acidified with HCl to yield **1** and **2** in the 6% and 4% overall yield, respectively (Scheme 3.2).

The ^{31}P, ^1H and ^{13}C NMR spectra of compounds **1** and **2** are presented in supporting information (Figure S3.1 and S3.2).

For structure **1**: R1 = Ethyl, R2 = Ethyl and R3 = H
For structure **2**: R1 = H, R2 = Methyl and R3 = Methyl
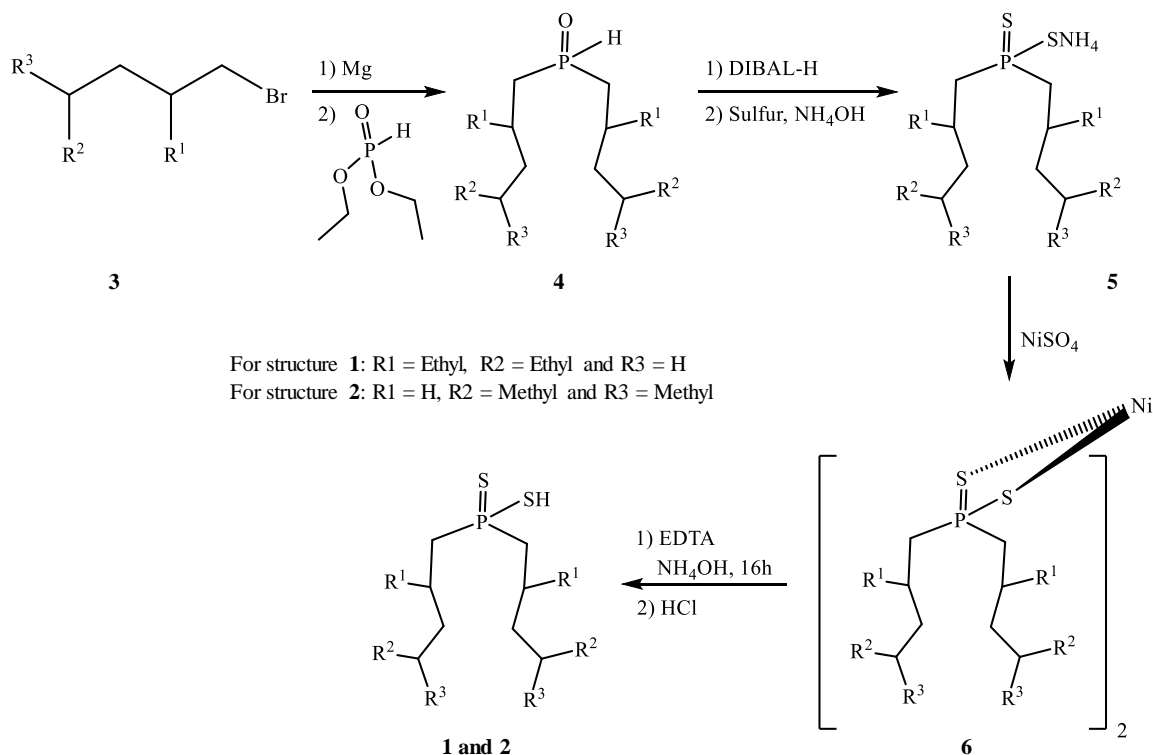
Scheme 3.2. Synthetic Procedure to prepare dialkyldithiophosphinic acids.

3.3.2. SAM Formation

We prepared gold films by electron-beam evaporation on silicon wafers with Ti adhesion layer (As-Dep gold) and Template-stripped (TS) gold films,[4] TS gold were made by evaporating 5000 Å gold on silicon wafer without an adhesion layer, a small

adhesive drop was applied to the gold surface followed by cleaned glass substrate, and cured the adhesive, stripped gold from the wafer. Then the As-Dep and TS gold films were used to prepare SAMs of these substrates by immersing the substrate into 1 mM solution of the DTPAs (**1** and **2**) in anhydrous toluene for 18-24 hrs. Substrates were then removed from solutions, rinsed with anhydrous toluene and dried under a stream of nitrogen.

3.3.3. Binding of the DTPAs Head Group to the Gold Surface

XPS survey scans of $(C_6C_2)_2$DTPA on the TS and As-Dep gold films detected carbon, sulfur, phosphorus and gold, consistent with SAM formation (Figure S3.3 and S3.4 in the supporting information). Oxygen was also detected in the survey scan. We used high-resolution XPS (HR-XPS) of the S 2p region to determine the binding state of the DTPA adsorbates to the gold surface. The electronic environment of the sulfur atom and the nature of the interaction between sulfur and gold surface atoms influence the S 2p binding energies. HR-XPS of the S 2p region can distinguish between sulfur atoms bound to gold (S $2p_{3/2}$ BE ~161–162 eV), sulfur species not interacting with gold (S $2p_{3/2}$ BE ~163–165 eV), and oxidized sulfur species (S $2p_{3/2}$ BE > 166 eV).[14,15]

HR-XPS spectra of the S 2p region of the DTPA SAMs on TS and As-Dep gold surfaces showed line shapes that we fit using one pair of S $2p_{3/2}$ and S $2p_{1/2}$ spin–orbit-split components by assuming a Gaussian/Lorentzian (70%:30%) line shape and a splitting energy fixed at 1.18 eV (Figure 3.1) and the data are summarized in Table 3.1.[16] The S $2p_{3/2}$ binding energies of the fitted peaks, assignments of these peaks, and the ratio of chemisorbed and non-interacting sulfur species for DTPA SAMs are shown in Table

3.1. The DTPA **1** SAM on As-Dep gold shows S $2p_{3/2}$ peak at ~161 eV corresponding to chemisorbed to gold through a gold-sulfur bond, and a non-interacting peak at ~163 eV, indicating monodentate adsorbates presented. This mixture of binding modes is consistent with previously reported SAMs of R_2DTPA and R^1R^2DTPA molecules on As-Dep gold.[1,4,5]

For the $(C_6C_2)_2$DTPA SAM on As-Dep gold, the chemisorbed sulfur:noninteracting sulfur ratio is approximately 70:30, corresponding to a bidentate:monodentate DTPA ratio of 40:60 (Figure 3.1 a). It has been demonstrated that the short hexyl chain does not block oxygen from penetrating the SAM,[9] however, it is interesting that the S 2p HR-XPS spectrum of the $(C_6C_2)_2$DTPA SAM on As-Dep gold does not show evidence of oxidized sulfur species, considering that oxidized sulfur species were detected in $(C_6)_2$DTPA.[9] It revealed that the branched ethyl chain on the hexyl chain helped to protect the sulfur atoms from oxidation better than single alkyl chain.

$(C_6C_2)_2$DTPA SAM on TS gold (Figure 3.1 b) showed the presence of only one type of sulfur atoms (chemisorbed sulfur), bonded to the gold surface, which means all the adsorbates are chelated to the TS gold surface. The absence of peaks at ~167–169 eV, due to oxidized sulfur species, is consistent with previous studies of R_2DTPA SAMs on TS gold, which showed all adsorbates chelate to gold surface and protected to headgroup from oxidation even for the shortest alkyl chain lengths (from C_6 to C_{16}).[17] On TS gold, chelation of the headgroup likely protect the headgroup from oxidation.
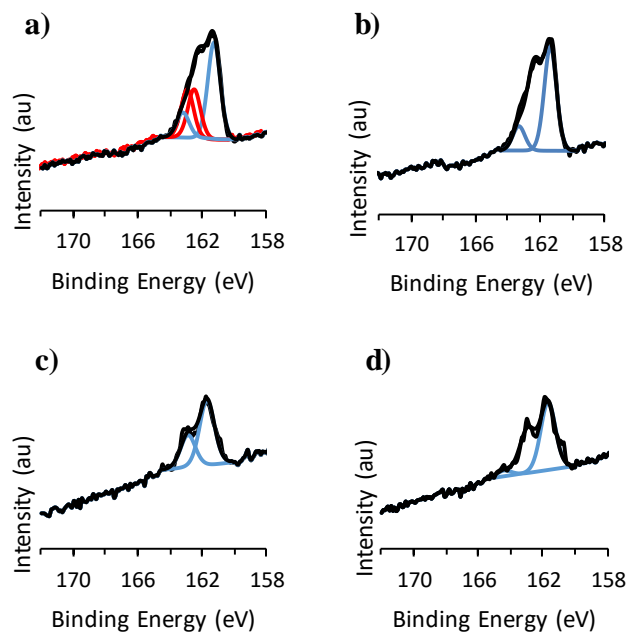
Figure 3.1. HR-XPS spectra of the S 2p region of $(C_6C_2)_2$DTPA (a,b) and C_6C_2SH (c,d) SAM on As-Dep gold (a,c) and TS gold (b,d).

	S 2p$_{3/2}$ Binding Energies (eV)			
	SAMs on As-Dep Gold		SAMs on TS Gold	
	$(C_6C_2)_2$DTPA	C_6C_2SH	$(C_6C_2)_2$DTPA	C_6C_2SH
Chemisorbed S (blue)	161.7	161.6	161.2	161.5
Non-interacting S (red)	162.4	-	-	-
Ratio of chemisorbed : non-interacting S	67:33	100:0	100:0	100:0

Table 3.1. S 2p$_{3/2}$ Binding Energy and the ratio of Chemisorbed : Non-interacting S species of $(C_6C_2)_2$DTPA and C_6C_2SH SAM on As-Dep and TS gold.

C_6C_2SH on As-Dep and TS gold shows the same results as the $(C_6C_2)_2DTPA$ on TS gold, only chemisorbed sulfur is observed and no oxidized sulfur (Figure 3.1 c and d). Because in thiolate SAMs, only one sulfur atom is presented in the molecule, which will always form a stable S-Au bond, no matter the gold surface is flat or with deep grains.

3.3.4. Organization of the Alkyl Chains

Reflection-absorption infrared (RAIRS) of SAMs provides information about the packing density, crystallinity and conformation of alkyl groups. By examining the frequencies of the asymmetric and symmetric methylene C-H stretches, we can assess the alkyl group crystallinity,[12] while the peak intensities in spectra of the C-H stretching are determined by two factors. One is the surface selection rule, where low methylene stretching intensities indicates less molecular tilt from the surface normal in the SAM. The second factor is that low density of alkyl chains results in low stretching intensities. The RAIRS spectra of the branched DTPA SAMs **1** and **2** on TS gold are shown in Figure 3.2, along with dashed lines at 2918 cm^{-1} and 2850 cm^{-1} that correspond to the peak positions of the $v_{as}(CH_2)$ and $v_s(CH_2)$ stretches for the crystalline chain of $C_{16}SH$ SAMs on gold for comparison. The organization of SAMs on TS gold shows that the short branched alkyl chain of both $(C_6C_2)_2DTPA$ and $(C_5C_1)_2DTPA$ SAMs are highly crystalline, which directly counters the $(C_6C_2)_2DTPA$ and $(C_5C_1)_2DTPA$ SAMs on As-Dep gold. The peak intensities of the SAM are low due to the presence of the few methylene groups. The methylene stretching frequencies of asymmetric and symmetric for SAMs **1** and **2** on TS and As-Dep gold are shown in Table 3.2.

