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Interface driven engineering of charge transport across molecular tunneling junctions

Jiahao Chen
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Interface driven engineering of charge transport across molecular tunneling junctions

by

Jiahao Chen

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

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Iowa State University

Ames, Iowa

2017

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ABSTRACT

Molecular electronics uses organic molecules to replace inorganic electrical components in circuits. Molecular electronics is a promising field that can extend the Moore’s law since scaling down transistors with molecules is comparatively easier than inorganic components fabricated using optical lithography.

This thesis describes a platform that can be used to study molecular electronics, which is self-assembled monolayers based large area tunneling junction with Eutectic Gallium Indium as top electrode and metal thin film as bottom electrode.

The role of interfaces in the junctions has been evaluated. The morphology of both bottom electrode and top electrode affects the charge transport behavior (in these system, it is quantum tunneling) across those molecular tunneling junctions. The effect of the bottom electrode morphology on the molecular structure of the SAM has been discussed in details.

Effect of molecular dipole on charge transport across the junctions has been studied. The dipole can affect the coupling between the molecule and the substrate and hence the charge transport. For a more complex system where the dipole has been decoupled from the substrate, the effect of dipole on tunneling can only be delineated from a statistical analysis.

From these studies, it has been acknowledged that interfaces plays an important role in molecular junctions. Therefore, to design or control the charge transport by engineering the interfaces is made possible.
OVERVIEW

Molecular electronics is an interdisciplinary field, founded on the notion that electrical components can be built from single molecules or a collection of molecules working in tandem. In 1974, Aviram and Ratner\(^1\) theoretically proposed a new type of rectifier based on a donor-sigma-acceptor molecule. This new concept of molecular electronics has been postulated as a potential solution to the extension of Moore’s law. Scaling-down with 2-terminal molecular rectifier is more likely than with the current silicon based transistors, whose scaling-down is heavily limited by material physics. The original promise of molecular electronics lies in the ability to engineer the wave-function of molecular components through organic synthesis. The biggest challenge in study of electronic behavior of single molecules, however, is in the ability to create electrical contact between molecules and macroscale electrodes, and in translation of molecular identity (structure, stereo-electronics, conformation etc.) into electric data/information.

To stabilize the molecules onto electrode(s) hence delineate electronic properties, two types of junctions are commonly used, \textit{viz.;} i) single molecule junctions, and, ii) large area molecular junctions. Single molecule junctions rely on trapping a molecule between two nanoscopic metallic wires while large area junctions are based on investigating an ensemble of molecules and averaging observed properties over the collection. Our research focuses on the large-area molecular junctions. A large-area molecular junction is normally based on a self-assembled monolayer (SAM), which consists of a top electrode and a bottom electrode with the SAM in between. The SAMs are typically chemically attached to the substrate that also serves as the bottom electrode. Coinage metals have been widely used as the substrates due to their ability to form strong covalent bonds with head groups like thiols, forming well-ordered and stable
SAMs. When a top electrode contacts the SAMs, a junction is thus formed by completing the circuit with the SAM as an integral part. Several methods have been developed to form a top electrode without damaging the SAM such as PEDOT:PSS, nanorods, nanospheres, liquid metals, among others.

Eutectic gallium indium (EGaIn, 75.5% Ga, 24.5% In), a non-Newtonian liquid metal at room temperature that has a thin (~0.7 nm) passivating oxides layer, has emerged as a robust top-electrode. The non-Newtonian nature of EGaIn means that it can be shaped into a sharp conical tip that can then be used to contact the SAMs to form a stable junction. The thin protective layer implies that the liquid metal core is not in direct contact with the SAM and forms a protective shell allowing for high yields of working junctions to be formed at ambient conditions. This translates to an ability to generate large quantities of data over a short period of time, and the reusability of the tips hence reliable physical organic studies. Presence of the oxide shell has been shown to play an insignificant role in the overall resistivity of junction since the SAM is orders of magnitude more resistive than this sub-nanometer tunneling layer.

This thesis will mainly discuss two parts. i) Understanding the role of interfaces in charge transport across SAMs. Nature of the substrate affects the chemisorbed bottom interface hence influences structure of the SAMs and hence the overall properties of the junction. From the hybridization of the head group to the SAMs cant angle, tilt angle, and packing density, the nature of the bottom interface plays a critical role in all these SAM properties on top of effects due to substrate defects and differential faceting. Similarly, the morphology and structure of the top electrode also affects nature of the physisorbed interface, hence, charge transport behavior across SAMs. To investigate the effect of these interfaces, which depend on the surface morphology of both electrodes, we desire to control surface roughness of the electrodes
to reveal finer molecular-level properties that significantly affect charge tunneling. The morphology of the top-electrode is critical in our definition of the contact resistance and differentiating geometric vs electrical contacts. As such, we developed a method to prepare smooth, low modulus—hence potentially compliant, EGaIn top-electrodes. Unfortunately, prior to this work, there were no literature methods to systematically prepare metal thin films of tunable surface roughness and morphology of relevance to this study, and as such no understanding of the role of substrate morphology in SAM packing and properties. We, therefore, had to invent a method of engineering roughness of the bottom electrode in a bid to understand the role of such roughness in the overall SAM structure. New understandings of the role of this roughness in SAM structure were delineated and form a basis for our understanding of SAMs. Follow-up studies will apply new information generated from this part of the work to engineer charge transport. ii) Understanding the role of subtle stereo-electronic perturbation to the molecules making up the SAM in controlling charge transport. Here we focus on two primary effects; i) the steric orientation of a terminal moiety in effecting charge tunneling. In this part, we focused on the rather simple n-alkanethiolate SAMs and investigated the odd-even effect, a consequence of the orientation of the terminal \(-\text{CH}_2\text{CH}_3\) moiety. ii) Effect of molecular dipole on charge transport by tunneling across large area junctions. The effect of molecular dipole in charge transport (current tunneling rate) was investigated by designing molecules with one or two well oriented molecular dipole(s). In the case of two dipoles, these were electronically isolated using hydrocarbon moieties and were either directionally aligned or misaligned. Molecular dipoles, however, depend on the orientation and packing of the molecule in a SAM, which in turn depends on the quality of the substrate on which the SAM is fabricated. Specifically, this thesis covers the following parts:
Chapter 1: Development of a technique to fabricate coinage metal substrates of various surface roughness and morphology. We employed lattice misfit, valence shell interactions, and defect propagation in thin films to induce surface reorganize on a deposited thin film of a coinage metal. To achieve this, a thin (10 nm) adlayer of a lattice mismatched element is deposited on a pre-deposited thin (200 nm on atomically flat Si wafer) film of the metal to be reconstructed. The film is then template stripped to reveal the reconstructed bare surface. For thin gold substrates, this technique can lead to increase or decrease of the root mean square, $R_{RMS}$, ($R_{RMS} \approx 1.8\text{Å} - 4.6 \text{Å}$). We demonstrated that lattice misfit energy is correlated to the roughness of the derived surface and hence the reorganization in the thin films.

Chapter 2: To study the dependence of interfacial properties (both wetting and charge transport) of SAMs on substrate roughness and morphologies. To delineate effect of roughness on SAM structure, we focus on understanding the effect of substrate roughness through a simple interface-dominated property, wetting behavior, and confirm our inferences using interface-specific spectroscopy (sum frequency generation). The properties are expected to differ due to the roughness dependence of the orientation of the terminal $–\text{CH}_2\text{CH}_3$—the so-called odd-even effect. On rough surfaces ($R_{RMS} \approx 2.2\text{nm}$), the SAMs are poorly ordered, and thus, the odd-even effect (both in wetting and SFG CH$_3$ asym vibration peak intensities) was not observed although it is observable on smoother surfaces (e.g. $R_{RMS} < 0.45 \text{ nm}$). Ability to prepare substrates with tunable surface morphology also allowed us to quantify the maximum difference in wetting for SAMs with odd or even number of carbons. Analogously, we were able to demonstrate that the odd-even effect in hydrophobicity cannot be observed for surfaces with $R_{RMS} \geq 1 \text{ nm}$. Comparing Au and Ag surfaces, we demonstrated a length-dependent limit to the observation of substrate effects, since differences in the odd-even effect in wettability of
n-alkanethiolate SAMs on the two substrates decreases with decreasing molecular length with a convergence at propanethiolate SAMs. By comparing SAMs on Ag and Au, we also predicted phase evolution in the nature of the SAM top-interface which we infer is related to evolution of gauche defects in the SAMs. Applying the well-known Young-Dupre wetting equation, we derived a non-dimensionless number to quantify conformational disorder (gauche defects) relative to an infinitely long and well packed (zero molecular vibrations) hydrocarbon SAM. This structural evolution bears an analogous periodicity to that observed in theoretical simulation of conformational order in gas-phase hydrocarbons hence its likely be related to the molecular level vibrational dissipation of energy in such of a global minimal- the cause of gauche defects in SAMs.

Chapter 3: To develop a tool for statistically analysis the raw data of charge transport.

Even with well-formed SAMs and smooth electrodes, for EGaIn-based large-area molecular tunneling junctions, the challenge lies in analyzing the large amount of data generated. Another challenge is the uncertainty in reproducible junction formation since there were no tools to qualitatively evaluate the nature of contact formed between the SAM and the top-electrode. The prevalent use of simple averages is not informative enough to characterize the quality of the junctions, and due to requisite Gaussian fitting, detailed information about the junction is lost. We desire to develop a statistical tool to evaluate nature of the contact and a data analysis/reporting method that shows all raw data with concomitant details of junction quality. For this we settled on 3D data representation in the form of heat-maps.

Chapter 4: To investigate the effect of smoothening both electrodes on charge transport:

Having prepared smooth substrates and developed an understanding of effect of substrate roughness on SAM quality, we investigated the effect of top electrode on charge transport. For
this study a non-Newtonian liquid metal (EGaIn -eutectic gallium indium) conical tip, prepared through breakage of an hour-glass shaped construct, was used as the top-electrode. This conical tip EGaIn top electrode, has a rough oxide shell, potentially also with whiskers at the point of breakage that can affect contact area, hence, charge transport properties. We desired to develop a universal method to polish the electrode, reduce the oxide layer at the tip to its native ~0.7 nm thickness, increase convergence of the geometric and electrical contacts, and maintain the low-modulus liquid nature of the electrode at the tip. With the help of a previously reported method—SLICE, to fabricate smooth EGaIn spherical particles, the tip was polished into a smooth well-rounded form. The polished EGaIn electrode enabled observation of finer details of the odd-even effect to a point that it can be correlated to inferences from wetting studies as detailed in chapter 2.

**Chapter 5: To study the effect of embedded molecular dipoles on charge transport behavior across molecular tunneling junction.** Understanding of the effects of molecular dipoles in charge transport are, at the very least, inconsistent. In some studies, the effect of embedded dipoles on charge transport behavior is very significant, but in others this effect is too subtle to be observed. We, however, believe that molecular dipoles (a vector quantity, hence ‘tensor-like’ in their effect) are effective in influencing charge transport in molecular tunneling junctions. To test this hypothesis, we used two system that are slightly different in molecular structure, but similar in junction structure (metal/SAMs//EGaIn). i) Molecular junction with low cooperativity. For those junctions, the effect of dipole on charge transport is subtle and may not be observed in average tunneling rates (second moment statistics) but will show in third and fourth moment statistical analysis (skewness and kurtosis respectively). ii) Junction with higher cooperativity. For these junctions, the effect of the dipoles are more
significant. We can compare the effect of the magnitude and direction of dipoles on charge transport characteristics across tunneling systems. In these junctions, effect of dipoles manifests in almost every mathematical moment of the data, hence, they do not required higher moment statistics to reveal effect of the dipole. As a consequence of this strong cooperativity, Fermi-level pinning and other associated dipole-dependent effects are expected and are discussed.

**Reference**

CHAPTER 1. DISSIPATION OF INTERFACIAL STRESS AS SURFACE REORGANIZATION IN METAL THIN FILMS

The structure of molecular assemblies and hence quality of molecular junctions are highly dependent on the substrate, especially its roughness and morphology. In this section, a fabrication technique was introduced to produce ultra-flat metal surface. These flat surfaces are ideal substrates for 2-dimensional materials such as self-assembled monolayers. This technique involves template striping a hetero-bimetallic thin film. The morphology of the derived thin films surfaces and the interface of the hetero-structure were characterized. The mechanism of the smoothening effect was explored through both experimental results and theoretical simulations. Effect of the resulting substrate roughness on SAMs will be discussed in Chapter 2.

1.1 Introduction

Co-deposited multi-metal thin films have been used in plasmonics, thermocouples, actuation, catalysis and materials synthesis. These applications often assume that the properties of the first deposited film do not significantly change upon deposition of a second layer, despite the generation of a new interface. Interfacial stress on co-evaporated films, however, is well documented especially in epitaxial film growth. Growth of bimetallic films (hetero-epitaxy) involves deposition of a thin layer of metal ($M_1$) on a host substrate, often silicon (111) or (100), followed by the growth or deposition of a second metal ($M_2$) to create three interfaces, viz; $M_1$/substrate, $M_1$/ $M_2$, $M_2$/air interfaces. In bimetallic film growth involving non-reactive metals, the strain in the plane of the hetero-interface ($M_1$/ $M_2$) can be estimated from the lattice mismatch, but the magnitude of the shear component of the strain depends on the faceting of $M_1$, inter-diffusion and propensity to reorganize. Studies on the resulting strain at the hetero-interface has, however, mostly focused on its effect on the growth/evolution of the $M_2$ film structure with no reports on its effect on the $M_1$/substrate interface.
We hypothesized that, assuming a perfect lattice at $M_1/M_2$ interface, the morphology of the $M_1$/substrate interface and the bulk properties of $M_1$ film can be affected, and therefore tuned, by misfit stress on the $M_1/M_2$ interface (either as point, $\sigma_z$, or plane, $\sigma_{x-y}$, stress). The misfit stress can lead to either plastic deformation (due to defect migration) or an increase in dislocation (or other defects) density in the material. Increase in dislocations as the material accommodates the resultant strain can lead to a decrease in the grain size on $M_1$ with concomitant decrease in grain boundaries hence lowering the overall surface energy of $M_1$ along the $M_1$/substrate (Figure 1.1a). Plastic deformation due to dislocation migration, however, can also lead to surface step-edge defects, or if the strain predominantly dissipates at high energy points (e.g. grain boundaries and other surface asperities) thermodynamically-favorable reorganization would lead to their annihilation. We hypothesized that plane-stress can be controllably introduced on the surface of a thin film through lattice constant mismatch (misfit stress). Since thin films (lamina) cannot bear significant load in the Z-direction without damage ($\sigma_z \approx 0$), the adlayer ($M_2$) has to be slowly sputtered onto the surface to avoid damage. Template-stripping would subsequently reveal a surface with different surface morphology relative to that of a similar film without the adlayer (Figure 2.1b). For a material like Au, with high mobility of atoms at the surface, the proposed reorganization would manifest as a change in surface roughness on the template-stripped film. Increase in defect density would also lead to hardening of the film hence a change in its elastic modulus.

### 1.2 Roughness of the fabricated surfaces

To test our hypothesis, we deposited 200 nm films of Au ($M_1$, lattice constant 407.82 pm) on an ultra-flat Si (100) wafer with its native oxide (substrate). A thin film $M_2$, either Fe (lattice constant 286.65 pm) or Al ($M_2$, lattice constant 404.95 pm), was then sputtered on two different
samples. The films were then template-stripped as previously described\textsuperscript{23-26} to expose the \(M_1\)-substrate interface, with or without an adlayer (abbreviated \(\text{Au}^{M\text{-TS}}\) and \(\text{Au}^{\text{TS}}\) respectively, \(m = \) metal making up the adlayer). Characterization of the resultant surfaces by atomic force microscopy (AFM) showed significant differences in surface morphology (Figure 2.1c-2.1e). The observed root-mean-square roughness (\(R_{\text{RMS}}\)) of the template-stripped surfaces were; \(\text{Au}^{\text{TS}}, = 0.39 \pm 0.05 \) nm, \(\text{Au}^{\text{Al\text{-TS}}} = 0.44 \pm 0.06 \) nm, \(\text{Au}^{\text{Fe\text{-TS}}} = 0.21 \pm 0.03 \) nm. Analysis of the surfaces using scanning electron microscopy (SEM), using the energy selective back scatter (EsB) detector, indicated polycrystallinity with or without the adlayer. Characterization by X-ray diffraction (XRD) showed that, as expected, the thermodynamically favorable Au (111) orientation was dominant for both \(\text{Au}^{\text{TS}}\) and \(\text{Au}^{\text{Fe\text{-TS}}}\) (Figure 2.1f). A close look at the XRD patterns, however, reveals that the \(\text{Au}^{\text{Fe\text{-TS}}}\) surface get slightly reorganized as capture by the relative decrease in intensity of the (200) and (311) peaks (Figure 2.1f). We confirmed differences in surface roughness using scanning transmission microscopy (STM) and found \(R_{\text{RMS}} = 0.22 \) nm for \(\text{Au}^{\text{Fe\text{-TS}}}\) irrespective of the size of the scanned area (Figure 2.1g). These results indicate that deposition of the adlayers leads to uniform reorganization of the surface, with concomitant increase (\(\text{Au}^{\text{Al\text{-TS}}}\)) or decrease (\(\text{Au}^{\text{Fe\text{-TS}}}\)) in surface roughness (as captured by the \(R_{\text{RMS}}\)). The difference in \(R_{\text{RMS}}\) indicates that the adlayer or the process of depositing \(M_2\), had an effect on the \(M_1\) film.
**Figure 1.1** The effect of adlayer metal on metal thin film reorganization. a) Schematic representation of the distribution of stress and strain on a thin film, b) Potential effect of deposition of a second layer of material to generate point stress (Kinetic energy transfer) or plane stress (lattice mismatch) due to interface lattice constant mismatch that leads to improved surface topography upon template stripping. Comparative analysis of resultant surface topography by AFM for; c) Au\textsuperscript{TS} (R\textsubscript{RMS} 0.39±0.05 nm), d) Au\textsuperscript{Al-TS} (R\textsubscript{RMS} 0.44±0.06 nm), and, e) Au\textsuperscript{Fe-TS} (R\textsubscript{RMS} 0.21±0.03 nm). f) Normalized XRD patterns for Au\textsuperscript{TS} and Au\textsuperscript{Fe-TS} indicate surface reorganization as exemplified by diminished intensity in (200) and (311) orientation, g) surface roughness analysis by STM concurs with that derived from AFM for Au\textsuperscript{Fe-TS}.

### 1.3 Discussion on the effect of adlayer on the substrate layer

#### 1.3.1 Interfacial stress or kinetic energy transfer

Since the host Au film is evaporated using e-beam evaporation but the adlayer is deposited using sputtering, we investigated whether the change in deposition technique was the cause of
the observed decrease in surface roughness. When 10 nm Au was sputtered onto an e-beam evaporated 200 nm thick Au, the $R_{\text{RMS}}$ increased from $\text{Au}^{\text{TS}} = 0.39\pm0.05$ nm to $\text{Au}^{\text{Au-TS}} = 0.61\pm0.04$ nm, suggesting that in absence of misfit stress, as expected, the sputtering process ($\sigma_z$) damages the film.

To delineate the origin of the reorganization, several metals – with different chemical (standard redox potentials), solid-state (crystal structures) and surface (lattice parameters) properties were used to create the adlayer. Adlayers of Ti (lattice constant 295.08 pm), Cu (lattice constant 361.49 pm), and Pd (lattice constant 389.07 pm) were deposited on 200 nm Au films. The reorganized surfaces had $R_{\text{RMS}}$ in decreasing order; $\text{Au}^{\text{Ti-TS}} (0.23\pm0.01 \text{ nm}) < \text{Au}^{\text{Cu-TS}} (0.26\pm0.03 \text{ nm}) < \text{Au}^{\text{Pd-TS}} (0.32\pm0.02 \text{ nm})$, indicating smoother surfaces than the Au$^{\text{TS}}$ (Figure 1.2a and Table 1.1). We observe that the variation in surface roughness correlates with the identity of the metal and, except for Al, all adlayers gave surfaces with lower $R_{\text{RMS}}$ than Au$^{\text{TS}}$ (Figure 1.1a). We observe that Au$^{\text{TS}}$ had the smaller grain areas (0.025μm$^2$) while Au$^{\text{Al-TS}}$ (0.046μm$^2$) and Au$^{\text{Fe-TS}}$ (0.052μm$^2$) had the largest grain areas (Figure 1.2b).

**Table. 1.1**: RMS roughness of selected substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>RMS roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS Au</td>
<td>0.39±0.05</td>
</tr>
<tr>
<td>TS Au-Al</td>
<td>0.44±0.06</td>
</tr>
<tr>
<td>TS Au-Pd</td>
<td>0.32±0.02</td>
</tr>
<tr>
<td>TS Au-Cu</td>
<td>0.26±0.03</td>
</tr>
<tr>
<td>TS Au-Ti</td>
<td>0.23±0.01</td>
</tr>
<tr>
<td>TS Au-Fe</td>
<td>0.21±0.03</td>
</tr>
<tr>
<td>AD Au</td>
<td>2.3±0.2</td>
</tr>
<tr>
<td>AD Au-Fe</td>
<td>1.9±0.1</td>
</tr>
</tbody>
</table>
1.3.2 Effect of sputtering rate and adlayer thickness

To understand the extent of the influence of $\sigma_z$ we investigated the effect of sputtering rate by depositing Ti adlayers at different rates (0.08, 0.2, 0.4 nm/s) and evaluating the resultant $R_{RMS}$ (Figure 2c). We observed a minima in the mean and variance of surface $R_{RMS}$ (Mean, $\bar{x}_{RMS} = 0.23$ nm, and standard deviation, $\sigma_{RMS} = 0.01$ nm) when the sputtering rate was 0.2 nm/s (Figure 2.2c). When the deposition rate was less or greater than 0.2 nm/s, the films had higher $R_{RMS}$ (0.29±0.02nm and 0.35±0.03 for 0.08 nm/s and 0.4 nm/s respectively). From these results, we infer that there could be multiple processes occurring simultaneously, resulting in a minimum in roughness at a deposition rate of 0.2 nm/s (Figure 2.2c).

Having established that the reduction in roughness is dependent on the rate of deposition, the effect of the adlayer thickness was investigated by sputtering 10-80 nm Ti on 200 nm Au films. Figure 2.2d shows that $R_{RMS}$ is more dependent on the rate of metal deposition than on the thickness of the film. When the sputtering rate was set at 0.2 nm/s, slight but statistically insignificant differences in $R_{RMS}$ were observed over different thicknesses. We observed the reorganization both on the $M/I$/substrate interface as discussed above, and also on the ‘as-deposited’ adlayer. Correlating the effect of deposition rate and film thickness indicates that evaporating Ti at 0.2 nm/s for a 10 nm thick film is sufficient to achieve maximum reorganization.

1.3.3 Surface reorganization is independent of location on the wafer

Since the films are fabricated on an atomically flat Si (100) wafer (with its native oxide), the effect of the position on the wafer was investigated. A sample of AuFe-TS from the edge, middle, and, central region of the same wafer was prepared and $R_{RMS}$ measured (Figure 2.2e). All samples were observed to have similar $R_{RMS}$ values (0.19 ± 0.01 nm) suggesting that the
Au film across the whole wafer reorganized evenly on deposition of the adlayer. These results suggest the reported approach to thin film smoothening described here can be used at any scale as long as the material forming the adlayer is uniformly deposited at the same rate across the Au film sitting on an atomically smooth substrate.

**Figure 1.2** Data derived from multiple samples that were collected randomly from at least three wafers of each surface. a) RMS roughness from all metals, except Al, were lower than those of Au\textsuperscript{TS}. b) Average grain areas were larger for all surfaces compared to the Au\textsuperscript{TS}. The size of defects, however, were larger for Au\textsuperscript{Al-TS} while they were very small in Au\textsuperscript{Fe-TS}. c) Analysis of the effect of deposition rate of the adlayer on the RMS indicated a minima at 0.2
nm/s, while d) comparison of effect of both deposition rate and film thickness shows no statistically significant change in the $R_{RMS}$ with increase in adlayer thickness. e) Sampling different regions of the Si wafer template showed that the surface reorganization occurs evenly across the whole wafer. No significant differences in $R_{RMS}$ were observed irrespective of the region of the wafer sampled. f) Post fabrication thermal annealing of the surfaces leads to an increase in $R_{RMS}$, but with increase in grain boundaries.

### 1.3.4 Effect of thermal annealing

Thermal annealing creates large grains on metal surfaces albeit with concomitant increase in the size of the grain boundaries – that is; on a large film as grains get larger, the spaces between two large grains increases.\textsuperscript{27-30} Success of thermal annealing depends on several factors, one of which is the quality of the film being annealed.\textsuperscript{29-30} Thermal annealing followed by template-stripping of Au\textsuperscript{Fe-TS} led to growth of significantly larger grains, with concomitant creation of atomically flat regions, albeit with increase in the size of the grain boundaries (Figure 2.2f). Thermal treatment led to an increase in $R_{RMS}$ from 0.22 nm to 0.68 nm, in part due to increase in the size of grain boundaries. We are, however, aware that differences in the coefficient of thermal expansion, $\alpha$, between the Fe (12 x 10\textsuperscript{-6} m/(mk)) and Au (14.2 x 10\textsuperscript{-6} m/(mk)), may have a major effect on the morphology of the annealed surfaces.

### 1.3.5 Simulating the $M_1/M_2$ interface

Having empirically shown that deposition of another metal on Au leads to significant reorganization of the opposite surface, we desired to understand the mechanism behind this reorganization. The extent of metal penetration upon sputtering can be a source of significant internal stress. We employed Ziegler’s SRIM (stopping and range of Ions in Matter) technique\textsuperscript{31-35} to simulate implantation and distribution of the adlayer atoms. The SRIM platform is built on the Bethe-Bloch and Lindhard, Scharff, and Schiott (LSS) theories (as opposed to Tilinin theory).\textsuperscript{36-37} We interpret our simulation results in light of the limitation of this theory, and
therefore, these data are not considered in isolation but is used to inform experimental data. We used it to simulate implantation of deposited atoms, ion distribution, and, Kinchin-Pease damage on Au thin films at different kinetic energy of the respective adlayer atoms — assuming that all generated defects are localized (Figure 2.3a-2.3f). For comparison purposes, Figure 3.3a-f show simulation of atom implantation on Au by Fe and Al, metals that gave smoother and rougher surfaces respectively. Figure 3a and Figure 3b shows that Al penetrated slightly deeper (peaked at 0.7 nm, Tailed off at 1.4 nm) into the Au film than Fe (peaked at 0.5 nm, tailed off at 1 nm) when the atoms were accelerated at 100 eV — which is significantly larger than would be observed in our sputtering system (~ 400 meV).38-40 For other adlayers, no significant variation in the penetration depth was observed despite differences in atomic properties. Although the penetration (Figure 3a and Figure 3b) and ion/atom range (Figure 3e and Figure 3f) seems to be limited according to these simulations, we calculated the recoil energy, which would inform us on the extent of stress due to mechanical implantation of the atoms (Figure 3c and Figure 3d). For neutral atoms, however, it is safe to assume that all energy dissipation is localized and only the ensuing strain, or its effect, can propagate into the bulk of the film. Kinchin-Pease damage – due to transfer of energy by an implanted atom/ion into the substrate, leads to point defects near the site of energy transfer.35,41-43 This energy transfer can lead to local atom migration creating a vacancy, or generate Frenkel pairs (vacancy-interstitials pairs) due to secondary recoils at higher energies.4445 In our case, however, since all atoms have no charge, the number of Frenkel pairs are predicted to be low.45 Calculating the primary recoil energy, and hence extent of Kinchin-Pease damage across the depth of the substrate film, we observe that Fe gave higher primary recoil energy (7.2 eV) compared to Al (2.4 eV) albeit with a lower propagation depth (Figure 1.3c and Figure 1.3d). These data concurs with our
hypothesis that Kinchin-Pease and Frenkel pair damages will be low in the Au\textsuperscript{M-TS} films. From these simulation, we observe that there is low penetration of the substrate by the adlayer (≤ 15 %) and there is a low possibility to form Frenkel pairs. Correlation of the simulated data with experiments is, however, needed to further delineate the mechanism of the observed reorganization.

Figure 1.3 Simulation of interaction of adlayer atoms with Au using the SRIM method. a-b) extent to which deposited atoms penetrate into the Au film albeit at higher energies than
expected in a sputter system. c-d) Extent of Kinchin-Pease damage due to primary recoil. Number of Frenken-pairs is predicted to be zero since all elements forming the adlayer have $Z_m = 0$ (no charge). e-f) the ion/atom range showing a penetration depth of $\leq 15$ nm. g) Depth profiling of elemental composition of the film using XPS confirms the theoretical predictions and shows little interpenetration. h) The surface roughness correlates well with the differences in lattice parameters (lattice mismatch) between the element making up the adlayer and Au.

1.3.6 Experimental characterization of the $M_1/M_2$ interface

To support the simulation results, X-ray photoelectron spectroscopy (XPS) was used to develop a composition depth profile for the surface by etching small layers and analyzing the elemental composition of the remaining surface. We adopt this technique acknowledging limitations due to differences in etchability and atomic quantification with XPS. We, however, infer that in a comparative study, obtained data can give insert to the nature of the interface especially when that is in agreement with other techniques. Figure 3g gives the elemental composition across the thickness of the film for $Au^{Fe-TS}$. As expected, Fe forms a thin ($<15$ nm thick) passivating oxide layer upon exposure to ambient conditions. This layer was found to be primarily $Fe_2O_3$ on the surface but rapidly turns into mixed oxides and sub-oxides with depth (Figure 2.3g). Beneath the oxide layer, the fraction of Fe metal gradually increases to a depth maxima ~ 10 nm then gradually decreases up to ~ 36 nm (Figure 1.3g). The general trend in these results concur with our simulations (Figure 1.3e vs Figure 1.3g), albeit with the oxide layer present in the experimental data and a difference in the degree of interpenetration (2 nm vs ~35 nm respectively). This difference is due to inherent limitations in each method viz; i) inability to create atomically smooth interfaces in our experiments, ii) assumption of atomically flat surfaces and an orthogonal deposition of the adlayer in the simulations, iii) presence of defects and polycrystallinity in real material as opposed to the singular faceting and defect free materials in the simulation.
Further depth profiling shows that Au gradually increases and becomes the only element at depths of ~ 35 nm (18 % penetration of the Au film by Fe), indicating small mixing of the two metals at the interface. Similar observations were made for Al, whose penetration is about 18 nm (See Supplementary Materials). As predicted in Figure 1.3a and Figure 1.3b, we observed that the penetration of the sputtered adlayer (Fe) into the host substrate (Au) is low (simulation ~15% and experiment ~20%), hence confirming that reorganization is not due to metal interpenetration. Although the small (~20 %) interpenetration can generate internal stress in the host substrate leading to re-organization. Since the surface of the as-deposited Au prior to deposition of the adlayer is significantly rough (2.3 ± 0.2 nm), the packing of the second metal cannot be expected to form an ultra- smooth interface and, as such, in the depth profile experiment Au will appear to be closer to the surface while Fe will appear to be deeper than would be expected.\textsuperscript{46} An asymmetric distribution of Fe is observed both in the simulation (Figure 1.3e) and experimental (Figure 1.3g) data. Similar observations were made for other metals, even with Al where $R_{RMS}$ for $Au^{Al-TS} > Au^{TS}$ Comparison of $Au^{Al-TS}$, $Au^{Fe-TS}$ and $Au^{TS}$ shows no correlation between penetration depth and changes in $R_{RMS}$ suggesting that the penetration depth is not a significant contributor to the observed reorganization.
Figure 1.4 STEM characterization of the as-prepared thin films. a) A thick layer of Pt is deposited on the AuFe-TS film and a thin cross-sectional slice, of the three metals and the silicon substrate, is prepared to expose the interfaces. b) Elemental mapping of the Fe-Au interface shows that the adlayer is localized on top of the Au, and does not significantly penetrate or diffuse into the Au film. c) Elemental analysis across the bimetallic interface shows the penetration of Fe into Au layer by both XPS and EDS analysis.

To understand the underlying mechanism to the surface reorganization at the $M_1$-substrate interface, the association between Au surface properties and properties of the atoms was investigated. Under the current experimental conditions Au, with its low reactivity, is unlikely to form intermetallic compounds, however, diffusion bonding cannot be ruled out although this is dependent on interatomic forces that are only effective over ~ 1 nm. We therefore sought to investigate other material properties that can help explain the reorganization. Figure 2.3h shows the correlation of the $\text{Au}^{mTS}$ and lattice constant mismatch between the Au and the metal used for the adlayer. We observe that the larger the lattice mismatch the lower the surface roughness, indicating that the lattice constant is an important parameter in tuning degree of surface reorganization. Although a decay is observed, the plot is analogous to that of interfacial
stress in hetero-epitaxy film growth in that,\textsuperscript{48} it asymptotes at $R_{\text{RMS}} = 0.2$ nm suggesting a maximum limit in reorganization at the interface.

In addition to the simulation and depth profile XPS analysis, we further confirmed the nature of the interface using scanning transmission electron microscopy (STEM).\textsuperscript{49} A thin cross-sectional slice of the composite film – supported by a thick Pt layer, was prepared (see Supplementary Materials) and, from the STEM image (Figure 1.4a), elemental mapping (Figure 1.4b) and elemental line analysis (Figure 1.4c), we observe that, as predicted by SRIM simulation and XPS, the Fe layer is localized on the surface of Au and does not significantly penetrate into the Au. Through the energy dispersive spectroscopy (EDS) elemental line analysis, the penetration of Fe into Au is estimated about 75 nm. Considering the spatial resolution of EDS and alignment of detector and sample, the actual thickness is expected to be less from the reading. The EDS agrees with XPS depth profile (Figure 1.4c) when we align EDS at maximum signal with most Fe-rich region from XPS. The effect of the deposited Pt layer can also lead to a slight reorganization at the Fe-Au interface, hence this STEM characterization should be interpreted as a compliment to the simulation and XPS depth profile analysis. The results, even with the limitation in resolution, confirm that the re-organization on the opposite face of the Au film is likely to arise from the interfacial stress generated upon deposition of an adlayer (kinetic energy transfer and associated damage) and from the penetration of the film by atoms making up the adlayer (physical disruption of the crystal lattice).