The previous papers showed that on As-Dep gold, the DTPA adsorbates provide a mixture of bidentate (60%) and monodentate (40%) to underlying as the number of

45

methylene units in the chain increase, the crystallinity of the alkyl group increase.[9,18,19] But on TS gold, because all the headgroups bidentate to the gold surface in the SAM, these SAMs exhibit an unusual trend in alkyl chain crystallinity; SAMs formed from adsorbates with short alkyl chains (n=5) are ordered and crystalline, and the alkyl increasingly disordered and liquid-like as the number of methylene units is increased.[11] It seems that the branched ethyl or methyl group in the alkyl chain does not break the ordered packing of the SAMs. So we assume the headgroups of both $(C_6C_2)_2DTPA$ and $(C_5C_1)_2DTPA$ adsorbates bidentate to the gold surface, and the short branched alkyl chains might fill the space in the SAM to increase the packing density of adsorbates in the SAM, with crystalline packing, comparing to $(C_6)_2DTPA$ on TS gold.
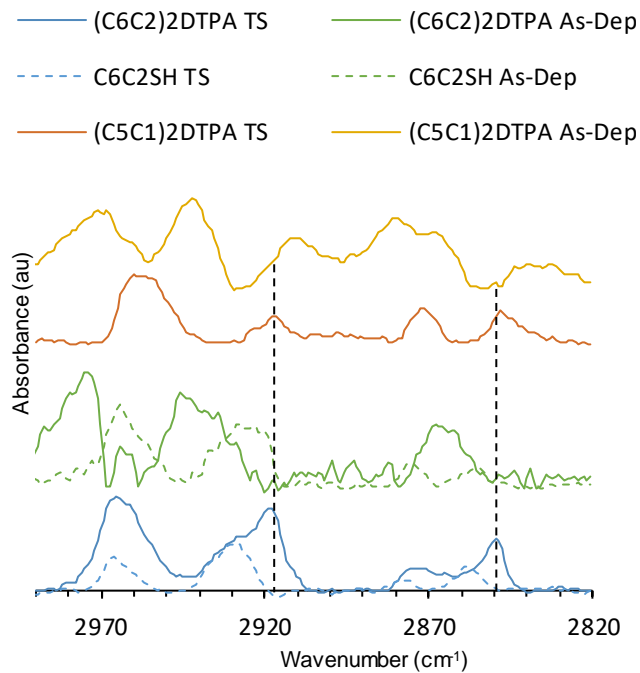
Figure 3.2. RAIRS spectra (2990-2820 cm^{-1}) of $(C_6C_2)_2$DTPA, $(C_5C_1)_2$DTPA and C_6C_2SH SAMs on As-Dep and TS gold. Dashed vertical lines indicate the positions of crystalline $\upsilon_{as}(CH_2)$ and $\upsilon_s(CH_2)$ of C_{16}SH SAMs on gold (2918 and 2850 cm^{-1}, respectively).

SAM	Peak Position (cm^{-1})	
	$\upsilon_{as}(CH_2)$	$\upsilon_s(CH_2)$
$(C_6C_2)_2$DTPA on TS Au	2918	2850
$(C_5C_1)_2$DTPA on TS Au	2917	2849
$(C_6C_2)_2$DTPA on As-Dep Au	2939	2865
$(C_5C_1)_2$DTPA on As-Dep Au	2941	2867
C_6C_2SH on TS Au	2927	2857
C_6C_2SH on As-Dep Au	2927	2855

Table 3.2. $\upsilon_{as}(CH_2)$ and $\upsilon_s(CH_2)$ peak positions of $(C_6C_2)_2$DTPA, $(C_5C_1)_2$DTPA and C_6C_2SH on TS and As-Dep gold.

	TS Gold			AsDep Gold		
	$(C_6C_2)_2$DTPA	C_6C_2SH	$(C_5C_1)_2$DTPA	$(C_6C_2)_2$DTPA	C_6C_2SH	$(C_5C_1)_2$DTPA
WATER						
Stationary	78° ± 3°	84°± 2°	81°± 1°	81° ± 1°	83° ± 2°	83°± 3°
Advancing	80° ± 5°	88° ± 1°	83°± 2°	83° ± 2°	82° ± 1°	87°± 4°
HEXADECANE						
	<15°	<15°	<15°	<15°	<15°	<15°

Table 3.3. Contact angles of water and hexadecane for $(C_5C_1)_2$DTPA, $(C_6C_2)_2$DTPA and C_6C_2SH SAMs on TS and As-Dep gold.

Hexadecane is more sensitive to small changes in the interfacial free energy due to its low surface tension, and the angles are all <15º with hexadecane. Hexadecane wets all these short-chain DTPA and thiol SAMs, which may result from that the hexadecane drop can penetrate the SAM and interact with the underlying gold.[19] The water contact angles of the $(C_6C_2)_2$DTPA, $(C_5C_1)_2$DTPA and C_6C_2SH SAMs (Table 3.3) have no big difference on both types of gold, θ_a (H_2O) is at the range of 80º - 87º. θ_a (H_2O) of $(C_6C_2)_2$DTPA SAM on TS gold is 80º, whereas the value is 87º on As-Dep gold, which is similar to that of C_6C_2SH on gold. This difference can be explained by the structure difference between $(C_6C_2)_2$DTPA on TS and As-Dep gold from RAIRS. However, all the adsorbates have short alkyl chains, the water can penetrate the SAM, like hexadecane, and result the hydrophilic SAMs.

3.4. Conclusions

We have shown that the synthetic flexibility of DTPA molecules permits synthesis of new DTPA adsorbates **1** $(C_6C_2)_2$DTPA and **2** $(C_5C_1)_2$DTPA. The branched $(C_6C_2)_2$DTPA SAMs bind exclusively in bidentate fashion on TS gold and exhibit mixed bidentate and monodentate binding modes on As-Dep gold. SAMs formed from adsorbate **1** on TS gold exhibit an ordered and crystalline alkyl layer, in contrast, it is liquid-like on As-Dep gold. The contact angles of the short branched DTPA SAMs on gold are very close, but can still prove the DTPA SAM structure difference between As-Dep and TS gold.

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3.7. Supporting Information

July 8
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31P 1D
300US

~70.08

BRUKER
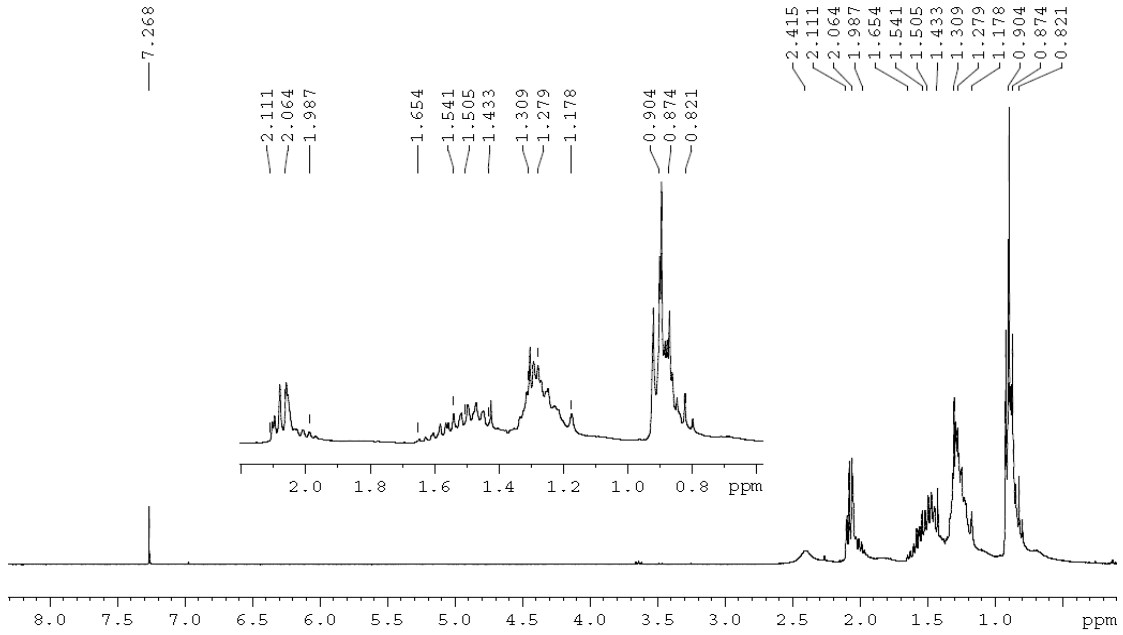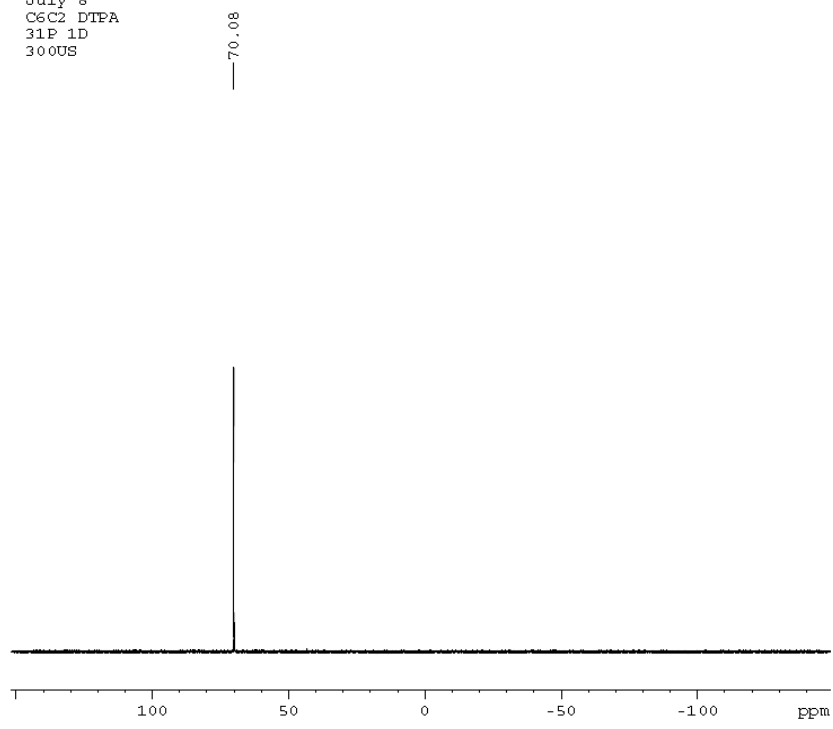
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FIDRES   1.113780 Hz
AQ   0.4489716 sec
RG   26008
DW   13.700 usec
DE   6.00 usec
TE   296.1 K
D1   1.00000000 sec
D11   0.03000000 sec
TD0   1

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PL1   0.00 dB
SFO1   121.4949575 MHz

======== CHANNEL f2 ========
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PCPD2   80.00 usec
PL2   0.00 dB
PL12   17.16 dB
PL13   24.00 dB
SFO2   300.1312005 MHz
SI   32768
SF   121.4947739 MHz
WDW   EM
SSB   0
LB   1.00 Hz
GB   0
PC   1.40

53

Ethylhexyl DTPA
1D 13C
DPX300

77.50
77.08
76.65
44.50
44.01
34.49
33.09
29.39
28.46
27.40
27.35
25.90
14.20
10.48

BRUKER

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NUC2   1H
PCPD2   70.00 usec
PL2   0.00 dB
PL12   14.30 dB
PL13   19.31 dB
SFO2   300.2323000 MHz

F2 - Processing parameters
SI   32768
SF   75.4928917 MHz
WDW   EM
SSB   0
LB   2.00 Hz
GB   0
PC   1.40

Figure S 3.1. ^{31}P, ^{1}H and ^{13}C NMR of (C$_6$C$_2$)$_2$DTPAs.