1.3.7 Mechanistic understanding of surface reorganization

We hypothesize that the mechanism of surface reorganization could be a manifestation of thermodynamic equilibration, in which an increase in internal stress due to the introduction of
the adlayer leads to surface reorganization and reduced surface energy. This reorganization entails minimizing the size of the grain and the grain boundaries, a process that induces surface re-organization, albeit on the parallel (opposite) surface of the film from one where the adlayer is deposited. Such a coupled process would require a concomitant increase in defect density upon deposition of the adlayer, followed by dislocation migration leading to dissipation of some of the generated strain. Increased density of defects would consequently lead to an increase in the materials hardness.

To test this hypothesis, we characterized the mechanical properties by nano-indentation. Figure 1.5a shows the correlation between the peak load (usually interpreted as the hardness of the material) and surface roughness of the AuM-TS films. The AuAl-TS shows comparable hardness with the control sample—AuTS, while the rest are harder than the original film. As the material gets harder, the surface roughness decreases following a trend analogous to that observed with the lattice mismatch (Figure 1.5b). These results therefore support our hypothesis that there is an increase in defect density upon deposition of the adlayer and, therefore, any associated defect migration leads to the observed reorganization.
**Figure 1.5** a) The roughness of the template stripped surface is correlated to the mechanical hardness of the material which is captured by the peak load in nano-indentation. b) The relation between lattice mismatch and the corresponding film surface roughness as well as the peak load (inset). Both peak load and lattice mismatch follow analog relations to the surface roughness.

### 1.3.8 Summary

We investigate the effect of interfacial stress in co-deposited metal thin films as captured by surface reorganization, change in mechanical strength, and surface roughness. We hypothesize that the observed changes in thin film properties upon deposition of a second layer is, in part, due to defect migration, that allows for strain relaxation/energy dissipation across the thin film. A minima, in both the mean and standard deviation of $R_{\text{RMS}}$ with varying sputtering rates (hence kinetic energy of adlayer atoms), we infer that the reorganization process has an energy barrier to overcome for optimal reorganization. As expected higher sputtering rates (high kinetic energy) led to film damage. Through nano-indentation, we observe that the thin films became harder which we infer to be due to an increase in defect density. A correlation between hardness, lattice mismatch, and degree of surface reorganization (decrease in roughness) is observed. We, therefore, believe that larger lattice mismatch leads to higher stress and more defects, inducing more surface reorganization, which concomitantly leads to a decrease in size of grain boundaries and, hence, a decrease in surface roughness.

### 1.4 Materials and methods

**Materials:** All metals were purchased from Ames National Labs or Sigma-Aldrich and were used as received. Some Au$^{m}$-TS ($m$= Fe, Ti, Cu, Pd, Al) substrates were independently custom prepared by Substrata Thin Film Inc. and used as received.
**E-beam evaporation of Au:** 99.99% pure Au was evaporated onto silicon wafer (*Temescal BJD-1800*). Silicon wafers were purchased from university wafer and used as received. The chamber was evacuated to high vacuum (<10^{-6} Torr) before the electron beam was turned on. The evaporation rate was determined at ~1 nm per sec.

**Example of adlayer sputtering procedure (Ti):** The Ti ad-layer was magnetron-sputtered onto 200 nm Au film on silicon (111) substrates. The chamber was evacuated until the vacuum reached 3x10^{-6} Torr. Sputtering was conducted at different rates, where depositing rate was calibrated by measuring thickness of a film using a contact profilometer. The Au ad-layer was sputter coated onto Au-silicon substrates using Quorum sputter coater. The chamber was evacuated and purged with Ar for plenty of times to minimize the amount of air. Deposition rate was estimated as 0.2 nm/s.

**SRIM:** The ion (atoms) penetration into gold film and the energy absorbed by gold film were simulated using the *SRIM software*. The ions were simulated at the given energy of either 100eV or 10keV. All data and figures were generated automatically by the software.

**Characterizations:** The thin film surface was characterized and analyzed by Atomic force microscopy (AFM), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray photoelectron microscopy (XPS), X-ray diffraction (XRD) and nano-indentation.

**Reference**


44. According to Norget's modification of the Kinchin-Pease expression, the energy required to remove an atom from its lattice position, Ed, is directly proportional to the charge, Zm, and mass, m, of the atoms involved in the collision. Based on this model, we infer that with neutral species, the primary recoil energy will be low, hence cannot meet the limit: \( E < 25 \text{ KeV.m.Z^4/3} \) needed to generate Frenkel pairs.


CHAPTER 2. INTRODUCTIONS TO SAMS STRUCTURE AND PROPERTIES

Since the discovery of molecular monolayers, self-assembled monolayers (SAMs) have emerged as a simple platform technology hence have been broadly studied. SAMs are also essential platforms in molecular electronics and, therefore, the quality of the molecular junctions is dependent on the structure of the SAMs. With advances in the state-of-the-art fabrication and characterization methods, new insights into SAM structure and related properties have been delineated albeit with some discrepancies and/or incoherencies. Some discrepancy, especially between experimental and theoretical work, are in part due to misunderstanding of subtle structural features like phase evolution or SAM quality. Recent work has shown that simple techniques, like measurement of static contact angles, can be used to delineate otherwise complex properties of the SAM especially when complimented by other more advanced techniques. In this section, we highlight effect of nanoscale substrate asperities and molecular chain length on SAM structure and associated properties. By deploying a well-known tensiometry technique (herein the liquid is used to characterize the solid, hence the term ‘inverse tensiometry’) to characterize the SAM, we demonstrate that complex molecular-level phenomena in SAMs can be understood through simplicity.

This chapter is modified from an article that has been submitted to Langmuir.

2.1 Historical review of development of self-assembled monolayers

Origin of research in organic thin films dates back to Franklin’s discovery of the calming effect of oil on water surface,\(^1\) where a monolayer of oil molecules was actually formed. The first reported monolayer film on solid substrate was fabricated by inserting a solid film into aqueous solution with organic components.\(^2\) This type of molecular monolayer, so-called Langmuir-Blodgget film, find their roots in Whilhelmy plate tensiometery technique.\(^3\) Studies of organic monolayer have been slowly but steadily carried out, with these original studies being based on physisorbed systems. Realization that certain organic moieties can covalently
bond to various substrates led to chemisorbed monolayers, from which the concept of self-assembly emerged in part due to a small metal - head-group foot-print on an otherwise large molecule. Over the last few decades, the field of self-assembled monolayers (SAMs) has rapidly evolved, especially for organosulfur compound on noble metals, where the fabrication/synthesis of SAMs has been established, and the structure of SAMs has been characterized by a combination of spectroscopies, microscopies, and extensive theoretical work. Meanwhile, SAMs have found broad interest in biological applications, materials surface functionalization, sensing, electronic/optoelectronic devices among others. A self-assembled monolayer is a 2-dimensional material that is formed on a substrate through a spontaneous assembling of molecules. Based on the type of adsorption (chemisorption and physisorption) of molecules onto the substrate, there are chemisorbed and physisorbed SAMs. The chemisorbed SAMs are the focus of this article. In chemisorbed SAMs, molecules are covalently bonded to the substrate (usually metal, such as gold and silver), leaving the molecules standing on the substrate due the secondary intermolecular interactions that induce order depending on the extent of relaxation that the molecules undergo. This relaxation is dependent on the degree of rotational freedom in the molecular structure, allowing the molecule to interrogate all the conformational energy space available, and where possible relaxing to a global minimum that maximizes the overall energy of the molecular ensemble. These conformational relaxation, in turn, affects the nature of interface created and can therefore manifest in the surface energy (wetting) properties of the SAM. Previously, studies on SAMs and new challenges in respective areas have been summarized in other review articles. In these reviews, characterizations of SAMs with vibrational spectroscopy, optical spectroscopy and scanning microscopy are discussed for structure
analysis and corresponding property studies are reported. Development of robust SAM-based
technologies has, however, been hindered by a lack of fundamental in SAMs processing-
structure-properties relationship. Unfortunately, literature on SAMs is riddled with reports of
‘conclusive’ studies on such topics as effect of substrate roughness on SAM structure, phase
evolution in simple SAMs, or even basic properties like wetting, yet agreement between
various reports is missing starting with the Whitesides-Porter odd-even discrepancy over 25
years ago. A major source of the differences is the state-of-the-art technologies at each
historical point that lead to misinterpretation or invalid conclusions. Advances in surface
fabrication and characterization techniques has, however, allowed for better and more accurate
characterization of the SAMs and is the subject of this report. We summarize our studies on
the simplest system, n-alkanethiols on gold (Au) and silver (Ag) substrates, aiming to
understand the processing-structure-properties relationship. By going back to the most basic
property of characterizing a modified surface, wetting behavior, we interrogate the surface
using various fluids and exploiting the surface related material specific property of the probe
liquid to understand the nature of the contacting surface. Fitting the obtained data into well-
established wetting theories and relating the deduced observations to the underlying molecules,
inferences on the nature of the SAM are deduced. We further support our inferences using
sum-frequency generation spectroscopy, allowing us draw bold conclusions about the nature
of the SAMs with changing molecular chain length (especially the so-called odd-even effect)
and substrate roughness or identity (Au vs Ag).

2.2 SAM wetting and the odd-even effect

The odd-even effect is a widely observed phenomenon in various areas, such as chemistry,
physics, biology and even evolution. In SAMs, the odd-even effect is described as a zig-zag
oscillation in material structure and properties depending on whether the number of a repeating unit, e.g. CH$_2$ in n-alkanethiols, in the molecules making up the SAM is odd or even. The odd-even effect has been observed in spectroscopy, wetting, frictions, mechanical properties, thermal properties, charge transport among other properties. The odd-even effect in SAMS has been well covered in a review by Tao et al., hence only necessary updates will be provided in this perspective.

Alkanethiolate-based monolayers on Ag or Au surface, are the simplest form of SAMS from a chemistry (saturated hydrocarbon) or structure (simple inter-chain van der Waal induced assemblies) point of view. The SAM/ambient interface is of most interest in various field, and has been carefully characterized and theoretically studied in a number of recent studies. Despite the fact that this surface-exposed interface is removed from the substrate, its properties are intricately tied to the substrate through the space unit, and as such depend on the nature (conformation, order, size, structure and orientation) of these spacers. Study of odd-even effect in alkanethiolate SAMs, therefore, needs to associate SAMs behavior with substrate surface characteristics and relate these to the role of the spacer unit(s).

### 2.2.1 Contact Angle—simple approach to delineating SAM interface structure

Contact angles are widely used to characterize materials surface properties, primarily due to their role in tensiometry. The Young’s Equation, (Eq. 1) is widely applied to correlate surface tensions/energies ($\gamma$) through observed contact angle ($\theta$), as schematically shown in Figure 1;

$$\cos \theta = (\gamma_{SG} - \gamma_{LS}) / \gamma_{LG}$$

(2.1)

Where $\gamma_{LG}$ is the surface tension of the liquid, $\gamma_{LS}$, the interface tension, and $\gamma_{SG}$ is the surface energy of the substrate.
The wetting behavior can also be characterized through the spreading parameter (Young-Dupre equation, Eq. 2) or through the work of adhesion (Eq. 3) with both parameters being derivatives of the Young’s equation.

\[
S = \gamma_{SG} - (\gamma_{LS} + \gamma_{LG}) = \gamma_{LG} (\cos \theta - 1)
\]

\[
W_a = \gamma_{SG} + \gamma_{LG} - \gamma_{LS} = \gamma_{LG} (\cos \theta + 1)
\]

The latter can further be elaborated through an understanding that ability to physisorb is directly dependent on intermolecular interactions across the interface – essential in the establishment of a static equilibrium. These intermolecular interactions (secondary bonds) can further be classified as polar (e.g. H-bonding, dipole-dipole) or non-polar (van der Waals type) interactions leading to re-expression of \( W_a \) as (Eq. 4);

\[
W_a = 2 \sqrt{\gamma_{LG}^p \cdot \gamma_{SG}^p} + 2 \sqrt{\gamma_{LG}^d \cdot \gamma_{SG}^d} = \gamma_{LG} (\cos \theta + 1)
\]

From a closer inspection, and upon simple rearrangement of Eq. 4, we recently demonstrated the derivation of a dimensionless parameter (\( \chi_c \)) that correlates with the nature of interactions at the liquid-solid interface (Eq. 5). In the case of SAMs, \( \chi_c \) relates to the quality of the monolayer hence, the nature of the substrate and molecular ordering. The \( \chi_c \) parameter is dependent on the probe liquid (\( \gamma_{LG} \)) and the interactions between the surface and said liquid.
\[ \chi_c = \sqrt[\gamma_L^P \gamma_S^p} + \sqrt[\gamma_L^d \gamma_S^d} \]  

For SAMs, since \( \chi_c \) is a surface sensitive parameter, it can be used to probed and/or qualify surface dipole, intermolecular interactions, and by extension gauche-defect density. From Eq. 5, if SAM interface has variance in polarizability/dipole moments (due to identity or orientation of the terminal moiety), the contact angle formed by a probe liquid will show an analogous fluctuation depending on their identity. In a well-ordered n-alkanethiolate SAM, for example, the odd-even effect in wetting can be presumed to be due to alternating dipole moments (orientation of the terminal \(-\text{CH}_2\text{CH}_3\)) at SAM/ambient interface for molecules with odd and even number of \(-\text{CH}_2-\) groups.
Early studies in wetting on SAMs of n-alkanethiolate, however, cast a shadow on the odd-even effect due to discrepancy in the general trends and an insinuation of possible contaminations. In one of the earliest systematic study of SAM wetting properties, Walczak et al.\textsuperscript{41} (Porter’s group) observed a zig-zag oscillation in contact angles (Figure 2a(iv), 2b(iv)), hence inferred an odd-even effect. An odd-even effect was observed in water $\theta$s with longer chain length (n>10), and in shorter chains (n<8) for hexadecane $\theta$s. A few months later, Laibinis et al.\textsuperscript{11} (Whitesides’ group), in an analogous study failed to observe an odd-even effect (Figure 2a(i, ii), 2b(i, ii)). A gradual increase in $\theta$s with chain length, however, is observed in lieu of the odd-even oscillation. These two studies constitute the so-called Whitesides-Porter discrepancy that has been revisited elsewhere.\textsuperscript{42} Analogous follow-up studies also failed to demonstrate an odd-even effect (Figure 2a(iii)) and b(iii)).\textsuperscript{40} In later work, Graupe et al.\textsuperscript{8} did not observe the odd-even effect with water $\theta$s (Figure 2a(v)) but observed it in hexadecane $\theta$s (Figure 2b(v)). A major caveat in most of these early studies is that no substrate roughness data were reported, making it challenging to deduce the quality of the SAMs formed. Limitation in the state-of-the-art surface fabrication techniques, however, can be hypothesized as the origin of these discrepancies. In later studies, it has been shown that substrate roughness has a significant effect in the observed contact angles. Comparison of wetting between rough ‘as-deposited’ (M\textsuperscript{AD}) and smooth template-stripped (M\textsuperscript{TS}) Ag and Au surfaces showed that, indeed, the challenge with these earlier studies was likely in the quality of substrates. An odd-even zig-zag oscillation in water contact angles for C\textsubscript{10}-C\textsubscript{16} SAMs formed on M\textsuperscript{TS} and not on M\textsuperscript{AD} was recently reported, as in Figure 2a(vi). Figure 2b(vi) shows that HD however gives an odd-even effect.
effect in contact angle regardless of the substrate roughness, although the magnitude of the odd-even effect is smaller on Au\textsuperscript{AD} than that on Au\textsuperscript{TS}. Interestingly, a gradually increase in the water contact angle, analogous to observations from most of the earlier studies, was also observed for the M\textsuperscript{AD} surface indicating that earlier studies may have used rough surfaces, an inference supported by the state of the art capabilities at that time.

2.2.2 Effect of substrate roughness on SAMs thermodynamics, structure and wetting.

**Figure 3.** The dependence of SAMs functional interface on substrate and the number of alkyl groups. a-b) Schematic illustrations of chemisorbed molecular assembly on flat and rough surfaces, respectively. Orientation of the terminal moiety is different for molecules with c) even number of CH\textsubscript{2} and d) odd number of CH\textsubscript{2}.

The SAM formation process is dominated by head-group substrate bonds and intermolecular forces to create an ordered structure\textsuperscript{12, 25, 43}, the latter being highly dependent on the relative distance between the chains. Surface texture, therefore, can perturb the degree of order\textsuperscript{12, 26, 44-}. 
in SAMs (Figure 3a and 3b). Molecules on rough surface are, therefore, not highly ordered or at least not universally ordered (ordered assembly may occur on local flat regions, forming “islands”\textsuperscript{50}). In well-ordered n-alky SAMs, the orientation of terminal moiety depends on whether the spacer has even or odd number of methylene (-CH$_2$-) units (Figure 3c and 3d).\textsuperscript{39} This oscillating behaviors manifest in various fields such as charge transport\textsuperscript{37-38, 51} and friction.\textsuperscript{33-34} Considering that “as-deposited” surfaces have root-mean-square roughness $>$ 2nm, a distant longer than a trans-extended C$_{18}$, it can be expected that deposition of such molecules on these surfaces will give low-quality SAMs while the inverse is true for truly flat surfaces.