54

C5C1 DTPA
20160715
1H 1D

7.276

2.120
2.113
2.096
2.076
1.599
1.582
1.575
1.557
1.533
1.513
1.488
1.466
1.443
1.320
1.309
1.295
1.263
1.245
1.221
1.198
0.938
0.919
0.913
0.902
0.895
0.888
0.865
0.841
0.816

2.2 2.0 1.8 1.6 1.4 1.2 1.0 ppm

7   6   5   4   3   2   1   0   ppm

4.000   2.409   12.211   12.330
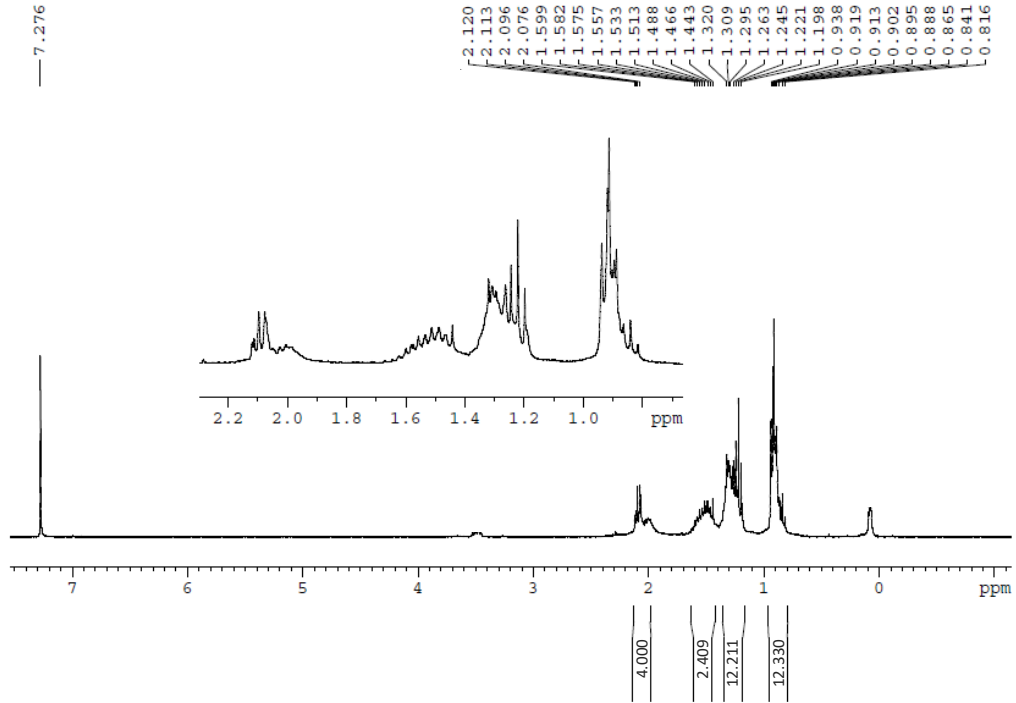
C5C1 DTPA
20160715
31P 1D

70.77

BRUKER
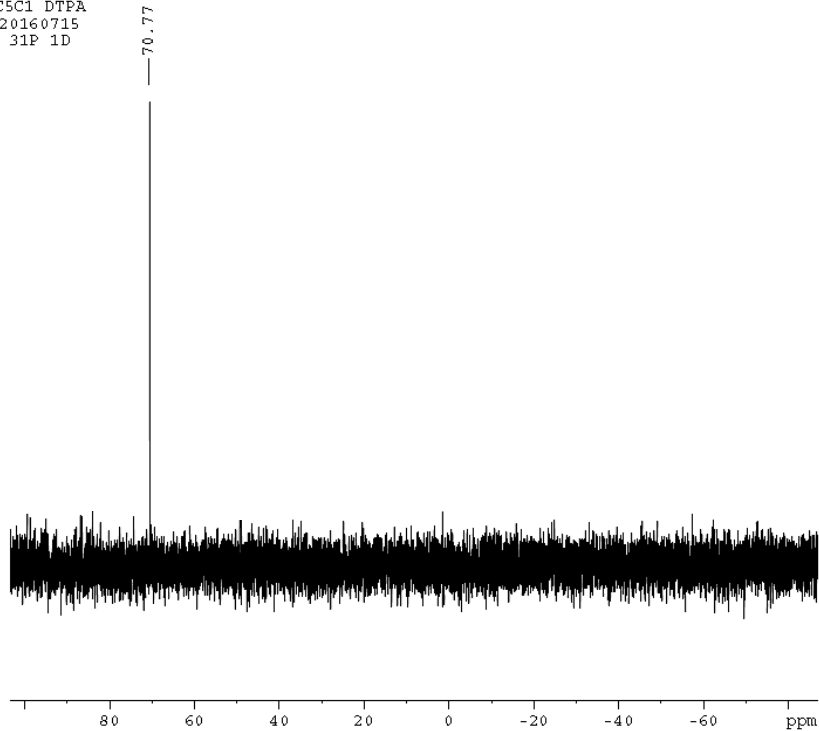
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EXPNO   1
PROCNO   1
Date_   20160715
Time   15.26
INSTRUM   spect
PROBHD   5 mm PABBO BB-
PULPROG   zgpg30
TD   32768
SOLVENT   C6D6
NS   256
DS   0
SWH   36496.352 Hz
FIDRES   1.113780 Hz
AQ   0.4489716 sec
RG   41285.1
DW   13.700 usec
DE   6.00 usec
TE   294.3 K
D1   1.00000000 sec
D11   0.03000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   31P
P1   10.85 usec
PL1   0.00 dB
SFO1   121.4949575 MHz

======== CHANNEL f2 ========
CPDPRG2   waltz16
NUC2   1H
PCPD2   80.00 usec
PL2   0.00 dB
PL12   17.16 dB
PL13   24.00 dB
SFO2   300.1312005 MHz
SI   32768
SF   121.4947696 MHz
WDW   EM
SSB   0
LB   1.00 Hz
GB   0
PC   1.40

80   60   40   20   0   -20   -40   -60   ppm
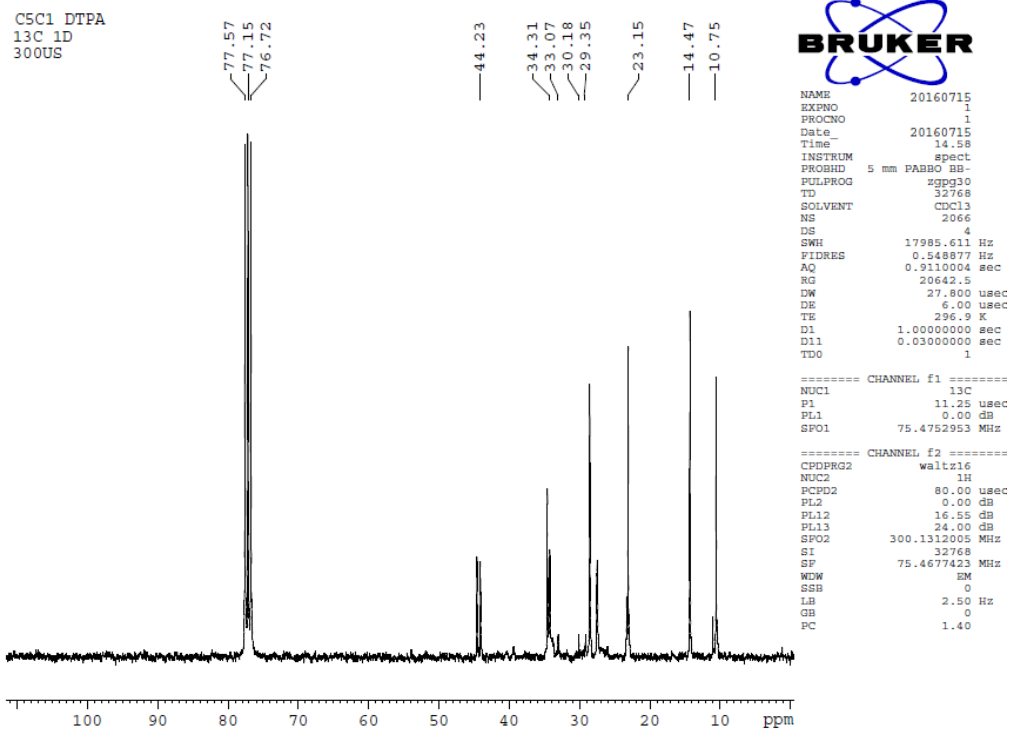
Figure S 3.2. ^{31}P, ^{1}H and ^{13}C NMR of $(C_5C_1)_2DTPAs$.
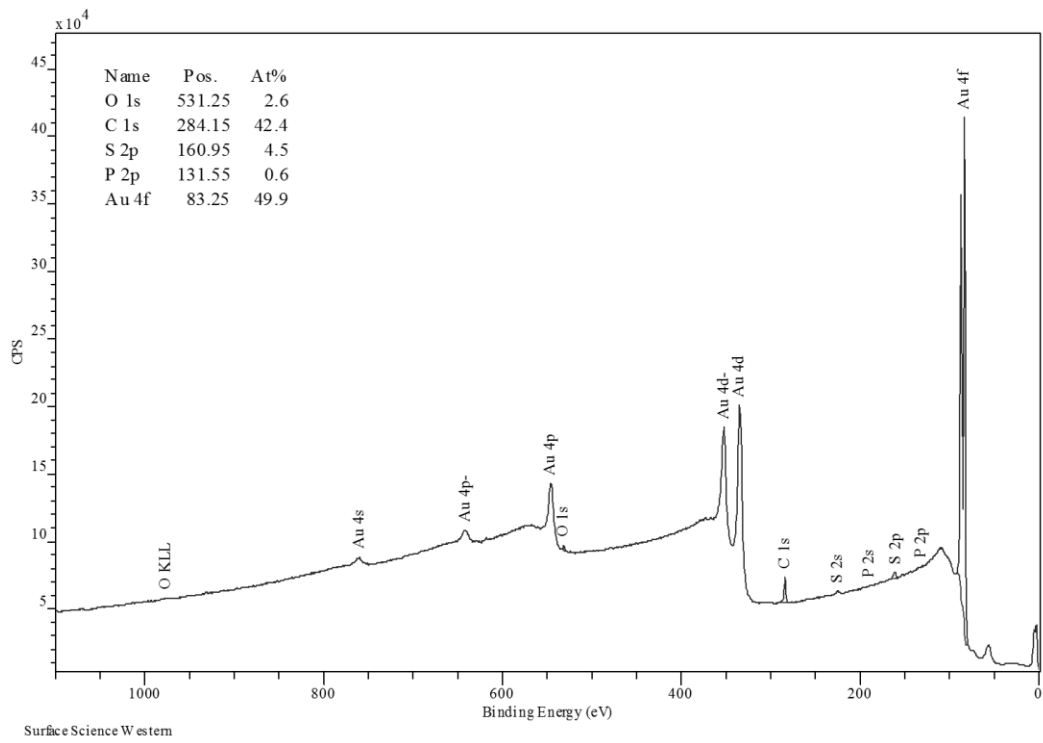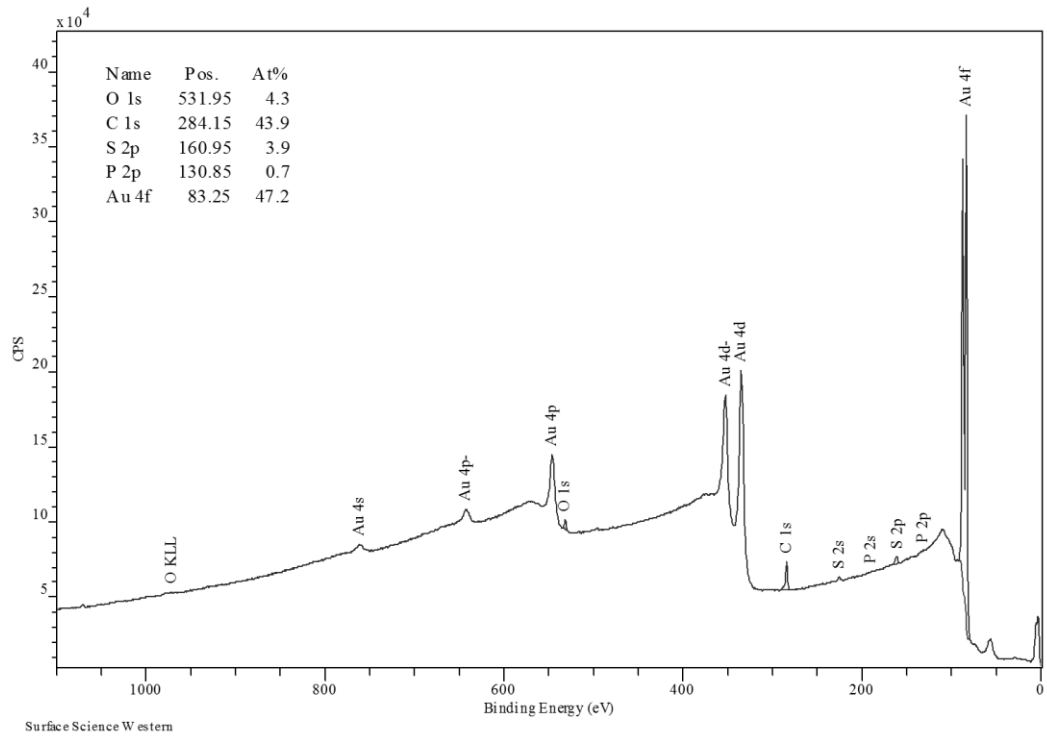
Figure S 3.3. XPS survey spectra of $(C_6C_2)_2$DTPAs on TS (top) and As-Dep (bottom) gold.
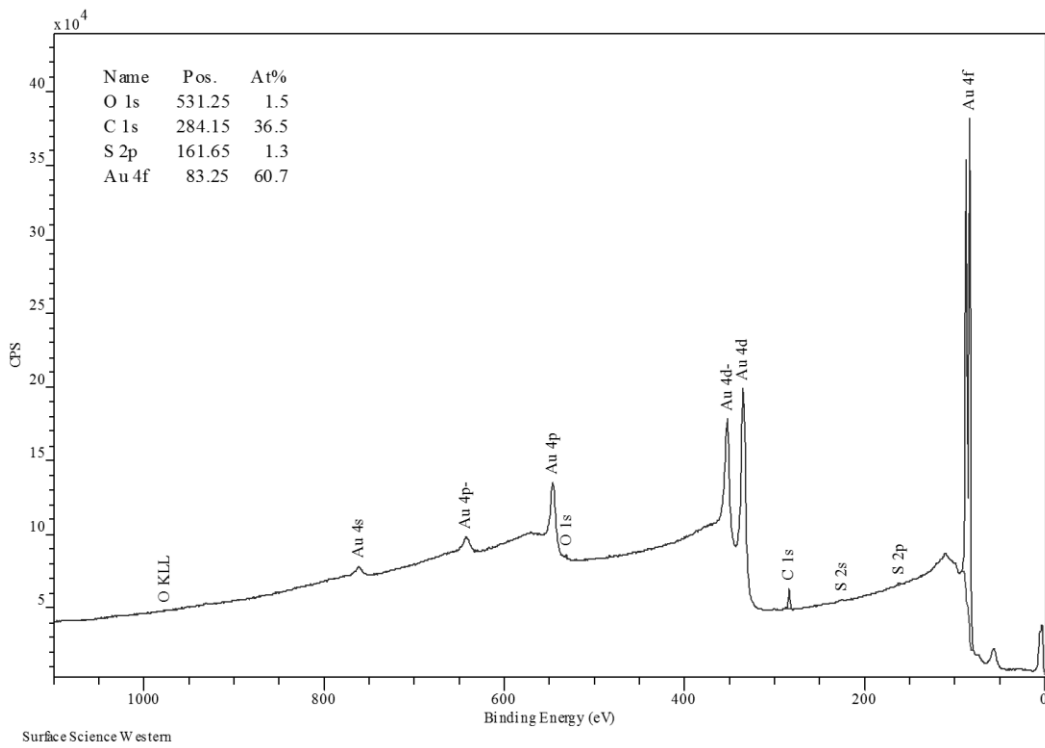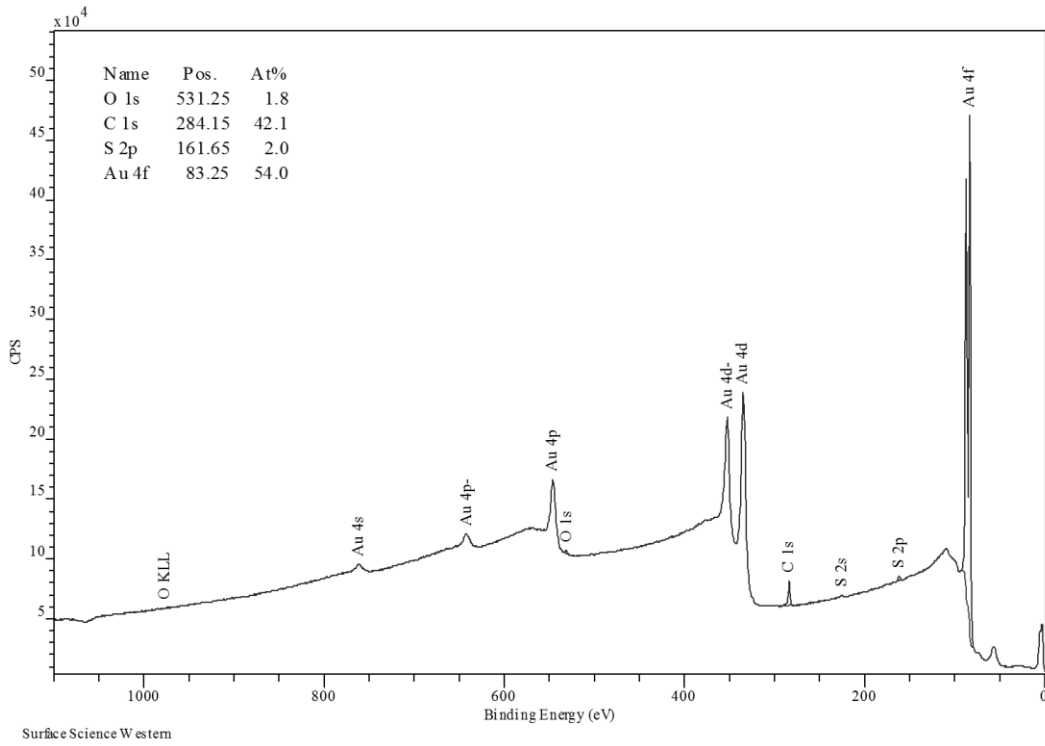
Figure S 3.4. XPS survey spectra of C_6C_2SH on TS (top) and As-Dep (bottom) gold.

Chapter 4

Stretchable Gold Film on Modified Silica Nanoparticles

4.1. Introduction

The development of stretchable electronics is very promising for the application in ultrathin electronic skin sensor, soft robotics[1-4] and human-machine interfaces,[5,6,7] which can withstand high elongation without significant changes to their electrical performance. One remarkable application is using the smart artificial skin with integrated stretchable sensors to cover a prosthetic hand, allowing the wearer to feel pressure between a soft touch and a firm handshake.[8,9]

The high conductivity of gold makes it ideal to be used as a conductor in comparison to the other frequently used materials, such as carbon nanotubes and graphene. Besides, gold is desirable in the soft electronics field since it is inert and will not be oxidized, which allows the devices to last longer. A free-standing metal film is inherently non-stretchable, electrically failing at 1-2% elongation. Deposit gold film on soft elastomeric substrates, such as polydimethylsiloxane (PDMS), can suppress the strain localization, which makes it possible to induce stretchability on the conductor. The challenge is that as the stretchability is increasing, the conductivity of the metal is decreasing rapidly, due to the cracks that propagate across the metal film as it is elongated and interrupt the conductive pathway. The distinction between methodologies to increase the stretchability of the elastomeric PDMS substrate is whether cracking is avoided or not. The first method, which is where cracking is avoided, can convert tensile strain applied to the film to bending strains of buckles on patterned serpentines. Pre-strained (stretch substrate at a certain strain before metal deposition and then release), buckled surface and serpentine routings[10-13] remain at low resistance up to a critical strain point, by accommodating the strain by flattening buckles or straightening the serpentines.[14] The resistance increases

dramatically beyond the critical strain point, due to the propagation of long cracks that interrupt the conductive pathway, which is a challenge for large-scale elongation. Mogul-patterned surface[15] can be reached by soft lithography to generate a maximum density of peak-valley hexagonal structure. The applied strain on the substrate can be efficiently absorbed by straitening the mogul-patterned structure, resulting in minimal interference with motion-induced stress. The second method is where cracking is permitted, Lacour *et al.* have identified stretchable metal with microcracks, where the metal network twists and deflects out of plane but remains bonded to substrate, and conductive up to 32% strain.[16] Several other methods that have been reported by changing the surface topography to affect the strain localization and create a favorable cracking pattern. Even when cracks form after stretching, the sample can still remain conductive. Sand-blasting and surface-etching can also reach a rough surface to preserve the conduction up to large strain.[17] Metal films on micropillar array PDMS substrate exhibit high electrical conductivity and can stretch reversibly to 20% without failing electrically. In which the cracks seem to start or stop at the closest pillar base at site of local strain maxima, the cracks widen but do not propagate at higher strain, and additional narrower cracks appear in between the pillars.[18] When metal films are deposited on pyramidal nanopatterned surfaces, the nanopatterned localize the microcracks that are formed during stretching, resistance increase by only 60% at 25% strain.[19] But these surface topography methods involve photolithography or chemical etching, which makes the fabrication process complicated.

Our group demonstrated the cracking permitted approach by creating topographical features on the surface of PDMS that provided numerous sites for strain localization in a

gold film deposited on the surface. Our method used spin-coating to deposit an aqueous emulsion of poly(vinyl acetate) (PVAc) – common, commercially available white glue diluted in water – onto an oxidized PDMS surface. The density of the PVAc globules depends on the concentration of the glue in the emulsion. From the three different dilutions (1:1, 3:1, and 5:1 v/v water:glue) that we tested, the diameter of the PVAc cluster range from ~ 40 µm to < 1 µm, and a film thickness from 3.5 µm to ~ 2 µm in height. When coated with gold, the least diluted structure (PDMS/glue$_{1:1}$) remains remarkably conductive up to 65% elongation, with an increase in resistance to only 23x the initial resistance of the film.[20]

Instead of the micro-structured PVAc glue, this paper uses MPTMS modified silica nanoparticles embedded in PDMS as an interlayer between gold film and the PDMS elastomeric substrate. After the gold deposition, these silica-based structures show an increase in resistance of 32x the initial resistance at 80% elongation. We further demonstrated that by altering the weight ratio of MPTMS modified silica:PDMS interlayer, the resistance change can be tuned, which leads to different functional samples.