\textbf{Figure 4.} Substrate morphologies and the SAMs wetting behaviors. a) Atomic force microscopies of template stripped gold surface (Au$^{\text{TS}}$) and as-deposited gold surface (Au$^{\text{AD}}$). b) Sum frequency generation spectroscopies of alkanethiolate SAMs formed on Au$^{\text{TS}}$ and Au$^{\text{AD}}$. (Copyright from RSC)
The structure of SAMs are well-studied using state of the art characterization techniques like scanning tunneling microscopy (STM), atomic force microscopy (AFM) and supported by theoretical simulations. Specifically, STM is used to study molecular packing and assembly, as well as some crystallographic structure of the SAMs. Detailed reviews of SAM characterization by advanced microscopy has been widely reviewed. Surface sensitive IR-based techniques examine rotational and vibrational structure of the molecules, from which intramolecular oriental structure and intermolecular “solvation” environment can be deduced. Using sum frequency generation (SFG) spectroscopy, we characterized both bulk and interface structure of n-alkanethiolate SAMs on smooth template-stripped (AuTS, \(R_{\text{RMS}}=0.4\text{nm}\)) or rough ‘as-deposited’ (AuAD, \(R_{\text{RMS}}=2.4\text{nm}\)) surfaces (Figure 4), by using the terminal –CH\(_3\) as a probe. Spectra were collected for C\(_9\)-C\(_{16}\) (except C\(_{13}\)) on both substrates. The intensity from the CH\(_3\) asym str peak at 2970 cm\(^{-1}\) on “smooth” AuTS showed odd-even oscillation (Figure 4). On the “rough” AuAD surface, however, no significant variance for this peak intensity with increasing chain length was observed (Figure 4). Besides revealing the interface structure, trends in peak width variations showed that the local chemical environment of the terminal –CH\(_3\) changes with surface roughness irrespective of surface roughness. This insight pointed to molecular length-dependent changes in the SAM and may be related to theoretical conformational dynamic studies like those of Goodman and Jorgensen.

Whereas the use of these advanced techniques to characterize SAMs is commendable, necessary, and illuminating, they did not help clarify the discrepancy in wetting properties of SAMs—A fundamental, and critical, property in our understanding and development of these platform technology. In the first two decades of the development of chemisorbed self-assembled monolayers, limited effort had been dedicated to understanding the role of substrate
roughness in the wetting properties, but with advances in scanning probe microscopy, it gained attention. It took 23 years for the first study on effect of roughness on SAM wetting to appear after the first published wettability reports by Porter and the latter by Whitesides and Nuzzo.42

2.2.3 But why a focus on wetting?

Wetting, is a simple but information-rich phenomena since it captures the intricacies of an equilibrium state between a two surfaces. Considering Gibbs free-energy of a sensille droplet (Equation 6), we observe that not only is the equilibria dependent on the surface energies of the surface and the substrate, but also on the size of the droplet (captured by the height at each point on the interface). Wetting, even in case of sensille droplets, can therefore be envisioned as a chemo-structural property, revealing not only the intricacies of molecule-molecule interactions at the interface but also the nature of the interface structure.

\[ G_{[h]} = \iint [\gamma \sqrt{1 + (\nabla h)^2} + (\gamma_{SL} - \gamma_{SV})] \, dx \, dy \]  

(2.6)

Where \( h \) is the height of the droplet at a point in the interface, \( \gamma \) is the surface energy, and \( G \) is Gibbs free energy.

It therefore follows that wetting can reveal characteristic properties of SAMs surface structure, and by extension, help indirectly deduce bulk structure. By analyzing contact angles, a SAM’s overall structure, or at least the interface structure, can be deduced. In linear n-alkanethiolate SAMs, the odd-even effect depends on the probe liquid and SAM order and therefore this phenomena is ideal for deducing SAM structural properties.

2.2.4 How rough is too rough for odd-even effect?

Since substrate roughness affects SAMs order and hence properties, several questions had remained unresolved until recently. These question are; i) since molecular bonds have a fixed
length, is there a limit below which substrate roughness can be overcome by conformational relaxations? ii) Analogous to (i), is there a limit beyond which substrate roughness dictates interfacial properties in SAMs? iii) What is the relationship between substrate roughness and size of the molecule making up the SAM? Does a molecular length-substrate roughness coupling effect exist? iv) Since interfacial Gibbs free-energy depends on the height (size) of the droplet and interfacial surface energy (Equation 6), is there a dependence of substrate roughness dependent properties on the surface tension of the probe liquid? v) Are there other substrate dependent variables that dictate interfacial properties of the SAMs besides roughness?

To answers these questions, surfaces with different roughness and morphology (grain size) are required. We, therefore, developed a technique to tune the surface roughness and/or morphology of a metallic thin film without damaging/contaminating the surface on which the SAM is to be fabricated.\textsuperscript{57} Using our method, roughness of either Au or Ag surfaces can range from 0.2 nm to 2.2 nm, with variable grain sizes but predominantly one faceted. With this tunability in substrate roughness, the effect of substrate roughness on the odd-even effect in wetting was investigated. Figure 5 summarizes wetting data as captured in water and hexadecane (HD) contact angle (C\textsubscript{10}-C\textsubscript{16}) across different surface roughness derived from both Ag and Au. Irrespective of the differences in cant angles for SAMs on Ag and Au, we observe that there is a clear limit to the empirical observation of the odd-even oscillation in contact angles at R\textsubscript{RMS} \textit{ca.} 1 nm.

\textit{Hydrophobicity.} On ultra-flat Au surfaces (R\textsubscript{RMS}=0.2-0.4nm), the odd-even effect was not significantly affected by substrate roughness (\(\Delta\theta_2 \approx 0.7^\circ/\text{Å} \), but rather showed a slight decline with increase in substrate R\textsubscript{RMS}. Extrapolation of the linear fits to the odd- and even-series led
to two main inferences, viz; i) the maximum differences in water contact angles between the odds and evens, $|\theta_s^{even} - \theta_s^{odd}| = 3^\circ$, ii) this difference diminishes with an increase in surface roughness eventually disappearing at $R_{RMS}$ ca. 1 nm. To empirically prove this predicted limit, and evaluate the role of molecular cant angle, a series of Ag substrates with roughness spanning the 1 nm mark (0.7nm-2.2nm as in Figure 5) were used to fabricate monolayers. Ag substrate with $R_{RMS} = 1.1$nm did not show the odd-even effect while one with $R_{RMS} = 0.7$ nm showed the odd-even effect. This observation confirmed that a roughness-dependent limit to the observation of the odd-even effect lies in the range $R_{RMS} \approx 0.7$nm-1.1 nm, which correlates well with the prediction.

**Oleophilicity.** Due to the favorable surface tension match between hydrocarbons, hexadecane (HD) on alkanethiolate SAMs shows lower contact angle (<50°)- that is, it wets the surface. With HD, the odd-even effect was not only observed over the range of substrate roughness (0.2nm-2.2nm) recently reported by Thuo and co-workers but also in other rough substrates. This behavior is contrary to the observations from water contact angle, where the odd-even effect is hypothesized to be useful in diagnosing the quality of the SAMs or interface structure. The presence of an odd-even effect in the HD aligns with the oscillation in peak widths observed in SFG suggesting, as expected, sensitivity to the local chemistries on the surface irrespective of surface morphology. Odd-even effect with water can be compared to analogous peak intensities on the suggesting sensitivity to the interface. This comparative association, therefore, poses as a quandary; can wetting and non-wetting probe liquids be used to understand complex interface chemistries? An understanding of role of interface structures and wetting is, therefore needed to resolve this quandary.
2.2.5 Effect of substrate structure beyond simple roughness.

In surface characterizing, the RMS roughness is undeniably one of the most important parameters. For wetting of volatile liquid, however, surface micro-structure play an important role due to capillary forces and hence adhesion force. Consider two solid surface that are sufficiently close to each other, vapor condenses into liquid following the Kelvin’s equation (Eq. 7). This phenomenon (capillary condensation), is important in describing some adhesion phenomena.

\[ RT \ln \frac{P}{P_0} = \gamma V_m \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]  \hspace{1cm} (2.7)

Where P and \( P_0 \) is the vapor pressure and saturation pressure, respectively. \( \gamma \) is the surface tension, \( V_m \) is the liquid molar volume, and \( r_1 \) and \( r_2 \) are principal radii of curvature. It therefore follows that, if surface asperities are very sharp (low radius), then propensity to condense vapor will be very high altering the surface energy of the substrate. Presence of a monolayer, however, may reduce the overall size of these crevices mitigating condensation of surface energy mismatched vapors.
But is a condensate a reason for concern in delineating surface properties? For a simplified case, the capillary force \( F_{\text{cap}} \) of a liquid in between two spherical surfaces is described as (Eq. 8);

\[
F_{\text{cap}} = 4\pi \gamma cR^{*}\left(1 - \frac{D}{V\sqrt{\pi R_1 + D^2}}\right)
\]

(2.8)

Where \( c \) is a constant associated with the contact angle of the liquid on the two surfaces. \( R_1 \) and \( R^{*} \) are the radius of one particle and the effective radii (derived from the radii of the two particles), respectively. \( V \) is the constant volume, and \( D \) is the distance of two surface. Detailed descriptions and explanations have been summarized by Butt and Kappel.\(^6\) The capillary force contributes to the adhesion force on a textured surface as captured in this relation (Eq. 9).

\[
F_{\text{adh}} = 4\pi \gamma cR^{*} = F_{\text{cap}}\left(1 - \frac{D}{V\sqrt{\pi R_1 + D^2}}\right)
\]

(2.9)

From this equation it is clear that the radii of the particles are affecting the adhesion force, suggesting that curvature (as surface morphology in some cases) matters in governing the nature of interaction between a surface and a probe liquid. To extend, beyond spherical surfaces, the geometries of the two surfaces also have significant effect on the adhesion force (Figure 6). Therefore, on surfaces that have micro-structure the effect of those structure on wetting should not be neglected. A challenge in this discourse is the role of nanoscale surface defects on adhesion and, by extension, wetting.
Extension of these macroscale phenomena is complicated by capillary effects once below the capillary length of the probe liquid. In other studies that are based on SAMs such as large area tunneling junctions, it has been shown that the entirety of surface morphology, rather than simple roughness, significantly affect the SAM structure as manifested in corresponding properties. Nijhuis and coworkers for example, observed that in addition to roughness, the number of grains and the width of corresponding grain boundaries can affect SAM packing, and therefore; i) affects the rectification ratio of molecular diodes, and ii) the yield of working devices. Bearing volume (BV), a parameter associated with grain size and boundary widths, was found to correlate with device performance.

The micro/nano-structure on the substrate surface, such as grain size and grain boundaries, in some case is independent from the RMS roughness. Figure 7a shows AFM images of two metal surfaces, the AuTS and AgFe-TS, which bear comparable R_{RMS} (~2.2nm). These two surface, however, have significantly different grain sizes, which can be directly observed from AFM images. The silver surface has larger grains than the gold surface but also deeper defects (at the boundaries). Due to the morphology, proposed formation of SAMs were illustrated in Figure 7a. AuAD, which has smaller grains and is considered defects dominant, does not have
flat regions to form ordered SAMs or at least islands of SAMs. $\text{Ag}^{\text{Fe-TS}}$, however, has considerably larger grains, which turns into flat region for ordered SAMs formation.

**Figure 2.7** The effect of grain size on contact angle. a) The morphology of two substrate surface. Similar $R_{\text{RMS}}$ but different grain structure, and the proposed SAMs formation at those two surfaces. b) The water contact angle on $\text{Ag}^{\text{Fe-TS}}$ and $\text{Au}^{\text{TS}}$, and a comparison with consideration of the packing and tilting effect.$^{32}$ (Copyright from ACS)

Difference in substrate surface morphology lead to difference in SAMs wetting properties. The water contact angle on SAMs on both substrates (Figure 7b) does not show an odd-even effect, indicating larger grains cannot compensate for the effect of roughness on SAMs structure and hence wetting (or analogous) properties. As previously shown, we can correct for differences in SAM packing densities on the contact angles (Figure 7b, triangles) but this does not account
for the differences between the wetting properties. This variance in hydrophobicity of Ag and Au rough surfaces can either be due to capillary force or differences in SAM structure.\textsuperscript{12, 29}

Figure 2.8. Effect of substrate nature and subtle change on molecular wetting behaviors. a) AFM images of Ag\textsuperscript{Al-TS} and Au\textsuperscript{TS}, whose surface morphology are similar, and Au\textsuperscript{Fe-TS} with lower roughness. b) Ideal SAM structure and molecular orientation on Ag and Au surface. c) The difference in contact angle on SAMs formed on Ag and Au surface with similar morphology and roughness. d) The difference in contact angle between Au and Ag substrates disappears at around C\textsubscript{3}. e) The change of contact angle on SAMs over slight substrate roughness variance. (Copyright from ACS)
As a molecular phenomenon, factors other than surface morphology that affects the molecular structure are important in the observed wetting results. Surfaces with similar morphology (roughness, bearing volume, coverage, etc.\textsuperscript{32}) but different identities, Au\textsuperscript{TS} and Ag\textsuperscript{Al-TS}, have been used as substrates for SAMs (Figure 8ai and 8aii). The ideal SAMs structure on these surface are expected to be different (Figure 8b) and, as expected, show differences in the oscillation in their odd-even effect (Figure 8c). Form this work, it was observed that the odd-even effects in hydrophobicity were due to difference in contact angles on SAM\textsuperscript{E}, but this difference decreases and vanishes at C\textsubscript{3}, as in Figure 8d.\textsuperscript{32} This observation of diminished effect of the substrate identity to the wetting properties of the SAM, may be in part due to decreased order in the SAMs suggesting that degree of SAM order will decrease with molecular length for shorter chain-length SAMs. We qualify this observation since for longer SAMs (>C\textsubscript{14}), the contact angles seem to be different for both SAM\textsuperscript{E} and SAM\textsuperscript{O}.

In addition, small changes in the morphology (mainly decrease in roughness by \sim 0.2 nm) of the surface also leads to slight changes in wetting results (Figure 8e). We have demonstrated that using substrate with reduced roughness, such as Au\textsuperscript{Fe-TS} (roughness RMS= 0.2 nm), the contact angle on the SAMs that are fabricated on these surface shows a roughness dependence (Figure 8e).\textsuperscript{30} Extrapolation of this data followed by empirical evidence over both Au\textsuperscript{30} and Ag\textsuperscript{31-32} suggests that there is a limit to the observation of the odd-even effect in hydrophobicity of these SAMs through sessile droplet contact angles.

### 2.3 Why different probe liquid behave differently?

From the preceding discussion it can be inferred that a roughness and chain-length dependent odd-even effect in hydrophobicity exists in SAMs. Changing the probe liquid to a non-polar one (hexadecane), however, the roughness-limit to the odd-even effect has not been
reported (Figure 5). This discrepancy between HD and water contact angles calls for more detailed evaluation.

**2.3.1 The hexadecane ‘anomaly’ in odd-even effect limits**

With HD as a probe liquid, odd-even effect is observed on all substrates irrespective of roughness and across the n-alkanethiolate chain lengths. From SFG spectroscopy, however, n-alkanethiolate SAMs formed on Au surface with $R_{\text{RMS}} \sim 2$ nm bear a highly disordered interface.\(^{26}\) Therefore, the odd-even effect observed from HD contact angle is not derived from interfacial interactions with the terminal moiety (i.e. not governed by orientation of these terminal moieties), but is likely from molecule-molecule interactions – a possible inference since HD wets the surfaces. With HD, therefore, there are two possible scenarios; i) Since HD wets these SAMs a closer contact can lead to probing of the variance in the local chemical environments of each of the surface exposed moieties.\(^{62}\) This variance in local chemical environment has recently been observed using peak-width at half-height in the SFG signals derived from the terminal $-\text{CH}_3$ moiety.\(^{26}\) An analogous behavior would not exist for a poorly wetting probe liquid. ii) Being apolar, HD does not have a polar component contributing to its surface tension and hence only bears a dispersive component. Molecular polar forces (Coulombic interactions) are generally more directional in their inter-molecular interactions, hence are better probe for order-dependent interfacial properties.\(^{63-64}\) Dispersive force (e.g. London dispersive forces and van der Waals interactions), on the other hand are more adaptable and responsive to local chemical environments. Thus contact angle (wetting) of HD is not only dependent on interface order/orientation of the SAMs but also on intermolecular interactions between the liquid and the SAMs irrespective of order. This inferences leads to a need to further deduce that by using either the polar or dispersive component of surface tension as a
‘probe’ to investigate wetting; not only can we reveal the nature of the top-interface of the SAM (polar component) but also delineate the degree of order/disorder in the bulk (dispersive component). The former is well known fact as it is the basis of spectroscopic methods like SFG (surface dipoles interacting with light), while the latter has not been reported until recently.