4.2. Experimental Methods

Poly(dimethylsiloxane) (PDMS) (Sylgard 184) was obtained from Dow Corning, Midland, MI. Fumed silica (Aerosil 200) was obtained from Evonik Industries, Parsippany, NJ. All other chemicals were obtained from Sigma-Aldrich and were used as received.

Preparation of PDMS Substrates PDMS (Dow Corning Sylgard 184) was prepared by mixing a 10:1 w/w ratio of prepolymer : curing agent, followed by degassing under vacuum to remove the bubbles. A smooth PDMS surface was obtained by casting 15 g of the mixture against a 9 cm diameter polystyrene Petri dishes and curing at 60 ℃ for at least 1 h.

Oxidation of Substrates PDMS substrates were exposed to an air plasma at medium discharge setting for 30 seconds at an air pressure of 10 psig (flow rate of 32 mL/min). (Harrick Plasma PDC32-G coupled to a PlasmaFlo gas flow mixer).

Preparation of Nano-interlayer Fumed silica was modified by mixing a 1 : 1 w/w ratio of fumed silica : 3-mercaptopropy-l-trimethoxysilane in toluene at 70 ℃ overnight. The solution was centrifuged at 3300 rpm for 15 mins to isolate the modified silica nanoparticles, which were dried in a vacuum oven at 100 ℃ for 6 h. Solutions of MPTMS-modified silica and PDMS were prepared by suspending the desired amount of MPTMS-modified silica (0.17 g, 0.26 g, 0.38 g, 0.50 g and 0.82g for 10%, 15%, 20%, 25% and 30%, respectively) in 10 mL n-hexane, and 1.50 g of a 10:1 w/w ratio of prepolymer : curing agent PDMS was then added into the modified silica suspension. Oxidized PDMS substrates were then spin coated with the MPTMS modified silica/PDMS mixture in hexane at 2000 rpm for 1 minute (Laurell Technologies WS-400A-6NPP). The resulting PDMS$_{Si}$ substrates were cured in the oven at 60 ℃ for at least 1 h.

Deposition of Metal Layer An e-beam evaporator was used to deposit 30 Å titanium, followed by 250 Å gold, onto oxidized MPTMS/silica/PDMS samples at a rate of 0.3 Å/s and 1 Å/s respectively under high vacuum (10^{-6} mbar).

Characterization Optical characterization was performed using an Olympus BX51 microscope and stereo microscope (Leica MZ6) both equipped with an Olympus Q-Color3 digital camera. A micro-vice stretcher (S.T. Japan, USA, Inc.) was mounted to the microscope stage and samples were clamped in the stretcher to obtain microscope images of stretched samples. AFM images were obtained using a Digital Instruments Multimode atomic force microscope in tapping mode. A silicon cantilever was used with a nominal tip radius of 10 nm, resonance frequency of 300 kHz and a nominal spring constant of 40 N/m. The AFM images were collected from three spots on each sample in an area of 10 μm × 10 μm using a scan rate of 1.0 Hz with a scanning resolution of 512 samples per line. Images were collected using Nanoscope 6 software and processed using WSxM 5.0 Develop 8.2 software.[21] Electrical characterization was performed using a Keithley 2601A source meter. Gallium-Indium (EGaIn) (~0.01mL) was first deposited by syringe to the corners (for sheet resistance) or ends (for resistance measurements) of the gold surface to facilitate electrical contact. Data sets consisted of a minimum of three samples, and the average was reported. For electrical measurements under strain, samples were clamped in a micro-vice stretcher (S.T. Japan, USA, Inc.) and the resistance was measured at 5% strain intervals increments.

4.3. Results and Discussion

Pyrogenic (fumed) silica is a nanoparticle (particle size: 12 nm) which is produced by the hydrolysis of alkylchlorosilane in an O_2/H_2 flame between 1200 and 1600°C and has a high surface area covered by silanol groups. This hydrophilic surface does not mix well with the hydrophobic PDMS polymer matrix.[22] The surface modification of silica with an organosilane, such as 3-aminopropyl-trimethoxylsilane, 3-methacryloxypropyl-trimethoxylsilane, ethyl triethoxysilane, octyl triethoxysilane and 3-mercaptopropyl-trimethoxysilane,[23,24,25] reduces the number of the superficial silanol groups, by grafting molecules with an organic nature. In this way, these silane coupling agents increase the surface hydrophobicity, therefore improving the Van der Waals interactions between the modified silica particles and PDMS polymer to achieve better dispersion. 3-methacryloxypropyl-trimethoxylsilane (MAPTMS) and 3-mercaptopropyl-trimethoxysilane (MPTMS) have less hydrophilic terminal groups then the other silane agents and MPTMS appears to be the most reactive by TGA analyses.[26]

The fumed silica was modified by stirring with the MPTMS coupling agent in toluene at 70 °C. Solution of different weight of modified silica (0.17 g, 0.26 g, 0.38 g, 0.50g and 0.82 g) and 1.5 g uncured 10:1 w/w ratio of prepolymer : curing agent PDMS were prepared in n-hexane. We then spin-coated these solutions onto cured PDMS substrates that were oxidized to enable wetting, and cured in the oven to get $PDMS_{xSi}$ samples ($PDMS_{xSi}$, where x = 10%, 15%, 20%, 25% and 30%, for different weight ratio of modified silica : PDMS). The dark-field optical micrographs of $PDMS_{xSi}$ samples show that the modified silica nanoparticles appear to form micron-scale clusters within the

PDMS/modified silica layer, coated on the PDMS surface (Figure 4.1). The density of the clusters depends on the concentration of silica nanoparticle in the PDMS mixture.
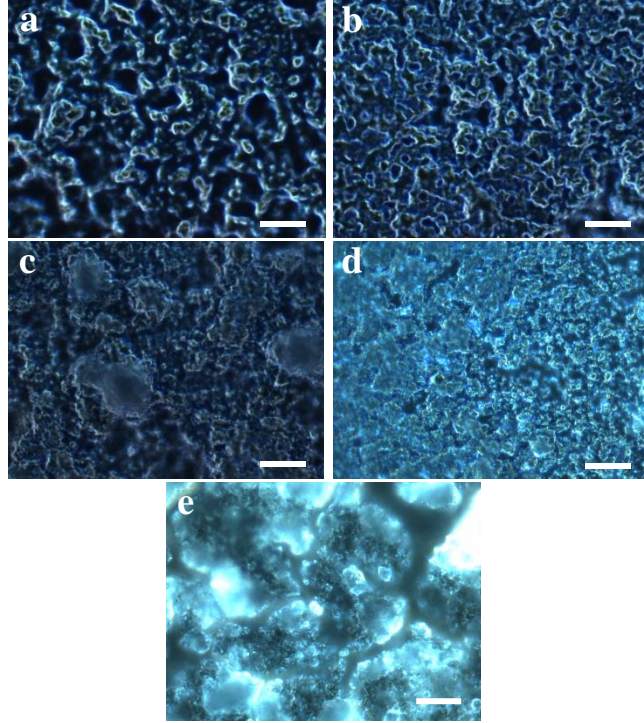
Figure 4.1. Dark-field optical micrographs of PDMS$_{10Si}$ (a), PDMS$_{15Si}$ (b), PDMS$_{20Si}$ (c), PDMS$_{25Si}$ (d) and PDMS$_{30Si}$ (e) samples before Au deposition. Scale bar –20 μm.

We used AFM to characterize the surface morphology. Figure 4.2 shows the images of PDMS$_{xSi}$ samples with cross sections. At the lowest concentrations of silica (PDMS$_{10Si}$), the surface consists of micron-scale clusters of modified silica which are separated by voids (bare regions with no topography) (Figure 4.2 a). Increasing the weight percentage of modified silica to 15% and 20% does not appreciably increase the cluster sizes, but the clusters on the surface increases as the weight percentage of modified silica increases

(overlapping clusters) (Figure 4.2 b, c). The optical and AFM images of these two samples (PDMS$_{15Si}$ and PDMS$_{20Si}$) both show a more agglomerated micron-scale clusters of modified silica covered onto the surface. For the PDMS$_{25Si}$ sample, it seems that the modified silica just covers the whole surface but with little cluster overlapped on top gives a rougher surface (Figure 4.2 d). At the highest concentration of silica, PDMS$_{30Si}$ sample (Figure 4.2 e), the surface of the substrate is covered with too much modified silica, which aggregates together to form big clusters over the homogenously bottom modified silica layer throughout the sample.
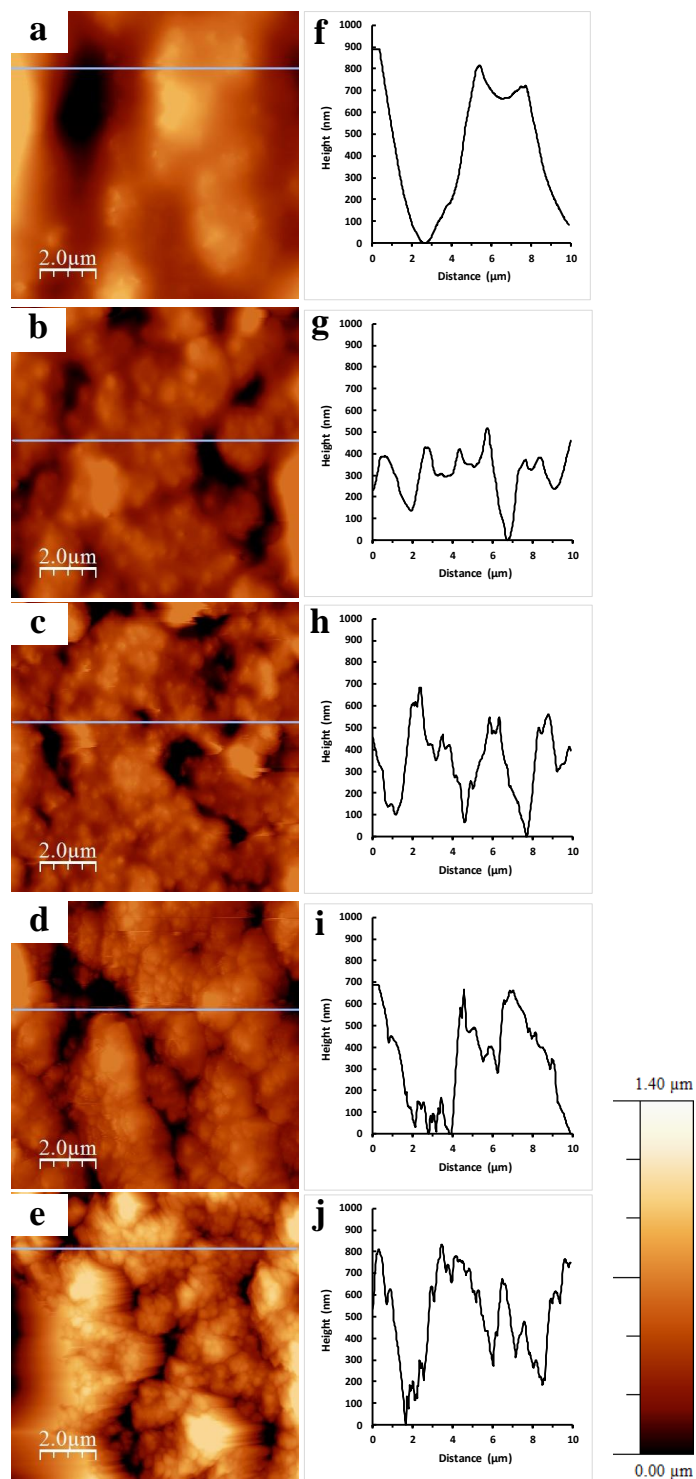
Figure 4.2. AFM images (a-e) and cross section (f-j) of PDMS$_{10Si}$ (a, f), PDMS$_{15Si}$ (b, g),

PDMS$_{20Si}$ (c, h), PDMS$_{25Si}$ (d, i) and PDMS$_{30Si}$ (e, j) samples before Au deposition.