### 2.3.2 Effect of the dispersive and polar components

As discussed in section 2.1, the contact angle of a probe liquid on a solid surface is dependent on both dispersive and polar interaction between the liquid and the solid surface. This relation is well-understood as captured in the Young’s equation and from the analogous Young-Dupre relation, effect of the polar and dispersive components to the contact angle can be deduced (Equation 10).\(^{28, 30, 65-66}\)

\[
\cos \theta = 2 \left( \sqrt{\gamma_{LG}^p \gamma_{SG}^p} + \sqrt{\gamma_{LG}^d \gamma_{SG}^d} \right) \frac{\gamma_{LG}}{\gamma_{SG}} - 1
\]

This relation, therefore, shows that the observed contact angles are a derived from a product of polar (\(\gamma_{LG}^p \gamma_{SG}^p\)) and dispersive (\(\gamma_{LG}^d \gamma_{SG}^d\)) interactions at the interface, and these would additively dependent on proportional contributions of each to the interaction. It can therefore be envisioned, as mentioned above, that HD would be a good probe to use to interrogate non-polar interfaces since there are no coupe polar-dispersive interactions. Presence of polar interaction, however, introduces a dependence of contact angle on polar component of the solid surface, \(\gamma_{SG}^p\). Of relevance to our discussion on n-alkanethiolate SAMs, as a simple model system for other SAMs, is the interfacial molecular dipole that is dependent on the orientation of the terminal moiety. Being a vector (tensor), the surface dipole is dependent on the orientation of the supporting moiety and, hence, the substrate roughness. Overall dipole moment can be estimated as (Eq. 11)
Effective dipole moment normal to the interface ($P \cdot \cos \theta$) and the density of the dipole ($N$), as in Eq. 2.4, where $\theta$ is the angle between dipole orientation and the interface normal. Change of orientation of the molecules leads to varying $\theta$ and hence affects the interfacial dipole as its result. Since dipole-dipole interactions are directional, disordered SAMs (disordered dipoles) cannot show odd and even oscillations in the requisite dipole-governed interactions. Thus water (or other polar liquids) shows strong substrate roughness dependence in odd-even effect while HD does not.

### 2.3.3 Effect of substrate roughness on wetting of different liquids.

Although the non-polar liquid does not show a dependence on substrate roughness in contact angle, it is well-established that substrate roughness affects SAM structure.\textsuperscript{12, 26, 44-49} Since the observation of the odd-even effect in hydrophobicity is roughness dependent and empirically disappears at $R_{\text{RMS}} \sim 1$ nm, a comparative self-referencing variable ($\Delta \theta_s$) is adopted to; i) compare changes in wetting for other probe liquids other than water; ii) deduce the effect of changing roughness on the wetting behavior of the expanded probe-liquid library. We proposed this as a characteristic wetting parameter based on an asymmetric gradual increase in $\theta_s^{\text{water}}$ that occurs for $<C_{14}$ that eventually asymptotes to a symmetric odd-even oscillation.\textsuperscript{11, 30-31, 40-41} An analogous transition was observed in the odd-even oscillation in peak-width of the terminal CH$_3$ asym vibration peak on SFG.\textsuperscript{26} By definition $\Delta \theta_s$ is the maximum change of contact angle ($\Delta \theta_s = \theta_{\text{max}} - \theta_{\text{min}}$) over a specified chain length, and for this discussion we focus on the C$_9$-C$_{13}$ chain-lengths—for reasons elaborated later (section 4.2), on Ag surfaces. Figure 9 shows the reported change in $\Delta \theta_s$ with changing roughness for three different probe liquids. For glycerol ($\gamma^p = 41, \gamma^d = 24$) there is no significant variation in
Δθs while there is an observed increase—albeit small, for water (γ^p = 51, γ^d = 22), and a
decreases for HD (γ^p = 0, γ^d = 28). The slight increase in Δθ_{water} can be inferred to be due
to enhanced capillary effect at these nanoscale roughness, akin to fabrication of texture driven
engineering of superhydrophobicity. At the irregular nanoscale roughness, the surfaces never
became superhydrophobic since the range of roughness is small. Further investigation of the
small gradual increase in Δθs showed that this is, in part, due to an asymmetric zig-zag
oscillation in θ_{water} that is; Δθ^E→O ≠ Δθ^O→E. An elaborate discussion on this asymmetry
is given in section 4 below. For HD, the decline in Δθs asymptotes at R_{RMS}~1.5 nm, suggesting
a roughness-dependent limit to the variability of θ_{HD} with changes in molecular chain length.
We infer this to be an effect of the SAM behaving like ‘fat’ on the rough surface since at high
roughness there is no order even though the molecules are chemisorbed to the surface. Since
interactions between the surface and HD are dictated by dispersive, non-directional,
interactions, we can infer that the observed decrease in θ_{HD} is likely due to a maximization of
these interactions suggesting a low into the values of contact angle that can be observed for
SAMs. This deduction allows us to infer that dispersive forces driven interactions can be used
to probe molecular level changes in a SAM and is discussed below (Section 4.1). To
summarize, substrate roughness has a diametric effect the behavior of the probe liquid, with
wetting surfaces spreading further and non-wetting surfaces beading up. This inference is,
however, not surprising bearing in mind that the free energy change upon contact (adhesion)
of a liquid on a surface is dependent on the fractional contact area as captured in equation 12.

\[ \Delta G_{adhesion} = \pi r^2 \gamma_L G \left[ \left( \frac{2a}{\sin \theta} \right)^{2/3} - a \right] \]  

(2.12)

Where ‘a’ is the effective surface area, and ‘r’ is the radius of solid-liquid interface (assuming
a completely flat surface). From this relation, it follows that wetting is spontaneous (-ΔG), but
from the HD data we observe that the wettability has a roughness-induced limit probably due to the slight dipole moment on the alkanethiol molecule upon chemisorption or some yet undefined capillary effect. It is therefore imperative that when discussing interface properties of SAMs, that surface roughness and morphology data be provided for comparative evaluation of obtained data.

![Image](image.png)

**Figure 2.9** The effect of substrate roughness on contact angle of water, glycerol and hexadecane. (Copyright from ACS)

### 2.4 Understanding asymmetry in the odd-even oscillation in water contact angle

For C$_9$-C$_{13}$ SAMs, a gradual increase in $\theta_s^{\text{water}}$ and a zig-zag odd-even oscillation are observed. The odd-even oscillation is, however, asymmetric with $|\Delta \theta_s^{E \rightarrow O}| < |\Delta \theta_s^{O \rightarrow E}|$. This asymmetry decays with increase in molecular length and for SAMs derived from $\geq$C$_{14}$ thiols, the odd-even oscillation is fully symmetric. This asymmetry is due to different nature of the evolving nature of the SAMs interfaces over this range of chain length. This variance in interface properties was deduced to emanate mostly from changes in local chemical environment of the molecules and a decrease in SAM defect density. With increase in intermolecular interactions (increased chain lengths), constrained molecular vibration (smaller
number of chemical environments) and less gauche defects (more close-packed) there is reduced conformity to water-SAM interactions, as previously inferred by Laibinis and coworkers from simulation. As a result, the contact angle on the SAMs will be increased with chain length, but asymptotes when no more interfacial changes are structurally possible.

This chain length dependence of interfacial properties is not only observed in $\theta^{\text{water}}_s$ but also in a number of experimental and theoretical studies. Scanning tunneling microscopy on alkanethiolate SAMs demonstrates several phase transitions with chain length. For example, SAMs of methyl-, ethyl-, and propyl-thiolates show a $(3\times4)$ phase, while butanethiol congeners give a $(3\times2\sqrt{3})$ phase. Fenter and coworkers, however, though X-ray diffraction analysis, reported two regimes in terms of phase change and SAMs structure, which are SAMs with chain length $n>14$ and SAMs with $n<14$. In this work, they also reported a coexistence of “solid” and “liquid” phase when changing the temperature. In SAMs based molecular tunnel junctions, Jiang et al. reported that SAMs with $n<10$ show liquid-like characteristics that can compensate for the effect of substrate defects while SAMs with $n>10$ behave like solids and are heavily affected by the substrate defects. In a theoretical work, Jabbarzadeh and coworkers employed molecular dynamics to simulate evolution of gauche defect density in SAMs, where they reported that short chain ($n<7$) has high defect density, while SAMs ($n\geq15$) gauche defect density are diminished. We can therefore infer that the asymmetry in the odd-even $\theta^{\text{water}}_s$ oscillation correlates with an evolving structure of the SAM and with felicitous choice of molecular chain lengths, can be used to qualitatively evaluate the state of the SAM interface especially in cases where a significant amount of gauche (or analogous conformational) defects are expected.
2.4.1 Phase evolution with molecular chain length

In the course of exploring chain-length dependence in contact angles (for both water and hexadecane) on SAMs of a large range of alkanethiol molecules from over C$_3$-C$_{17}$ on Au$^{TS}$ substrates, the data binned into 4 regions showing coherent behavior (Figure 10a-b). The observed regimes are: i) ≤C$_3$—a hydrophilic regime ($\theta_s^{HD}$ and $\theta_s^{water}$ are <90°); ii) C$_4$-C$_8$; a linear increase in $\theta_s$ region where the odd-even effect was not observed; iii) C$_9$-C$_{13}$—an asymmetric odd-even ($\Delta \theta_s^{E\rightarrow O} \neq \Delta \theta_s^{O\rightarrow E}$)$^{30-31}$ regime where like the preceding region the value...
of the contact angle is gradually rising albeit with a gradual decay; iv) ≤C\textsubscript{14} SAMs—where a symmetric odd-even effect ($\Delta \theta^E_{s \rightarrow O} = \Delta \theta^O_{s \rightarrow E}$)\textsuperscript{30-31} is observed but the preceding region.

In regime I, similar to what was observed in STM,\textsuperscript{52} there is transition from C\textsubscript{3} to C\textsubscript{4} in SAM structure (organization on the surface). The hydrophilic nature of the surface (total wetting for HD) is mainly due to either; i) the poorly defined SAMs interface, or, ii) a different electrostatic potential at the interface that could emanate from the structural order of the chemisorbed molecules. The former reasoning, supported by literature data on the structure of the SAMs, let to labeling this region as a pseudo-formed SAMs, that is; the molecules though ordered do not behave as though they are a coherent unit. But even though a SAM forms, the SAMs are amphi-phobic with contact angles being <90°, which led to the conclusion that the substrate must be playing a significant role – potentially through hyper-conjugation since the anti-bonding $\sigma^*_{Au-S}$ and the $\sigma_{C_2-C_3}$ are well positioned for such a through space interaction. Such a hyperconjugation would significantly deplete electron density from C\textsubscript{3} rendering the generated interface hydrophilic (large $\Gamma^p$). Introduction of positive inductive effects (e.g addition of a –CH\textsubscript{3}) lessens the effect of the hyperconjugation and may account for the observed phase change across the C\textsubscript{3}-C\textsubscript{4} region.

In regime II, the increase in contact angle correlates with the decrease in gauche defects observed by Jabbarzadeh, and may therefore be due to an increase in rigidity of the SAM. Presence of a significant amount of gauche defects and lack of odd-even effects suggests that the terminal moiety is likely stochastically oriented, although some order may be gradually building in with increase in molecular length. This implies that molecular rotations are not fully inhibited hence the SAMs are likely “liquid-like”.
Regime III is likely a transition zone. As the chain length of the molecules increase, intermolecular interaction in the SAMs grow and beyond certain point (here $\geq C_8$), the interface start to bear order (defects at the interface are no longer dominating) hence it shows solid-like characteristics and odd-even oscillation starts to appear. Presence of the odd-even oscillation implies that the interface structure of SAM$^O$ and SAM$^E$ are different, but gauche defects are still present. This inference is drawn from the fact that SAMs in this regime show roughness-dependent and roughness-independent odd-even effect in SFG signals associated with the interface (peak intensity of the CH$_3$ asymmetric stretch) and local chemical environment (Peak width at half height for the CH$_3$ asymmetric stretch) respectively (Figure 4, section 2.2). This region is categorized as a transition between the liquid-like region II and the crystal-like region IV, hence for brevity it was named the ‘wax-like’ regime.

Regime IV is characterized by a plateaued values of contact angle and symmetry in their oscillation between the odds and the evens. We observe that the even-numbered molecules gave higher contact angles than the odd numbered congeners, a consequence of molecular symmetry.

The structure properties observed across the four regimes are not unique to n-alkanethiolate SAMs wetting properties, but analogous symmetry driven trends have been in melting points ($T_m$) of unbound hydrocarbons, as in Figure 10c.$^{71}$ In the melting point studies, the role of symmetry in the trans-extended n-alkane accounted for variation in $T_m$. Odd-even oscillations in $T_m$ were attributed to the fact that the van der Waal surface of an n-alkanes with an even number of carbons bears a C$_{2h}$ point group (D$_{2h}$ in three dimension) while an analogous odd numbered molecule occupies a C$_{2v}$ point group. Since gauche defects are prevalent in $<C_{15}$ SAMs deviations from this fully symmetry-driven property oscillations is expected hence some
correlation with conformational-driven molecular relaxation is expected. A correlation to conformational dynamics should allow for a correlation of contact angle data to the density of gauche defects, if symmetry is also considered.

2.4.2 The local chemical environment of the terminal groups.

It has been shown that the chain length dependence in SAMs leads to 4 regimes, in which SAMs tend to have different structure and properties. These 4 regimes shows the transition with chain length from disordered SAMs and poorly-formed interface to well-ordered SAMs with predictable interface properties. As depicted in Figure 10a, the 4 regimes for alkanethiolate SAMs are; pseudo-formed, liquid-like, wax-like and crystal-like. In previous studies, SAMs are only classified by liquid-like and crystal-like. We, however, show there is a transition region between liquid-like to crystal-like that captures properties of both.

An SFG studies on alkanethiolate SAMs on Au show similar transition at the around C₁₃, where the SFG band width analysis helps empirically understand the SAMs interfaces. From the SFG spectra of alkanethiolate SAMs on AuTS (Figure 4), the largest peaks (CH₃ asymmetric stretch band) are selected for analysis, whose fluctuation in band widths at half-height, indicating a phase transition at around C₁₃ (Figure 10d). The band width at half-height is associated with local chemical environment of the probe moiety – in this case the terminal methyl. Like in wetting (Figure 10a), the odd-even effect was observed for C₉-C₁₂. The odd-even effect, however, disappeared beyond n≥13, which we believe is attributed to the crystallization of the SAMs. The terminal CH₃ stretch in the crystalline-like SAMs is exposed to air, as such the chemical environment is consistently the same.
2.4.3 A quantitative parameter for gauche-defects

To further understand and parameterize chain length dependence of interfacial structure and properties (continuing from Section 2), a re-evaluation of not only the equilibria state (sessile drop contact angles) but also the adhesion informs the nature of the interaction. Through a simple extension of the Young-Dupre equation by considering the proportional contribution of dispersive and polar components of surface tension to interface interactions, a parameter that captures the evolving nature of the interface, $\chi_c$ (Eq. 5), was deduced\textsuperscript{28} by simply focusing on the case where $\gamma_p=0$ (HD, section 2.1). Focusing on the simpler case of HD, a simple proportionality can be deduced (Eq. 12);

$$\chi_c^2 = \frac{\gamma_{LG}}{\gamma_{LG} \cdot \gamma_{SG}}$$  \hspace{1cm} (2.12)

Based on the preceding discussion, however, the dispersive component ($\gamma_{SG}$) of the SAMs surface energy is dependent on the length of the molecule, $n$, and can be expressed as such (Eq. 13):

$$\gamma_{SG}^d = f(n)$$  \hspace{1cm} (2.13)

Since $\gamma_{LG}$ is known for a specific liquid and hence is a constant, Eq. 12 was rearranged into Eq. 14, by combining Eq. 13.\textsuperscript{28}

$$\chi_c^2 = \frac{1}{\gamma_{LG}} \cdot f(n) = a \cdot f(n)$$  \hspace{1cm} (2.14)

A plot of $\chi_c^2$, calculated using this simple extension of the Young-dupre equation, against $n$ (Figure 11a), gave an empirical exponential decay (Eq. 15);

$$\chi_c^2 = A e^{-\frac{n}{t}} + \epsilon_0$$  \hspace{1cm} (2.15)

Where $A$, $t$ and $\epsilon_0$ are fitting parameters. From this expression, when $n \rightarrow \infty$ (SAMs with infinite long chain are assumed fully crystalline), then $\chi_c^2 = \epsilon_0$, hence, by definition $\epsilon_0$ is the
maximum dispersive contribution to surface energy of a fully crystalline SAMs surface. As a result, \( (\chi_c^2 - \varepsilon_0) \) was attributed to the effect of molecular (primarily gauche) defects, which decrease with an increase in chain length. From an empirical point of view, it can also be deduced that since the exponential term decays rapidly, \( \chi_c^2 \) approaches the crystalline state over a significantly short chain length (e.g. for C\(_{10}\), \( e^{-\frac{n}{\tau}} = 1.13 \times 10^{-5} \) and \( 5.15 \times 10^{-10} \) for C\(_{20}\)).