The AFM image that we took has a geometrical area of 10 µm × 10 µm, but the actual topographical surface area is larger than the geometrical area. The developed interfacial area ratio (S_{dr}) is the percent increase in topographical surface area compared to the geometrical area. It expresses the roughness and density of topographical features on the surface. As more modified silica particles are added to the PDMS surface by increasing the modified silica weight percentage in the surface layer, the larger value it will be for the S_{dr}.

Sample	RMS Roughness (nm)		S_{dr} (%)	
	Without Au	With 250 Å Au	Without Au	With 250 Å Au
PDMS$_{10Si}$	105.8 ± 21.1	106.7 ± 6.8	8.2 ± 2.4%	6.2 ± 1.1%
PDMS$_{15Si}$	177.7 ± 31.5	169.1 ± 39.1	13.3 ± 1.8%	14.3 ± 0.9%
PDMS$_{20Si}$	180.4 ± 39.1	230.6 ± 62.9	26.5 ± 6.3%	27.5 ± 5.5%
PDMS$_{25Si}$	212.7 ± 42.3	268.3 ± 40.7	36.7 ± 11.8%	39.6 ± 2.0%
PDMS$_{30Si}$	328.4 ± 50.5	275.5 ± 30.6	52.1 ± 6.1%	49.7 ± 5.9%

Table 4.1. RMS roughness S_{dr} value of PDMS$_{xSi}$ samples with and without Au deposition.

The PDMS$_{10Si}$ sample has root-mean-square roughness of 105.8 ± 21.1 nm, S$_{dr}$ value of $8.2 \pm 2.4\%$ and peak-valley distance of 900 nm, with agglomerates as large as ~ 24 μm in diameter (Figure 4.1 a and 4.2 a, f).

As weight percentage of modified silica increases (15–30%), the topography becomes more detailed and complex, with layered micron-scale clusters. The entire surface of these samples is coated with modified silica micron-scale clusters. Peak-valley distances of the samples decrease to < 550 nm. All the clusters are < 16 μm in diameter on PDMS$_{15Si}$ sample; on PDMS$_{20Si}$ sample, the clusters are < 24 μm in diameter (Figure 4.1 b, c and Figure 4.2 b, g and c, h). These two samples (PDMS$_{15Si}$ and PDMS$_{20Si}$) have very similar RMS roughness and surface topography referring to Table 1, although more modified silica is coated for the PDMS$_{20Si}$ sample (larger S$_{dr}$ value, $26.5 \pm 6.3\%$ for PDMS$_{20Si}$ and $13.3 \pm 1.8\%$ for PDMS$_{15Si}$). The size of the clusters is < 40 μm for PDMS$_{25Si}$ (Figure 4.1 d), with the peak-valley distance ~ 690 nm (Figure 4.2 d, i) and a root-mean-square roughness of 212.7 ± 42.3 nm (Table 4.1). At the highest concentration of PDMS$_{30Si}$ sample, the size of the cluster ranges in diameter from ~ 60 to < 16 μm (Figure 4.1 e), with a peak-valley distance of ~ 850 nm (Figure 4.2 e, j) and a root-mean-square roughness of 328.4 ± 50.5 nm, S$_{dr}$ % value of $52.1 \pm 6.1\%$ (Table 4.1). In this paper, the S$_{dr}$ value presents the progress of the sample features as the concentration of modified silica increases (Table 4.1). As the modified silica concentration goes from 10% to 30%, the S$_{dr}$ values increase from $\sim 8\%$ to $\sim 52\%$, which means the actual surface area is increasing due to the greater percentage of particles at the surfaces. So as the concentration of modified silica increases, the RMS roughness and S$_{dr}$ values increase.

We used an e-beam evaporator to coat $PDMS_{xSi}$ surfaces with a 30-Å-thick layer of titanium as an adhesion promoter followed by a 250-Å-thick layer of gold. AFM images show that the metal coats the surfaces with topographical features that are indistinguishable from those of unmetallized $PDMS_{xSi}$ surfaces (Figure S4.1). The RMS roughness and S_{dr} % value for each $PDMS_{xSi}$ sample before and after gold deposition are also similar (Table 4.1). However, optical images of the $PDMS_{xSi}/Au$ samples (Figure 4.3) show that there are cracks formed during the deposition of gold onto the $PDMS_{30Si}$ sample. The high concentration of modified silica nanoparticles can produce an extremely rough and brittle surface, which may crack due to the expansion of PDMS from heating during the gold evaporation process. In addition, the $PDMS_{25Si}/Au$ sample has some cracks (smaller than $PDMS_{30Si}/Au$) which might be why the sheet resistance value (R_s) is higher than the lower weight percentage sample ($PDMS_{20Si}/Au$) (Table 4.2). Photographs of the resulting gold films are shown in Figure 4.4. Increasing the percentage of silica increases the roughness and texturing of $PDMS_{xSi}/Au$ samples, which changes the reflective and scattering properties of the surface.
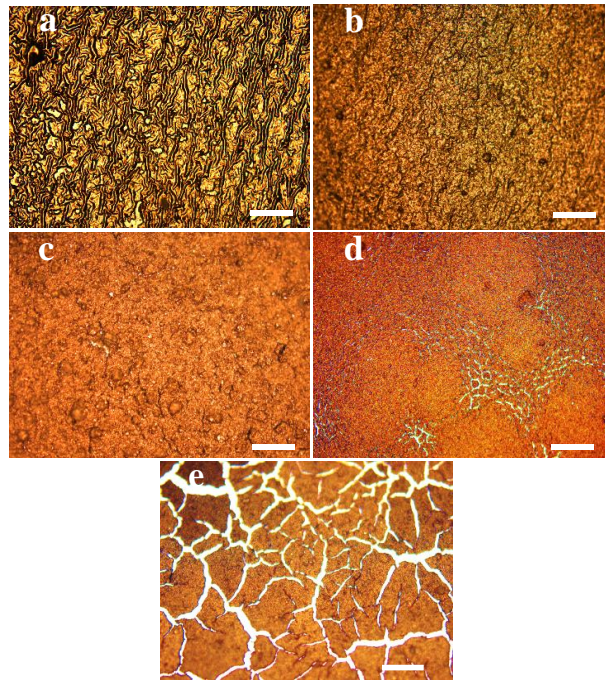
Figure 4.3. Optical images of PDMS$_{xSi}$/Au samples captured without stretch PDMS$_{10Si}$/Au (a), PDMS$_{15Si}$/Au (b), PDMS$_{20Si}$/Au (c), PDMS$_{25Si}$/Au (d) and PDMS$_{30Si}$/Au (e). Scale bar – 200 μm.
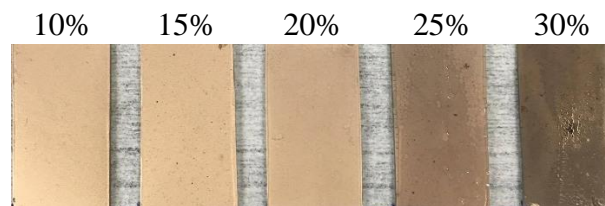
Figure 4.4. PDMS$_{xSi}$/Au sample images.

Sheet resistance (R_s) is not measurably affected by the topography difference for PDMS$_{10-20Si}$/Au samples. While the rougher sample (PDMS$_{30Si}$/Au) has a slightly larger R_s value, the PDMS$_{30Si}$/Au sample is not conductive at all (Table 4.2). From the results of the sheet resistance measurement and optical images, we chose PDMS$_{25Si}$ as the upper concentration limit.

Substrate	R_s ($\Omega/\square$)
PDMS$_{10Si}$/Au	1.2±0.5
PDMS$_{15Si}$/Au	0.6±0.2
PDMS$_{20Si}$/Au	0.8±0.03
PDMS$_{25Si}$/Au	1.8±0.2
PDMS$_{30Si}$/Au	GΩ

Table 4.2. Sheet resistance (R_s) of 250-Å-thick-gold PDMS$_{xSi}$ samples.

We stretched all the PDMS$_{xSi}$/Au samples under microscope, it showed that the topography of the nano-interlayer on PDMS substrates changes how the cracks initiate and propagate. Optical microscope images of PDMS$_{10-25Si}$/Au samples taken at 5%, 50% and 70% strain (Figure 4.5) show a trend that the rougher the topography is, the more sites are for strain localization and new crack nucleation.
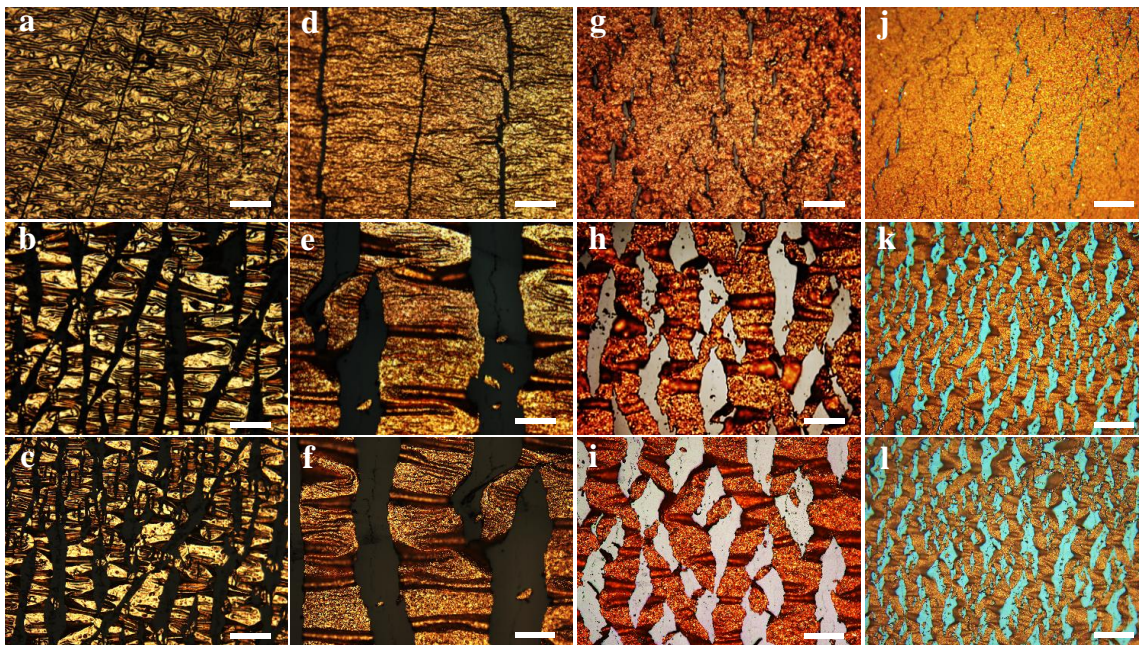
Figure 4.5. Evolution of cracks on PDMS$_{xSi}$/Au samples with stretching. Optical images captured at 5% (top), 50 % (middle) and 70% (bottom) strain for PDMS$_{10Si}$/Au (a-c), PDMS$_{15Si}$/Au (d-f), PDMS$_{20Si}$/Au (g-i) and PDMS$_{25Si}$/Au (j-l) samples. In all images, the samples were stretched in the horizontal direction. Scale bar – 200 μm.

From the stretching images of PDMS$_{10Si}$/Au and PDMS$_{15Si}$/Au samples (Figure 4.5), there are narrow and long cracks propagated through half the field of a 10x microscope objective, which is ~ 700 μm in length, at low strain of 5%. For PDMS$_{10Si}$/Au sample, the number and width of cracks increases with further elongation to 70%, but the long cracks fail to propagate at a certain site in the metal film, resulting in more individual cracks rather than fewer long cracks. The cracks in PDMS$_{15Si}$/Au are observed to be transitioning from those appearing in PDMS$_{10Si}$/Au to those in PDMS$_{20Si}$/Au. This may

be a result of the intermediate distribution of strain-relieving locations in the surface of the film creating a unique intermediate morphology.

The cracks that formed by $PDMS_{20Si}$/Au and $PDMS_{25Si}$/Au samples are totally different than that of $PDMS_{15Si}$/Au sample (Figure S4.2). At 5% strain, the cracks are much shorter (~ 333 μm). As for the stretching micrograph of $PDMS_{20Si}$/Au and $PDMS_{25Si}$/Au samples, it is clear that the crack density is increasing as the strain is increasing, but the width (< 30 μm) and the length (< 333 μm) of the cracks remain small. These narrow, short cracks have a "zigzag" appearance that retains gold bridges between the cracks. In contrast, $PDMS_{10Si}$/Au and $PDMS_{15Si}$/Au samples have long (~ 700 μm) cracks with no visible bridges in the region that we focused by the time we get to 70% strain, but must be few bridges since both samples are still conductive vide infra.
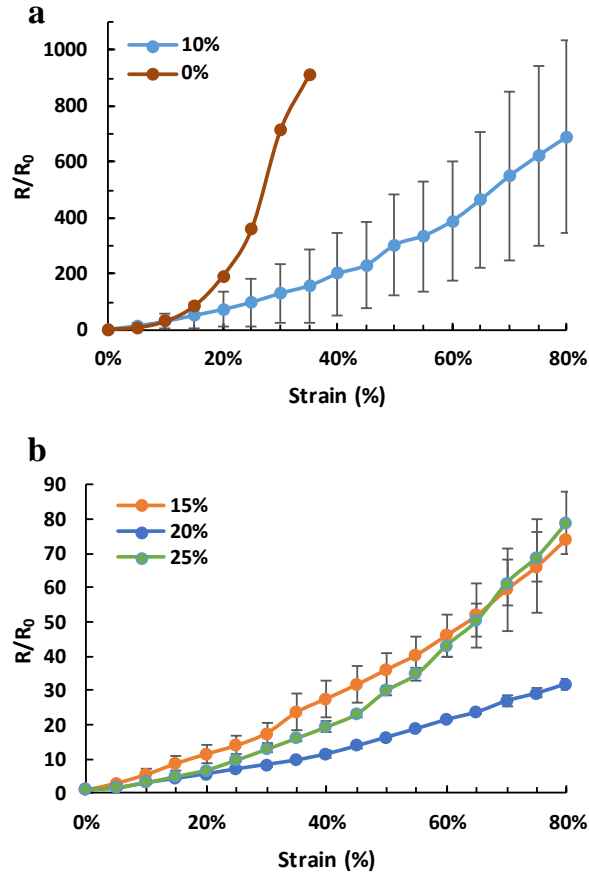
Figure 4.6. Plot of normalized resistance as a linear strain for 0% (Au/PDMS sample) and PDMS$_{10Si}$/Au (a) and PDMS$_{15Si}$/Au, PDMS$_{20Si}$/Au, and PDMS$_{25Si}$/Au (b) samples.

A comparison of the plots of the change in resistance of gold on flat PDMS and PDMS$_{xSi}$/Au samples (Figure 4.6) reveal that the resistance changes of gold film with stretching can be modified by varying the modified silica : PDMS weight ratio in the interlayer. Without an interlayer, the resistance of gold on flat PDMS rises rapidly to 909 times the initial value at small strain (35%), the cracks propagate to form lots of long and straight cracks at this strain, which causes the electrical failure (Figure S4.3). The sample

is not conductive after further stretching. At the lowest concentration of silica ($PDMS_{10Si}$/Au) sample, the modified silica in the interlayer has an effect on the gold conductivity with stretching. $PDMS_{10Si}$ gold sample remains conductive to higher elongation than gold on flat PDMS without silica (80% vs. 35%). The R/R_0 value for $PDMS_{10Si}$/Au is lower ($R/R_0 = 157$) than that of gold on flat PDMS at 35% strain (Figure 4.6 a). While of $PDMS_{10Si}$/Au sample, the nanoparticle sites prevent the formation of long cracks (compared to $PDMS_{0Si}$/Au sample, but the crack are still long) that break the conductive pathway, it remains conductive up to 80% elongation, and the R/R_0 value is 690 (Figure 4.6 a).

For $PDMS_{15-25Si}$/Au samples, the R/R_0 all remain under 100 up to 80% elongation (Figure 4.6 b). The $PDMS_{20Si}$/Au sample shows the best electrical stretching behavior among all the concentrations. At 5% elongation, the R/R_0 value are similar (~2) for all the three modified silica gold samples (Figure 4.6 b). At 50% elongation, the $PDMS_{20Si}$/Au sample is slightly different than the $PDMS_{15Si}$/Au and $PDMS_{25Si}$/Au samples. The R/R_0 value is 16 ± 0.6 for $PDMS_{20Si}$/Au sample, but the R/R_0 value for 15% and 25% gold samples are 36 ± 4.7 and 30 ± 1.5, which are ~ 2x higher than that of the $PDMS_{20Si}$/Au. As the elongation goes up to 70% strain, the R/R_0 value for the $PDMS_{20Si}$/Au sample continues to increase at a slower rate, which is just 27 ± 1.7. While at 70% elongation, the R/R_0 values are 59 ± 11.8 and 61 ± 6.6 for the $PDMS_{15Si}$/Au and $PDMS_{25Si}$/Au samples, respectively.

The cracks showed in optical images (Figure 4.5) appear very different after $PDMS_{15Si}$/Au, which does not reveal the cause of similarities or differences in R/R_0. We used stereomicroscope images, which provide a larger field of view (5.6 mm).

We stretched the $PDMS_{15Si}$/Au, $PDMS_{20Si}$/Au and $PDMS_{25Si}$/Au samples under stereomicroscope (Figure 4.7), the modified silica nanoparticles were aggregated in the interlayer which initiate and terminate the crack propagation at the edge of the isolated modified silica. It is interesting that $PDMS_{15Si}$/Au and $PDMS_{25Si}$/Au samples are indistinguishable in terms of R/R_0 vs. strain, but are completely different in cracking. The width of the crack of $PDMS_{15Si}$/Au sample increases from ~114 to ~570 µm as the sample is stretching up to 70% strain and some of the cracks get interrupted and new cracks formed (Figure 4.7 a-c). For $PDMS_{25Si}$/Au sample, the cracks are much smaller than the big long cracks that $PDMS_{15Si}$/Au sample has. At low strain (5% elongation), the $PDMS_{25Si}$ gold sample has some short cracks (< 110 µm) formed and gold film delaminated in some regions (Figure 4.7 g). At higher strain (70%) elongation, the short cracks are getting wider (< 460 µm), however, the gold film in some regions seemed to be out of plane, i.e. the gold film is peeling off while stretching the brittle modified silica surface (Figure 4.7 i and Figure S4.2 c). This can explain why $PDMS_{25Si}$/Au sample has a higher R/R_0 value (61) than that of $PDMS_{20Si}$/Au sample (27) at 70% elongation, and also explain why it is comparable to $PDMS_{15Si}$/Au at this elongation.

For the $PDMS_{20Si}$/Au sample, although the crack density is increasing as the strain is increasing just like $PDMS_{25Si}$/Au sample, the size of the short cracks remains small (< 229 µm), even at 70% elongation. From Figure 4.7 f, the gold film is still connected to continue the conductive pathway. The concentration of modified silica is lower in $PDMS_{20Si}$/Au sample than that of the $PDMS_{25Si}$/Au sample, so the surface is less brittle, which can withstand the high strain without peeling off the gold film. This support the view that the $PDMS_{20Si}$/Au sample has the best stretchable electrical performance.
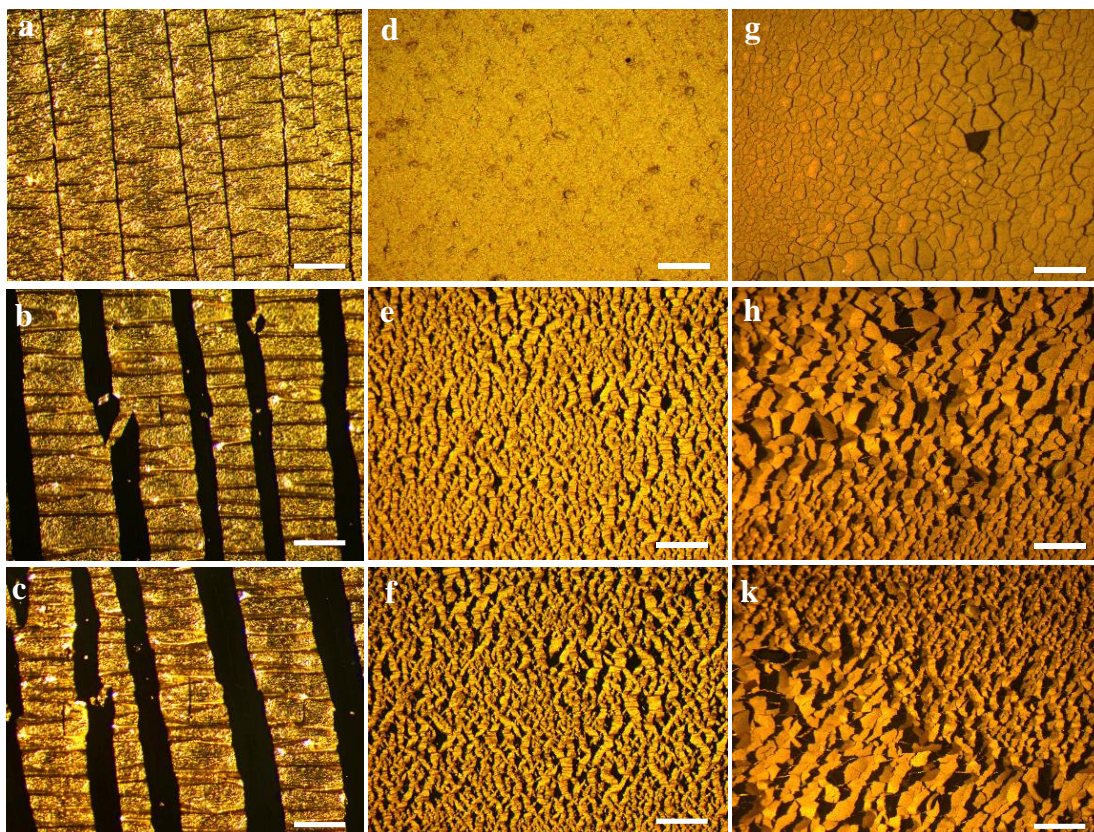
Figure 4.7. Evolution of cracks on PDMS$_{xSi}$/Au films with stretching. Optical images captured at 5% (top), 50% (middle) and 70% (bottom) strain for PDMS$_{15Si}$/Au (a-c), PDMS$_{20Si}$/Au (d-f) and PDMS$_{25Si}$/Au (g-i) samples. In all images, the samples were stretched in the horizontal direction. Scale bar – 800 μm.