Re-arranging Eq. 15, to introduce the deviation from a fully crystalline SAM, \( \Delta(\chi_c^2 - \varepsilon_0) \), a linear logarithmic relation was deduced (Eq. 16), showing that the SAM tends toward a crystalline form with increase in chain length as discussed in section 4.1.

\[
\ln(\chi_c^2 - \varepsilon_0) = \ln A - \frac{1}{\tau} \cdot n
\]  

(2.16)

**Figure 2.11** The chain length dependence in SAMs interfacial structure and properties. a) The \( \chi_c^2 \) shows the odd-even effect and a chain length dependence. b) The defect density, described by \( (\chi_c^2 - \varepsilon_0) \), shows an odd-even effect and chain length dependence.

The rate of \( \Delta(\chi_c^2 - \varepsilon_0) \) with chain length (slopes of the linear fits in Figure 11b) are different for odds and evens. These difference can be attributed to difference in symmetry between the odds and evens (C\(_{2V}\) and C\(_{2h}\), respectively) and the effect of this symmetry in conformational relaxations. To further affirm the latter, the exponential fitting parameter, \( \tau \), shows a geometric progression that correlates well with Goodman’s molecular conformation twists limits.\(^{28,55}\) We
can therefore infer that the introduced parameter can be used to quantify deviation from the fully ordered crystalline phase due to defect density, and may also be capturing frustrations towards conformation-relaxations due to presence of neighboring chains and chemisorption to the substrate.

Figure 2.12 The chain length dependence in SAMs structure and corresponding behavior and properties. a) The chain length dependence and the odd-even effect in the rectification ratio of ferrocene SAM junction on both Ag and Au substrate.\(^72\) b) The rectification ratio and the odd even effect is influenced by the location of bipyridyl group in alkanethiol, another chain length dependence.\(^73\) c) The calculated surface coverage of alkylamine SAMs formed on graphene.\(^74\) d) Calculated packing energy and adsorption energy.\(^74\) (Copyright from ACS)

2.5 Summaries and perspectives

The effect of orientation of terminal groups in SAMs has been observed with a large head group, ferrocenes (larger than \(-\text{CH}_3\)),\(^75\) and this manifests in the rectification ratios of molecular diodes (Figure 12a). This phenomena has also been reported in capacitance and
contact resistance. All these studies have, however, been on SAMs formed on Au or Ag (hard) substrates. Recently, it has been shown that even for flexible substrates the odd-even effect persists. The alkylamine SAMs formed on graphene demonstrates such phase evolution with chain length, as reported by Song et al. The calculated coverage of molecules on surface was estimated through molecular dynamics, showing three regions (Figure 12c) transitioning from comparatively low coverage ($\leq C_3$) to a higher coverage ($\geq C_{16}$). In addition, this transition was also observed in the calculated packing energy ($E_{\text{pack}}$) and the physisorption energy ($E_{\text{ads}}$) as shown (Figure 12d).

Besides wetting and charge transport properties, the odd-even effect – which as discussed above is dependent on the symmetry and conformation of the molecules in question, has been observe in other molecular properties. The odd-even effect in crystallization rate was observed in $\alpha,\omega$-bis-(pentane-2,4-dione-3-ylmethylsulfanyl)alkanes using polarized optical technique.

In biological applications, the cell parameters (cell volume, $\beta$ angle, space group etc.) is dependent on the number of carbons in the ester groups in chiral crystal solids, which shows odd-even oscillation. Even in amorphous materials, an odd-even effect was observed in the glass transition temperature of network-forming ionic glasses.

One can thus conclude that the chain length dependence is a universal properties for molecular assemblies, especially the alkyl chain based molecules, which is irrelevant to substrates nature. The chain length affects the intermolecular interaction and the inherent structure of the assemblies and the corresponding properties.
Reference


CHAPTER 3. REVEALING THE QUALITY OF LARGE AREA TUNNELING JUNCTIONS THROUGH HEAT-MAP REPRESENTATION OF RAW DATA

In this chapter, a statistic tool was developed, along with its application in diagnosing the reproducibility and statistical relevance of large volume data, for mechanistic understanding of charge transport behavior of large area molecular junctions. Even with the development of stable liquid metal electrode (EGaIn), challenges still lies in an inability to diagnose the quality of contact between the top-electrode and the SAMs. Since tunneling currents are dependent on the distance between the two electrodes, we demonstrate that by analyzing all raw unfitted data derived from a measurement using heat-maps, one can deduce the quality of contact and other minor bias-dependent fluctuations in the charge transport behavior. We demonstrate that the use of 3D plots would be challenging to interpret but adoption of heat maps clearly captures minor fluctuations and junction quality irrespective of the total size of the dataset or molecules used.

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3.1 Large area molecular junctions and EGaIn technique

The promise of molecular electronics rests on the ability to engineer molecular wave-function through organic synthesis. For some time, however, the main challenge was a need for platforms to reproducibly and reliably study unimolecular systems. The liquid top-electrode platforms, especially with EGaIn (eutectic gallium indium alloy) pioneered by Whitesides (Figure 3.1a-b), have offered promise in their ability to rapidly collect large volumes of stable, reproducible and statistically significant data.\(^1\)\(^-\)\(^5\) As the technique develops, improvements in characterization and understanding of different components is vital. For example, the nature of the top-electrode upon contact is still an on-going study. Alongside this, challenges in
processing large volumes of data and validating the obtained data will enable design of tools and molecules for mechanistic studies needed for the translation of the obtained information into working devices.\textsuperscript{6}

3.1.1 Background of large area junctions and EGaIn technique.

There are two main classes of molecular junctions, \textit{viz}: i) small area junctions, and, ii) Large area junctions. Small area junctions, usually single molecule junctions, are mainly based on the break junction technique - which include mechanically controllable break junctions (MCBJs) and electro-migration break junctions (EBJs).\textsuperscript{7-8} Despite the fact that break junction techniques can produce large data sets,\textsuperscript{9} challenges in the fabrication process, difficulty in identifying the contact configuration, low-yield of working junctions, and, limited compatibility of molecules to electrodes (types of bifunctional molecules) make the derived data suffer from either large fluctuation (i.e. junction-to-junction variation) or small-volume of high quality information rich data.\textsuperscript{9-10} To overcome the fluctuations, conductance histograms have been adopted in most of the statistical data analysis.\textsuperscript{11-12}

Large area junctions (predominantly self-assembled monolayer (SAM) based), are formed by introducing a top electrode in contact with a uniform assembly of many molecules (SAM) fabricated on a bottom electrode (predominantly Au or Ag). Large area junctions, therefore, measure the average properties across many molecules to rapidly accumulate reproducible and statistically relevant data. The presence of defects in the SAM (Figure 3.1c), however, results in variability between junctions fabricated on the same surface, primarily due to the nature of contact (hence the differentiation of surface defects to thin-area and thick-area defects).\textsuperscript{13,14} Defects in organic molecular junctions include; grain-boundaries, step edges, adventitious impurities, and, molecular back-folding of long-chain molecules, can have different effect on
the data from measurements.\textsuperscript{4,15} Inspecting and analyzing the whole range of data, however, can distinguish measurements made on defective areas from those made on fairly uniform junction areas. A large amount of data is, therefore, required to statistically minimize the effects of defects and overcome the resulting variance.

The hanging mercury (Hg) drop electrode (HMDE) technique, due to its relative simplicity and compatibility with a large selection of molecules, is a good tool for molecular junction studies.\textsuperscript{7,16-17} Use of Hg is, however limited by major drawbacks that include; i) Hg is toxic, ii) Hg is volatile, iii) Junctions are complicated by Hg electro-migration, and, iv) amalgamation with entire surface upon failure.\textsuperscript{18} The EGaIn technique, as an alternative to Hg, has been widely adopted for its stability, high yield and reproducibility.\textsuperscript{16,19-20} EGaIn is a non-Newtonian liquid metal at room temperature and can be shaped into a conical probe that can be used as the top electrode, forming a Metal-SAM//Ga_2O_3-EGaIn junction (Figure 4.1 a-b).\textsuperscript{4,21-23}

The current EGaIn technique also has its own challenges, for example, the lack of an ability to make uniformly configured top electrodes and the difficulty in defining the influence of morphology of the tip on measurements.\textsuperscript{23} Degree of force applied on the top electrode to establish contact, or the method to prepare the top electrode, induces variant amount of stress on the SAM resulting in discrepancies in distribution of data between users or labs. An example is the magnitude of the widely-observed odd-even effect in SAMs and in charge transport across the alkanethiolate junctions.\textsuperscript{1,4,21,24-29} Disregarding the fact that a defective/rough surface will increase the chance to diminish the alignment of molecules and break the structure of SAMs, the origin of the recent discrepancy in the magnitude of the observed odd-even effect in charge transport has not been established. Thuo et al.\textsuperscript{4} and Jiang et al.\textsuperscript{1} reported the odd-
even oscillation of tunneling current across Ag\(^{TS}\)-SC\(_n\)//GaO\(_x\)/EGaIn junction (Ag\(^{TS}\) is the template stripped Ag surface and SC\(_n\) is the n-Alkanethiolate SAMs) using soft contact, while Baghbanzadeh et. al.\(^{24}\) showed an absence of the effect when they altered the method used to prepare the top-electrode. A closer look at the three data sets shows that where the odd-even effect has diminished, the variance in data point is small (\(\sigma_{log} = 0.3\), and reproducible not only across different molecules but across different substrates, suggesting that the data is precise. In the case where the odd-even effect was observed, the standard deviations varied across different molecules with Thuo et. al., using the conical tip electrode, reported the largest variance (\(\sigma_{log} = 0.2\) - 1.1) while Jiang et. al., with microfluidics-based top electrode reported slightly lower range (\(\sigma_{log} = 0.12\) - 0.57). The variations in the latter two studies indicates less precise measurements. We hypothesized that the nature of contact between different electrodes might be the origin of the observed difference and that analysis of the raw data set can reveal the nature of the contact based on the distribution of the outliers and the skew of the distributions in counts. We inferred that with the different types of interfaces, judgement of the nature of non-optimal contacts, which is either hard or soft, would be manifested in either a domination by high or low value outliers respectively.
Figure 3.1 Schematics of molecular tunneling junction and diagrams of analysis of tunneling currents thought the junctions. a) Schematics of performing current measurement using EGaIn tip. b) The formation of M-SAMs//Ga$_2$O$_3$/EGaIn junction and interface 1 and 2. c) A schematic representation of defects in metal substrate and SAMs.

The EGaIn junctions generate a large volume of data, hence Gaussian fits (that assume a stochastic process) and related plots (Figure 3.1d-f) have been deployed as reliable platforms for reporting charge transport data.\textsuperscript{1-6, 21, 30-31} Although these data representations allow for
valuable comparisons, for example through comparison of Gaussian fits (J-V) and associated Gaussian mean, standard deviations and medians,\textsuperscript{1-2, 4-6, 21} the eliminate outliers (through the fit or by the user) and often override skewness, key parameters in establishing bias in the measurements. To take advantage of this information, J-V data needs to be represented in a single plot that includes total counts at each bias. Since current methods of representing data (Figure 3.1d-f) are insufficient, while a simple 3D plot is difficult to decipher (Figure 3.1g), deploying heat-maps - a planar version of the 3D data, we could not only capture the average J-V trace (Figure 3.1e), but also capture the skewness and outliers (that could be due to nature of contact or defects in the SAM) in a single figure. The ability to display the raw data also eliminates any bias associated with the quality of a fit, or the fitting algorithms employed.

3.2 Experimental design for data diagnostics

The experimental data was gathered using the EGaln technique, as previously reported.\textsuperscript{4, 21, 23-24} The plots were created using an in-house developed Matlab program, large area junction analysis (LAJA). Data was sorted into a hierarchal folder setup. A dataset contains molecules that contain samples that contain junctions that contain traces, enabling LAJA to analyze the data at different experimental levels by separating out unique samples, junctions, or molecules. The program allows users to specify relevant variables like voltage ranges, plots to produce, and current density ranges. LAJA can generate all of the data analysis figures shown in this work as well as a 3D scatter plot of the histogram, a table of the statistical analysis, and a 3D scatter plot of every individual trace divided up by molecule. The program uses a window-based system where each command, specification, and file is accessed sequentially by its own window, taking the user through the analysis. All SAMs and charge transport measurements
were performed as previously reported with modifications described in the text of this publication.

### 3.3 Results and discussions in diagnostics

We demonstrate the diagnostic/quality-control capability of this simple approach to data analysis and representation, a Matlab based *Large Area Junction Analysis (LAJA)* method, by analyzing data collected from junctions of n-alkanethiolate SAMs (Au$^{TS}$-SC$_n$/Ga$_2$O$_3$/EGaIn) with; i) different levels of experimental quality (molecule quality, hence, quality of the SAM, different expertise, different experimental conditions), ii) a molecule that is known to back-fold (SC$_{19}$) upon self-assembly, and, iii) soft or forced contacts (that is, we barely bring the top-electrode into contact with the SAM or push the top-electrode beyond what is normally considered a good physical contact).

First, we intentionally fabricated junctions under different experimental conditions using a medium chain length even-carbon molecule (SC$_{14}$), and many of the conditions are known to affect the SAM quality (did not purify the thiol, data was corrected at different humidity and temperature conditions, and no vibration isolation), and, data was collected by users with different levels of expertise. We represented the data in both 2D and 3D formats to illustrate how low quality data (Figure 3.2). The obtained data is at least bimodal, that is, there are two dominant distributions with ‘shadow’ peaks on lower and higher end of each distribution, suggesting a skewness. We hypothesized that this skewness is an indication of the origin of the adjacent major distribution, with the higher log|J| values being from thin-area defects and, similarly, the lower log|J| values being from thick-area defects.

The conventional method using Gaussian fits at a single bias fails to capture the extent of the noise in the data, especially when the data is fitted to a single Gaussian. To interpret the
data, a 3D histogram of the distribution of current density with voltage (Figure 3.2a) was generated from LAJA, showing the discrete multimodal J-V distribution, a simple 3D histogram is challenging to decipher. In contrast, the corresponding heat-map (Figure 3.2b), generated from an aerial top or bottom) view of that ‘skyscraper’ histogram plot is clearer and not only gives the data distribution but also captures any variations across all the biases. For data that are this noisy, a J-V trace generated from a single Gaussian fit is also equally effective at showing that the data is not scientifically sound (Figure 3.2d). The poor quality is only revealed upon plotting data across the span of the bias ranges, but the J-V trace fails when a shorter bias range is use. It is common in the area of large-area junctions to consider data at a narrower bias range, e.g. ±0.1V,7 but this can be misleading due to inclusion of a poor data set. For example, in the current data set data within ±0.2V gives a well-defined J-V trace erroneously suggesting that this data set is reliable. Using the standard deviation (slog) from a single Gaussian fit at ±0.2V J-V trace, also erroneously suggests that the data has a narrow distribution (Figure 3.2cii). These behaviors, therefore, highlight the limitations to adopting distributions and/or data at a single bias as a representation of the whole and, we infer, that a method that represents all data points without fits or pre-selection is desired.
Figure 3.2 Discrete data from unhealthy measurement of tunneling junctions. a) Histogram diagram of J-V in terms of counts. b) Corresponding heat map diagram of tunneling current vs applied voltage. c) The Gaussian fitting curves at each voltage step. i) Fitted into curves with two Gaussian peaks, ii) Fitted into curves with a single Gaussian peak. d) The J-V curve by plotting Gaussian mean current density value with applied voltage.
4.3.1 Understanding the nature of contact in EGaIn-based junctions

The convention in understanding conical tip based junctions is that a physical contact is established when the shaped liquid metal merges with its own reflection on a metal surface. Electrical contact is confirmed by running a single J-V trace and the stability of the junction ascertained by running at least 20 traces. The success of the visual method of establishing contact between a hundreds of microns wide electrode and often a nanometer thick monolayer is surprising, but also a potential major source of variances between users or between different laboratories. The challenge in learning what a reliable contact is has led to development of other methods of introducing the top-electrode that is independent of the user. Despite this development, the conical tip is rapid, easy to use and does not require any pre-fabrication or advanced fabrication techniques, and hence the method is of continued interests. Based on the dependence of the current density on distance, thick- and thin-area defects can be observed from the direction of the skew in the data and from the associated outliers, in which case the accumulation of outliers on one side of the dominant distribution would indicate either thin- or thick-area defects. In cases where the substrate and SAMs are of high quality, the thin- and thick-area defects would be associated with ‘hard’ and ‘soft’ contacts respectively. We define hard contacts as junctions formed when there is significant pressure applied on the top-electrode leading to deformation of the SAM (we infer the shear modulus of EGaIn, ≈0.5 N/m, is larger than the energy causing C-C to rotate forming Gauche, ≈0.21 for alkanethiolate SAMs on Ag from an estimation). Figure 3a shows data derived from a hard contact, in which there are significant shorts and a skew of the data towards high values of J. A simple 3D plot (Figure 3.3d) or the conventional J-V trace (Figure 3.3g) do not give valuable information on the quality of the junction. Most current density data collected from a soft contact (Log |J| (A/cm²)) is almost 3 orders of magnitude lower than those from a hard contact.
A generated Gaussian mean J-V curve from hard contact shows a reversed configuration than observed in most dielectric devices (Figure 3.3g). The abnormal current density peak at -0.1 V is caused by calculating the Gaussian mean with the inclusion of the asymmetrically distributed and abnormally large shorting current in the device. Figure 4.3b shows the analogous case when the electrode barely merges with its reflection on the surface (soft contact). A skew towards lower currents, and a large number of low-current outliers, is observed. For a control experiment, we collected data from C19 thiol, a molecule that is known to back-fold and therefore a source of thin area defects. As expected, the data was bimodal with a large distribution at higher currents. Although the fully extended chains dominated the current, a small but significant amount of current was observed through the thin-area regions. Unlike in the hard contacts, we did not observe a large number of shorts junctions (log|J| ≥ 2). The ‘skyscraper’ 3D histograms (Figure 3.3e-f) and J-V curves (Figure 3.3h-i), as expected, failed to illustrate the quality of the junctions but the heat-maps clearly showed the variances and as such can be used to inform the quality of the experiments.
Figure 3.3 Typical defective junctions diagnosed by heat map, 3D histogram and Gaussian value curves. a-c) The heat-maps of current density across molecular junctions with hard contact, soft contact and back-folding molecules, respectively. d-f) The corresponding 3D histogram associated with to the heat-maps. g-i) The plots of current density, calculated from Gaussian average, against voltage.

Besides revealing the quality of the contacts through capturing thin-area and thick-area defects, the deployment of heat-maps as a mean to represent charge transport data enables visualization of a large volume of data, especially from a homologous series. Figure 4.4a-b show the tunneling current though a C_{10} SAM junction in heat-map format and the corresponding 3D histogram. The heat-map clearly shows median log|J| at each bias, and where a purely stochastic process occurs, the mean and median overlap are very close. A similar inference can be draw by looking at the Gaussian fits to log|J| at each bias Figure 4.3c. For single molecule measurements, not only is the nature of the contact revealed, but any voltage dependent fluctuations will also be revealed – in this data set, there are no statistically significant voltage dependent fluctuations.
**Figure 3.4** Single-molecule and multi-molecule analysis of tunneling current through junctions using versatile 3D-viewing tool. a-c) analysis of tunneling current across decanethiolate (C_{10}) molecular junction, including heat-map, 3D histogram and Gaussian curves. d-f) analysis of all the tunneling current data obtained for molecular junctions from nonanethiolates to hexadecanethiolates (C_{9}-C_{16}), including heat-map, histogram and Gaussian curves.

In the case of a many molecules study, data from all the molecules can be presented in a single heat-map to inform homogeneity in the data set and/or pin-point variations that might bias any statistical comparisons between molecules. Figure 3.4d-f summarizes a multi-molecule data set containing 147,000 data points, a statistically relevant volume. Figure 3.4d, shows all the raw data (C_{9}-C_{16}) represented in a heat map, allowing for identification of regions with low or high data points – hence likely to dominate volume-dependent comparative parameters, for example calculation of mean. Unlike the commonly used stacked histograms
at a single bias (Figure 3.4e), the heat-maps allows for comparison across all biases while also revealing differences that could be attributed to differences in data volume. In the heat-map, a well distributed data should have an equal distribution of data across the biases, which would result in a Gaussian distribution of the current densities allowing for the data set to be treated as one. This type of distribution can be revealed at every bias using a heat-map (Figure 3.4d).

4.3.2 Conclusion

We demonstrate that the adoption of a simple data presentation can reveal otherwise concealed information in charge transport measurements. By converting an otherwise uninformative ‘skyscraper’ histogram into a heat-map, thin- and thick-area defects in molecular junctions can be revealed, allowing for the nature of contact between the SAM and top-electrode to be evaluated. Besides unveiling the SAM-electrode contact, other thick area defects like molecular back-folding have also been demonstrated. These heat-maps can be used with single or multi-molecule data sets.

Reference


CHAPTER 4. EFFECT OF SMOOTHENING ELECTRODES ON REVEALING FINER MOLECULAR INFORMATION IN CHARGE TRANSPORT ACROSS TUNNELING JUNCTIONS

Since substrate (bottom electrode) morphology affects SAM structure and interface (wetting) properties (chapter 2), similar effects are expected in charge transport properties with the added effect of the bulk structure since decay in tunneling probability depends on the nature of the barrier width. In large area molecular tunneling junctions, the top electrode (here EGaIn tip) also affects the structure and properties of the junctions. That is mainly due to the nature of the electrode-SAM interface that plays a major role in the tunneling behaviors across the junction, and manifests in properties like electrode/molecule coupling. In this chapter, effect of smoothening both top and bottom electrodes on tunneling behavior across the junctions is discussed.

4.1 Introduction to the odd-even effect in charge transport

Liquid metals have recently received increasing interest for use as conformal top-electrodes in large-area junctions.\textsuperscript{1-5} Besides the toxic hanging mercury drop top electrodes,\textsuperscript{6-8} eutectic gallium indium (EGaIn - 75.5 wt % Ga and 24.5 wt % In) has emerged as a more liable, safer and easier to use alternative liquid metal top electrode.\textsuperscript{1-5} Other approaches to fabricating top-electrodes in large area junctions include evaporated metal electrodes,\textsuperscript{9-14} nano-scale self-assembled monolayers (SAM) interfaced contacts,\textsuperscript{15-16} conductive scanning probe microscopy tips,\textsuperscript{17-19} multi-layer graphene,\textsuperscript{20} and spin-cast conductive polymer film (PEDOT:PSS).\textsuperscript{21} Most of these, like placing a conductive polymer film on top of a SAM, introduce unresolved ambiguities in the system and generates data that deviate from the inter-platform consensus (e.g. discrepancy in charge tunneling decay constant, $\beta = 0.66 \pm 0.04 \text{ C}^{-1}$ vs $\beta = 1 \text{ C}^{-1}$ in n-alkanethiolate SAMs).\textsuperscript{22}
The EGaIn-based systems, developed by Whitesides and co-workers,\textsuperscript{1,2} has a liquid-metal top-electrode with an oxide shell in contact with the SAM surface. Current density, $J$ (A/cm$^2$), is measured across self-assembled monolayers (SAMs) as a function of the applied bias, $V$, and is affected by the resistance of both the SAM and the contact.\textsuperscript{5} Figure 1a schematically illustrates the idealized EGaIn-based junction with a smooth SAM-oxide interface on a well-ordered defect-free monolayer. The electrodes and the SAMs are, however, usually defective and significantly deviate from this ideal (Figure 1b). Most of the top-electrode defects are inherent to the fabrication method with the native conical shaped tip being most defective. The EGaIn conical-tip electrode has, therefore, been shown to have a low true geometric (hence low electric) contact area, in part, due to a convoluted surface oxide structure.\textsuperscript{23} These asperities lead to large distribution in the observed data (Figure 1c). Use of low-oxidizing microfluidic environments\textsuperscript{24} and/or tip pre-flattening through electrostriction of the oxide layer\textsuperscript{23,25} have been deployed to engineer this interface and narrow the spread in obtained data (Figure 1d and Figure 1e respectively). Other approaches to mitigate defects on the SAM include use of super-flat substrates and understanding evolution of gauche/conformational defects in SAMs in order to mitigate their contributions.\textsuperscript{26-27}
Figure 4.1 Alkanethiolate SAMs based tunneling junctions with EGaIn top electrodes and the charge transport behaviors. Schematic illustrations of an a) ideal junction with perfect electrodes and b) realistic junctions with defects on both electrodes affecting the SAMs structure and the contact. c-e) The odd-even effect in charge transport behavior across n-alkanethiolate SAMs based junctions with different test-beds.\textsuperscript{3, 5, 25} f) The derived injection current $J_0$ and decay constant $\beta$ for both the odds and the evens from the three test-bed. The thin oxide electrode share similarity in value while the thick oxide electrode has different values.

The odd-even effect in charge transport has been observed in tunneling across n-alkanethiolate SAM junctions.\textsuperscript{3, 5, 25} These alkanethiolate junctions have, however, led to variable results even on similar test-beds with the only difference being top-electrode processing. Consider, for
example, the case where template-stripped silver (Ag\textsuperscript{TS}) was used as bottom electrode and EGaIn as top electrode.\textsuperscript{3,5,25} Thuo and coworkers\textsuperscript{3} first reported the odd-even effect in charge tunneling rate across alkanethiolate SAMs based molecular junctions using a native conical EGaIn tip (Figure 4.1c). The results have large distributions partially due to the vast amount of data collected, number of personnel involved in data collection, and variation in the nature of the SAM-EGaIn interface (Figure 4.1c).\textsuperscript{3} Although the simplified Simmon’s model (Eq. 4.1) was used to fit the data, no significant difference was observed in both the injection current $J_0$ or decay constant $\beta$, across the two series, and neither is the origin of this difference delineated using the expanded model (Eq. 4.2).\textsuperscript{28-30}

\begin{equation}
J = J_0 e^{-\beta d}
\end{equation}

\begin{equation}
J = A^*T^2 e^{-\beta D} e^{-\frac{-q \Phi_{bb}}{k_B T}}
\end{equation}

Jiang et al.,\textsuperscript{5} however, used microfluidic device to study Ag\textsuperscript{TS} n-alkanethiolate SAMs inferring that this would lead to less defective junctions. They observed the odd-even effect in a large range of alkanethiols (C\textsubscript{2}-C\textsubscript{18}) and with significantly lower dispersion in obtained data (Figure 4.1d). The odd-even oscillation decrease with decreasing chain length, especially when n<8. These two test-beds (Thuo et. al. and Jiang et. al.), although slightly different in raw current density values, yield comparable $\beta$ and $\log|J_0|$ for both odds and evens (Figure 4.1f).

Recently, Baghbanzadeh et al.,\textsuperscript{25} used a pre-flattened conical EGaIn tip (with presumed thickening of the oxide) as top electrode to form a junction. Although the bottom electrode remains similar to the previous two studies (Ag\textsuperscript{TS}), the odd-even effect is not observed with this “thick-oxide contact”.\textsuperscript{31} The current densities are also significantly larger with the thick-oxide than the other two (approximately 2 orders larger). The estimated $\log|J_0|$ and $\beta$ from
thick oxide tip are also significantly different from those derived from the other test-beds that has thin oxides (Figure 4.1f).

Previous experimental work on the odd-even effect in charge transport by tunneling can, at the very least, be considered wanting and partially inconsistent.\textsuperscript{24} We hypothesize that this is due to limited understanding of molecular level or nano-scale features in device fabrications and testing.\textsuperscript{32} We therefore infer that charge transport is not only affected by the material physics/chemistry of the electrode but also the morphology that varies with different preparation methods. We, therefore, desire to design a universal method to fabricate electrodes with consistent properties. One approach to achieving this goal is polishing the oxide shell on EGaIn and re-establishing while the liquid is distended in the shape that it shall be used.

4.2 Polishing the EGaIn electrode

We recently reported a method to prepare EGaIn nano- and micro-particles by shearing the liquid metal in acidic solution, the so-called SLICE method.\textsuperscript{33} The particles fabricated using this method consists of a uniform thin oxide layer (Ga\textsubscript{2}O\textsubscript{3}) with liquid metal core and did not collapse/coalesce even after months of ambient storage (Figure 4.2a). Inspired by this work, we developed a method to polish/smoothen the EGaIn top electrode via an etching-oxidation process. Figure 4.2b shows the schematic illustration of the EGaIn tip smoothening processing. First a native EGaIn conical tip is prepared by rupturing an hour-glass shape of the non-Newton metal as previously reported. Then gallium oxide shell, together with the asperities and the whiskers, at the tip are removed by etching with a dilute acid solution, allowing the liquid core to relax into an optimized smooth cone depending on how much of the tip-oxide is stripped during the etching process. Due to the liquid nature, the EGaIn tip will reorganize due to gravity
(F_g), surface tension (γ_int) and adhesive/capillary forces (E_{ad}). Upon re-oxidation, a smooth curved surface is formed (Figure 2b).

Figure 4.2 The design of polishing the EGaIn tip with acid etching. a) The EGaIn particles prepared using SLICE with a smooth and homogenous surface. (Copyright from ACS). b) The whiskers and asperities on the EGaIn tip surface concomitantly formed during the preparation of the tip, were removed by using etching. The conical EGaIn tip was imaged by c) optical camera and d) scanning electronic microscopy (SEM). Similarly, the EGaIn tip after acid etching was imaged by e) camera, and e) SEM, respectively.
4.3 Results and discussion

We fabricated the described tips by first preparing a conical tip as previously reported.\textsuperscript{2-3} High resolution optical camera (\textit{HITACHI KP-D20BU}) image (Figure 2c) shows a sharp conical tip. This preparation process makes complex non-uniform oxide structure on the surface of the tip.\textsuperscript{23, 36} A rough oxide surface and a whisker (\textit{ca.} 50\textmu m) were observed from scanning electron microscopy (SEM) image (Figure 4.2c). We then etched off the tip of the conical tip using dilute (5\% acetic acid in ethanol) to reveal a smooth tip, albeit no longer sharp but round (Figure 4.2e). Due to challenges in imaging the gravity-distended tip by scanning electron microscope (SEM), the tip was inverted to reveal a much smoother oxide surface (Figure 4.2f) compared to the unpolished tip (Figure 4.2d) (albeit with some wrinkling due to turning the tip upside down and collapse from the distended Figure 4.2e shape due to gravity). A close evaluation of the SEM image shows the extent of the acid treatment, which manifests as a step in the continuity of the oxide skin. From this data, we can infer that the fabricated tips as significantly smoother, and based on the earlier work with SLICE,\textsuperscript{33, 37} the oxide layer should be consistently smooth and elastic around the re-formed tip. This conformal interface should, therefore, reveal interfacial molecular features in a more reliable and consistent way.

The smoothened EGaIn/Ga\textsubscript{2}O\textsubscript{3} tips fabricated by this method were then used as top electrode to form a molecular tunneling junctions. Well-studied template stripped silver surface (Ag\textsuperscript{TS}) and titanium pre-annealed gold surface (Au\textsuperscript{Ti-TS}) were used for as SAMs substrate for tunneling junctions. The surfaces were characterized using AFM, as shown in Figure 3a, and the roughness analysis showed that root-mean-square (rms) roughness of these two surfaces were 0.63nm and 0.22nm, respectively. Figure 4.3b shows the 3D view of the AFM images of the surfaces, indicating that both surfaces are ultra-flat with Ag\textsuperscript{TS} slightly rougher than Au\textsuperscript{Ti-TS}. 
Although the surfaces are not single crystal, but the faceting of the substrate film was dominated by (111) directions, as revealed by wide angle X-ray pattern (Figure 4.3c).

Figure 4.3 Surface characterization of substrates. a) AFM images of the template stripped surface Au\textsuperscript{Ti-TS} and Ag\textsuperscript{TS}. b) 3D view of the AFM images, demonstrate the surface morphology of the surface. c) Wide angle X-ray diffraction pattern of the Au surface and Ag surface indicating that the surface with (111) oriented.

First, for a comparative study, we chose mid chain length molecules. Tunneling rates across C\textsubscript{10}-C\textsubscript{17} SAMs with applied voltage were recorded and were statistically analyzed using LAJA, where the heat-maps and histogram can also be generated, as discussed in Chapter 3. Figure 4.4a shows the plot of calculated Gaussian mean current density with applied voltage.
Figure 4.4 Charge tunneling across alkanethiolate SAMs formed on Ag\(^{TS}\) using polished EGaIn tip as top electrode. a) The plot of the tunneling rates (Log|J|) of alkanethiols (C\(_{10}\)–C\(_{17}\)) vs applied voltage. b) Water contact angle on alkanethiolate SAMs of different chain length formed on Ag\(^{TS}\).[ref]

4.3.1 Solid SAMs region.

We have previous explored the effect of chain length on the SAMs structure and properties, where it has been shown that there is 4 regions with different surface properties, depending on the gauche defect density (associated with chain length).\(^{26}\) Figure 3b shows the contact angle measurements on alkanethiolate SAMs on Ag\(^{TS}\). When the chain length \(n \geq 10\), there is obvious odd-even effect, which as we believe is the sign of solid nature of the SAMs. When \(n < 10\), the odd-even effect was not observed (but some random fluctuation), due to the high density of
gauche defects that makes the SAMs “liquid-like”. This study mainly focus on SAMs with solid nature, and hence \( n \geq 10 \), since liquid-like SAMs have more comprehensive and less explored.

The tunneling rate of various junctions at -0.5 volt were plotted in Figure 4c. A clear odd-even oscillation was observed, which grows even more significant with increasing chain length. Linear fits were generated for the odds and the evens, respectively, with confidence \( R > 99\% \). When comparing to the tunneling results from previous studies, as in Figure 4d, it has been shown that the general tunneling rates across different studies share comparable values. Reducing the roughness of EGaIn electrode or the oxide thickness does not significantly affect the tunneling rates across the junctions, and this is because that the resistance of the Ga\(_2\)O\(_3\) is not important in alkanethiolate molecular junctions and the effective electric contact area does not changes significantly.\(^{23}\) Therefore, we believe the effective electric contact area is not dominated by the EGaIn but the SAMs.