4.4. Conclusion

All the PDMS$_{xSi}$/Au samples that we have tested (10, 15, 20 and 25%) can prove the success of achieving high conductivity of thin gold film on elastomer substrates by simply varying the weight ratio of modified silica:PDMS interlayer between metal and substrate. The PDMS$_{20Si}$/Au sample has the best stretchable electrical behavior and highest stability.

We can reach highly stretchable and conductive gold film on PDMS with less rough surface (the peak-valley distance < 550 nm for the PDMS$_{20Si}$/Au sample), comparing to PDMS/glue paper by Filiatrault *et al*. in our group (the peak-valley distance < 3.5 μm for PDMS/glue$_{1:1}$), by using a nanoparticle as an interlayer. The PDMS$_{20Si}$/Au sample can persist high conductivity at 80% elongation, which is 32× the initial resistance with negligible standard deviation (R/R$_0$ = 32 ± 1.6).

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4.6. Supporting Information
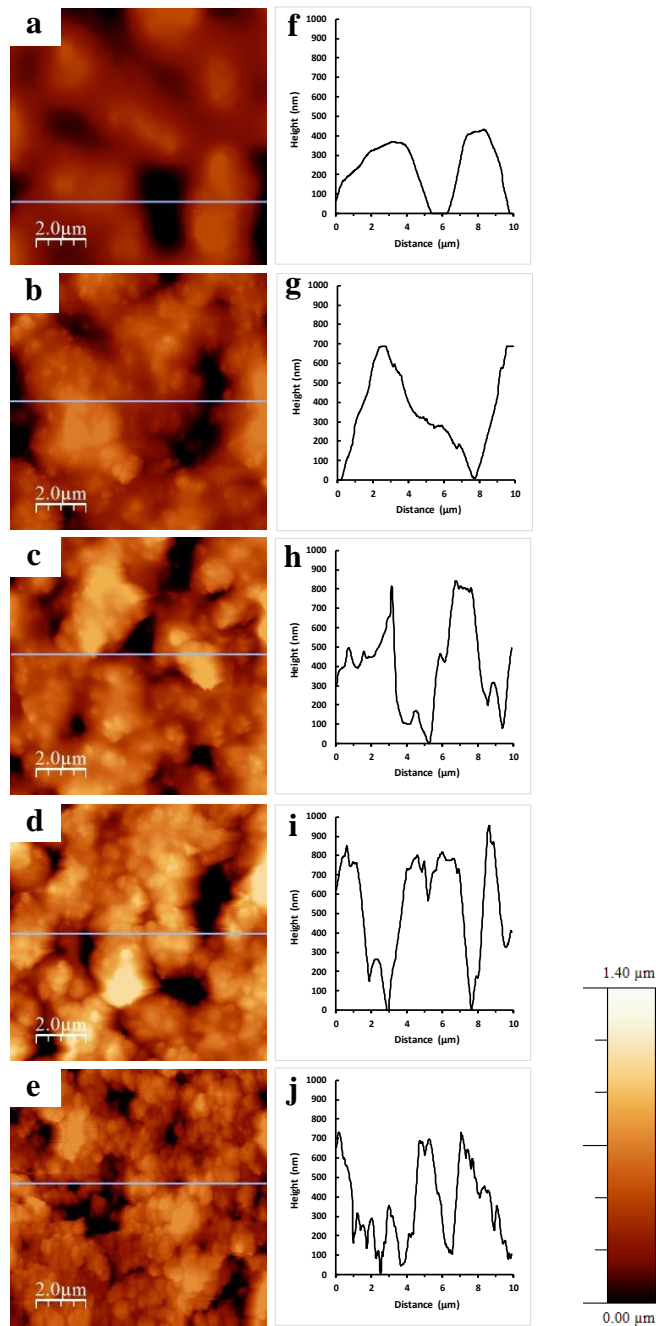
Figure S 4.1. AFM images (a-e) and cross section (f-j) of 10% (a, f), 15% (b, g), 20% (c, h), 25% (d, i) and 30% (e, j) PDMS$_{xSi}$ samples after 250 Å Au deposition.
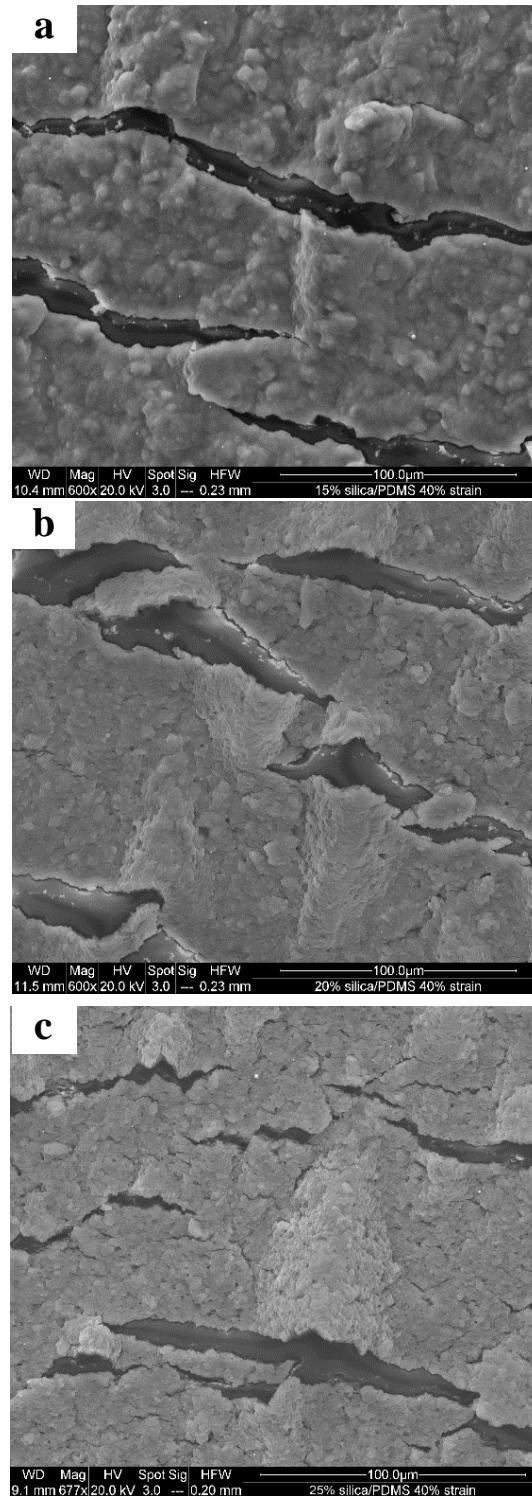
Figure S 4.2. SEM images of 15% (a), 20% (b) and 25% (c) PDMS$_{xSi}$/Au samples

under 40% strain. In all images, the samples were stretched in vertical direction.
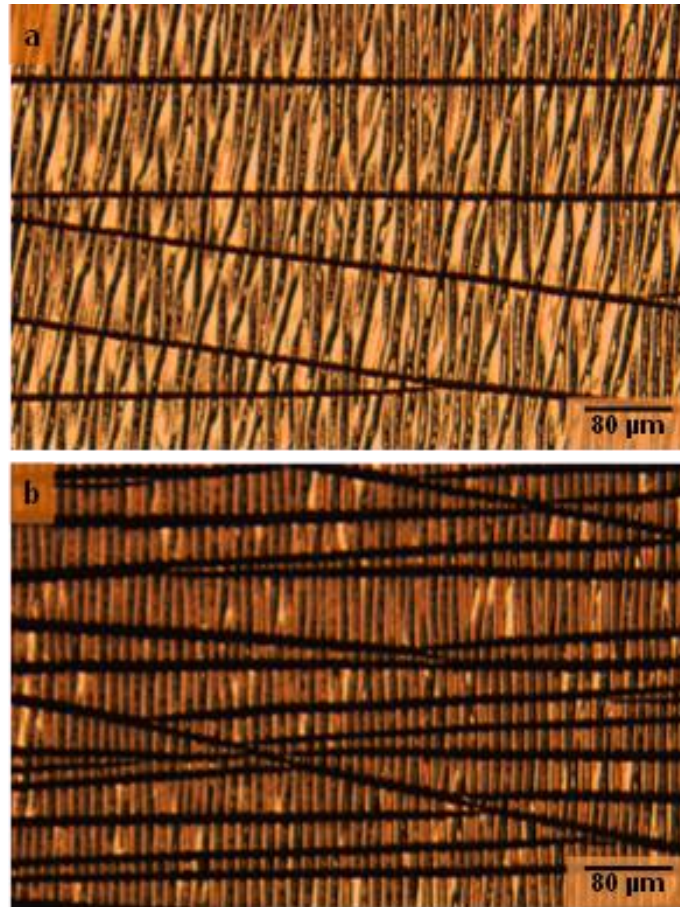
Figure S 4.3. Evolution of cracks on PDMS/gold structures with stretching. Optical images captured at (a) 5% strain and (b) 25% strain. In all images, the samples were stretched in vertical direction.

Chapter 5

Outlook

5.1. Branched DTPAs with Other Terminal Groups or Chain Length

It is reported that fluorocarbon-terminated molecular layers offer lower surface energy and interfacial friction compared to CH_3 – terminated analogues.[1] As the packing densities of molecules with identical chain lengths but different terminations (i.e., CF_3 vs. CH_3) were found to be indistinguishable by atomic force microscopy (AFM), the increased of friction in the case of CF_3 – terminated SAMs has been related to an increase in the interaction between adjacent CF_3 – terminal groups.[2,3,4] SAMs formed from fluoroalkyl thiols have been shown to be more hydrophobic than the analogous alkane thiols, thus higher contact angles are excepted.[5] It would be interesting to demonstrate the formation of branched DTPA SAM on TS gold by fluorinating the terminal methyl group or part of the methylene groups in the SAM molecular chains to reach high crystalline DTPA SAMs with similar surface coverage and more hydrophobicity than the non-fluorinated branched DTPA SAMs.

If we can successfully synthesize longer branched chain DTPA molecules, we can form SAMs that have larger contact angles. The tradeoff would be the increased steric demand of long alkyl chains on TS gold resulting in liquid-like and disorder chain organization SAMs. It is interesting to alternate the length of main chain and investigate how much space could we fill with branched chain before we perturb the chelation of the molecules on TS gold. If we can find the effective chains that can fill the space and allow the crystalline organization, we might expect the contact angles to change, because the gold would be shielded by the crystalline but short alkyl chains.

5.2. Ways to Increase Stretchability of PDMS$_{xSi}$/Au Samples

Even though we used nanoparticles as the interlayer to increase the stretchability and conductivity of the metal film, the roughness for the sample is still too high for these films to be used as electrodes in stretchable devices. However, we can probably reduce the size of silica clusters that form on the surface by changing the organosilane coupling agents used to study the relationship between roughness and gold cracking (and R/R_0). It would also be interesting to see how the sample will behave without the Ti adhesive layer before gold evaporation, since the silica layer could act as the adhesive layer as well. Future work will involve embedding the silica nanoparticles in a shallow layer of PDMS at the surface, which we hypothesize will generate a smooth surface while simultaneously retaining the strain-relieving effects of silica suspensions in PDMS.

The stretchability of the PDMS$_{xSi}$/Au sample is also limited by PDMS substrate. Besides PDMS, Ecoflex is researched in our group as a substrate for constructing devices and thin films. This elastomer can stretch up to 900% tensile strain without breaking, so it seems very promising that by using Ecoflex as the elastic substrate would remove substrate stretchability as a limitation on the performance of the conducting layer.

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