4.3.2 The chain length dependence in odd-even effect.

In Figure 4c, the fits of tunneling rates with chain length converges at \( n < 9 \). This observation is similar to findings from a theoretic work showing that the odd-even oscillation in charge transport across alkanethiolate junctions on Ag disappears with \( n \leq 10 \).\(^{24}\) In addition, our recent reports show that from both sum frequency generation (SFG)\(^{38}\) and wetting\(^{26}\), the SAMs structure demonstrates a chain length dependence, where longer molecules tends to form more close-packed and less defective SAMs. A phase transition between “liquid-like” SAMs and “waxy” SAMs occurs at around \( n=9 \) for SAMS on silver, below which the odd-even effect in water contact angle disappears.\(^{26}\) Similarly, the disappearance of odd-even effect in tunneling rates (\( n<9 \)) is most likely due to the lack of ordered or well-defined SAM/ambient
interfaces. With a polished tip which has smooth and thin oxide layer and shows liquid nature, finer molecular information can thus be manifested from measurements.

4.3.3 Soft EGaIn electrode—a comparison

According to Simmon’s equation (Eq. 1), the tunneling rate is affected by the injection current ($J_0$) and a decay constant ($\beta$). Table 1 summarized the $\beta$ and $J_0$ derived from alkanethiolate junctions on Ag substrate with thin oxide EGaIn electrode prepared using different methods. We obtained the tunneling data of C$_{10}$-C$_{17}$ from literature and re-estimated the value for $\beta$ and $J_0$. It is found that this work gives larger odd-even difference in both the decay constant ($\Delta \beta$) and the injection current ($\Delta \log|J_0|$). Using the polished EGaIn electrodes, the $\beta_{odd}$ has been increased than the others, while, the $\beta_{even}$, surprisingly, is comparable to the rest. Similarly, the $\log|J_0|$ has comparable values in SAM$^E$ but a larger value with polished electrode in the SAM$^O$. By polishing the EGaIn, reducing the asperities and possible residual oxides, it seems the odd-even difference from junctions is enlarged, although the average tunneling rates across junctions are similar (Figure 4.4d).

Table 4.1. Summary of tunneling parameters derived from junctions with polished electrodes and from literature with electrodes prepared with different methods.

|            | $\beta_{odd}$ (n$_c^{-1}$) | $\beta_{even}$ (n$_c^{-1}$) | $\Delta \beta$ | $\log|J_0|_{odd}$ (A/cm$^2$) | $\log|J_0|_{even}$ (A/cm$^2$) | $\Delta \log|J_0|$ |
|------------|-----------------------------|-----------------------------|----------------|-----------------------------|-----------------------------|----------------|
| This work  | 1.25±0.07                   | 0.96±0.05                   | 0.29±0.12      | 3.61±0.33                   | 2.57±0.25                   | 1.04±0.58 |
| Thuo et al.| 1.07±0.05                   | 0.99±0.04                   | 0.08±0.09      | 2.13±0.34                   | 2.52±0.23                   | 0.39±0.57 |
| Li et al.  | 1.07±0.01                   | 0.99±0.03                   | 0.08±0.04      | 2.21±0.08                   | 2.29±0.19                   | 0.08±0.27 |

4.3.4 Tunneling across Au/SAM//EGaIn junctions.

To further understand the chain length dependence and also the odd-even effect in charge transport, alkanethiolate SAMs (C$_{10}$-C$_{17}$) formed on Au$^{Ti-TS}$ were used to form a molecular
junctions. \( \text{Au}^{\text{Ti-TS}} \) has smaller roughness as in Figure 3a-b (~0.23nm), and thus can yield more ordered SAMs with less defects.\(^{39}\) Polished EGaIn tip was used as top electrode to collect tunneling measurements. Tunneling rate across each molecule at -0.5V were plotted and fitted as in Figure 5a (heat-maps and histograms were in SI). Similar to Ag, the odd-even effect in tunneling for Au also shows a chain length dependence, whose magnitude, in general, increases with molecular chain length and disappear at around \( n = 9 \). This convergence (both in Ag and Au) is in agreement with findings from our earlier wetting studies, where we noticed that the alkanethiolate SAMs undergo a phase transition at around \( C_9/C_{10} \) from a gauche defect dominant liquid-like SAMs to less defective solid-like (or “waxy”) SAMs.\(^{26}\) For liquid-like SAMs, the lack of interfacial order induces a loss of the odd-even effect (in contact angle) owning to scrambling of the orientation of the terminal \( \text{CH}_2-\text{CH}_3 \).

To better understand these phenomenon and the correlation with wetting results, we extend the range of molecules used for junctions by adding \( C_9 \) and \( C_8 \) (Figure S4-6). It has been shown that \( C_9 \) stays in the expected range, where the two fits merge. Junctions of \( C_8 \), in contrary, starts to show significant amount of short circuits during the measurements and higher current pathways as indicated by the large outliers (Figure S4).

**4.3.5 Comparison of tunneling across SAM/Ag and SAM/Au junctions.**

In general, the tunneling rates across Ag samples show more resistive characteristics than Au samples (lower current), as shown in Figure 5b. Disregard the different packing structure of the SAMs on Ag and Au (111) surface, in terms of grafting density of alkanethiolate on metal surface, Ag \( (N=4.6x10^{18} \text{ m}^{-2}) \) share same value as Au \( (N=4.6x10^{18} \text{ m}^{-2}) \). In addition, the odd-even effect magnitude for Ag is, surprisingly, much smaller than Au, as demonstrated in Figure 5b. The odd-even variance in terminal methyl group tilt angle is larger on Au than on
Ag due to a larger tilting angle of alkanes on Au. (It is well-known that alkanethiolates on Au are tilted ~30°, but tilted ~11° on Ag.)\textsuperscript{40} The contact angle results show that alkanethiolate SAMs on Au have large odd-even magnitude than on Ag, while the phenomenon in tunneling rates is the opposite. We, therefore, believe that other than the packing density and the molecular orientation, there is more influencing the tunneling behavior and the odd-even effect in those junctions.

Table 2. Comparison of tunneling parameters of alkanethiolate junctions on Ag and Au substrates.

|        | $\beta_{\text{odd}}$ (n$^{-1}$) | $\beta_{\text{even}}$ (n$^{-1}$) | $\Delta \beta$ (n$^{-1}$) | $\log |J_0|_{\text{odd}}$ (A/cm$^2$) | $\log |J_0|_{\text{even}}$ (A/cm$^2$) | $\Delta |J_0|$ (A/cm$^2$) |
|--------|-------------------------------|-------------------------------|-----------------|---------------------------------|---------------------------------|-----------------|
| Ag$^{TS}$ | 1.25 ± 0.07 | 0.96 ± 0.05 | 0.29 ± 0.12 | 3.61 ± 0.33 | 2.57 ± 0.25 | 1.04 ± 0.58 |
| Au$^{Ti-TS}$ | 0.87 ± 0.08 | 0.96 ± 0.04 | 0.09 ± 0.16 | 2.42 ± 0.42 | 2.77 ± 0.23 | 0.35 ± 0.65 |

To further investigate the phenomenon, we first compare the $J_0$ and $\beta$ for those two junctions on Au and Ag substrates. Table 2 summarizes the derived results from fitting data to Simmons’s model (Eq. 1). Interestingly, for SAM$^E$, Ag and Au share similar $J_0$ and $\beta$ values, while for SAM$^O$, Ag and Au have distinct $J_0$ and $\beta$. The tunneling rate results in Figure 5b also indicate that SAM$^E$ for Ag and Au are almost aligned while SAM$^O$ for Ag and Au has significant difference, $\Delta J_S = |J_{Au} - J_{Ag}|$. And this $\Delta J_S$ shows a chain length dependence, where the $\Delta J_S$ increases with chain length. The magnitude of the odd-even oscillation in tunneling rate on Ag is significantly larger than that on Au, as suggested by $\Delta \beta$ in Table 2. In wetting behavior on SAMs, however, the magnitude of odd-even oscillation in contact on Au is significantly larger than on Ag.\textsuperscript{41-42} Thus, we infer that the odd-even effect in tunneling is not simply dominated by the orientation of the terminal group in the SAMs.
Insight into molecular information in the junctions such as odd-even effect\(^3\) and dipole effect\(^{43}\) is limited using Simmons model, a more common coherent molecular model is adopted for analysis. Current injections (or leakages) at two interfaces affect the total tunneling rates. For brevity, we first define the interface at S-Metal bond is the interface1 and the interface between CH\(_3\)/EGaIn the interface2, as schematically shown in Figure 5e. In charge transport across molecular junction, the low bias conductance (G) can be described using the Landauer formula,\(^{44-47}\) as in Eq. 3;

\[
G = \frac{e^2}{\pi \hbar} T(E)
\]  

(4.3)

\(T(E)\) is a transmission coefficients, which is dependent on the energy \(E\). A Lorentzian is commonly used to describe the transmission coefficient, such as Eq. 4 for HOMO mediated tunneling systems (such as alkanethiol based junctions);

\[
T(E) = \frac{\Gamma_1 \Gamma_2}{\left(\frac{\Gamma_1 + \Gamma_2}{2}\right)^2 + (E - E_{\text{HOMO}})^2}
\]  

(4.4)

\(\Gamma_1\) and \(\Gamma_2\) are the coupling strength (\(\Gamma\)) between the molecules and the electrode at interface1 and interface2, respectively, which depict the energy barrier between the molecules and the electrodes (E-E\(_{\text{HOMO}}\)).\(^{48-49}\)
Figure 4.5 Odd-even effect in tunneling rates across alkanethiolate molecular junctions formed on Au and Ag surfaces. a) Odd-even effect in tunneling rates at -0.5V across junctions on Au surface. b) Comparison of tunneling rates at -0.5V of junctions on Au and Ag substrates. c) The tunneling rates of the evens for Au and Ag are comparably similar. d) The tunneling rates of the odds for Au and Ag are very different, whose variance shows a chain length dependence.

4.3.6 The even behaviors of the evens, the odd behaviors of the odds.

The asymmetry of the junction leads to uneven distribution of the coupling strength. The interface1 (chemisorption) has larger coupling strength than interface2 (physisorption), $\Gamma_1 >> \Gamma_2$. And hence, Eq. 4.4 can be simplified as:

$$T(E) = \frac{\Gamma_2}{\frac{\Gamma_1}{4} + (E-E_{HOMO})^2}$$

For the same molecule, $E_{HOMO}$ remain unchanged. As a result, the term $(E-E_{HOMO})^2$ can be treated as a constant ($\phi$) at a specific field, as follow;

$$T = \frac{4\Gamma_2}{\Gamma_1 + 4\phi}$$

Let’s first focus on the interface1. Due to the strong binding of S-Au or S-Ag bond, there is significant electronic state overlap and hence the coupling for both are high.\textsuperscript{48} Au-S has a
significant large bond energy than Ag-S,\textsuperscript{50} and in principal has a stronger coupling. In addition, the dipole, induced by the adsorption of S at the metal, however, also affect the electronic state at the interface. We have recently shown that stronger dipoles at the interface will reduce the coupling, which is caused by a Fermi level pinning barrier.\textsuperscript{43} According to previous study, the S-Au interface has a smaller dipole than the S-Ag interface.\textsuperscript{51} We, herein, infer that at interface1, $\Gamma_{1-Au} > \Gamma_{1-Ag}$. The odd-even variation in surface normal dipole will lead to small perturbation to the value of the coupling. According to literature, SAM\textsuperscript{E} on Ag has larger surface normal dipoles than SAM\textsuperscript{O}, while it is the opposite for SAMs on Au. From this, we can derive the order of coupling strength:

$$\Gamma_{1-Ag}^{E} < \Gamma_{1-Ag}^{O} < \Gamma_{1-Au}^{O} < \Gamma_{1-Au}^{E}$$  \hspace{1cm} (4.7)

or

$$\frac{1}{r_{1-Ag}^{E}} > \frac{1}{r_{1-Ag}^{O}} > \frac{1}{r_{1-Au}^{O}} > \frac{1}{r_{1-Au}^{E}}$$  \hspace{1cm} (4.8)

At interface2, however, the CH\textsubscript{3}/EGaIn is a weak van der Waals type binding for both Au and Ag based junctions. Neither orbital mixing nor Fermi level pinning is present at the contact between the SAM and EGaIn. Thus, a Schottky-Mott rule applies at that interface, where the vacuum level should be aligned, as shown in Figure 5e. Generally, EGaIn has work functions of approximately 4.5eV, while Ag with alkanethiols has lower work function than SAMs modified Au (with same molecules).\textsuperscript{51-52} As a result, the barrier between EGaIn and Ag is generally larger than that for Au-based junctions, and hence $\Gamma_{2-Au} > \Gamma_{2-Ag}$. Despite the effect of the chain length of the molecules on the work function of the substrates, the odd-even variation in dipoles lead to perturbation to the work function in a similar way, where SAM\textsuperscript{O} on Ag (SAM\textsuperscript{E} on Au) has comparatively larger barriers, which corresponds to previously reported work by Nijhuis and coworkers\textsuperscript{5} that on Ag SAM\textsuperscript{O} has larger contact resistance than SAM\textsuperscript{E}. 
With the guidance from literature, it leads us to the derivation of the order of the coupling strength;

\[ \Gamma_{2-Ag}^O < \Gamma_{2-Ag}^E < \Gamma_{2-Au}^E < \Gamma_{2-Au}^O \]  \hspace{1cm} (4.9)

According to Eq. 6, the transmission coefficient \( T \) is proportional to \( \frac{1}{\Gamma_1} \) and \( \Gamma_2 \);

\[ T \sim \frac{1}{\Gamma_1} \cdot \Gamma_2 \]  \hspace{1cm} (4.10)

According to the relation in Eq. 8 and Eq. 9, chances are high for a comparable transmission coefficient for \( \text{SAM}^E \) on Au and Ag, while SAME on Au has smaller transmission than \( \text{SAM}^O \) (an opposite case for junctions on Ag). Based on evidence, we infer;

\[ T_{Au}^O > T_{Au}^E \approx T_{Ag}^E > T_{Ag}^O \]  \hspace{1cm} (4.11)

This trend in transmission coefficient reflects the same trends in tunneling rates, which correlated well with our results.

4.3.7 Effect of intermolecular interactions on tunneling.

So far we have shown that interfacial coupling strength induced by dipole is the most important parameters for observations of the odd-even in those junctions. Those arguments are based on the assumptions that SAMs are perfectly ordered on the substrates, where a parallel-separated odd-even effect should be expected.

In SAMs, the gauche defect density evolves with a decrease of intermolecular interaction (van der Waals interactions for saturated chains). Disordered molecules lead to a poor alignment of dipoles, and for highly disordered “liquid-like” SAMs, the subtle odd-even variation in surface normal dipole will be diminished, leaving no odd-even oscillation in the tunneling rates, as discussed before (Figure 4.4).

The rate in change of intermolecular interactions with molecular chain length (\( \Delta E \)) is, however, not equal, which depends not only on whether \( \text{SAM}^E \) or \( \text{SAM}^O \) but also the substrate. We twenty-six, thirty-eight
and others$^{53}$ have reported that on Au SAM$^E$ is more favorable to increase inter-chain interactions with chain length than SAM$^O$ (the reverse case for Ag). A larger tilt angle in molecules generally gives smaller van der Waals interactions,$^{53}$ and therefore, if not considering odd-even oscillation, SAMs on Ag have larger inter—chain interactions. We infer that for intermolecular interactions; $\Delta E_{Ag}^O > \Delta E_{Ag}^E \approx \Delta E_{Au}^E > \Delta E_{Au}^O$. Thus, as shown in Figure 5b-d, the change of tunneling rates with chain length (the slope) correlated with the change of intermolecular interactions, where the largest change of intermolecular interaction (SAM$^O$ on Ag) has the largest change of tunneling rates with chain length.

The odd-even effect disappear at around C$_9$ for Au and Ag, while the limit to observe the difference between SAM$^O$ on Ag and that on Au is around C$_8$. The disorder in dipole in SAMs undermines the distinction between Ag and Au based junction, showing a similar tunneling rate. Jiang et al., observed similar phenomenon that with short-chain molecules (<C$_9$), the junctions did not distinguish the difference between smooth and rough surface.

4.4 Conclusion

With the polished EGaIn tip, finer molecular information has been derived from a qualitative but thorough mathematical analysis of electrical measurement data. The insight into the molecular junction tunneling and a comparison with literature lead us to the conclusions as follow;

i) **The nature of the oxides on EGaIn electrode does affect the tunneling across molecular junctions.** The “pre-flattened” thick oxide electrode$^{25}$ gives higher precision in data collection, but leaves behind some molecular information such as the odd-even effect. Chemical polishing provides electrodes with smoother surfaces and
thinner oxide shell. Although those electrodes do not provide better precession, they do yield better information about molecular detail.

ii) **Both interfaces between electrodes and the monolayer affect the odd-even effect.**

The fine molecular information from these measurements are not easily explained by the Simmon’s model, but the coherent tunneling model provides greater insight into the observed phenomena. Through estimating the contribution of the coupling strength at two interfaces in charge tunneling, one can conclude that both interfacial coupling strength parameters affect the tunneling rates and are responsible for the odd-even effect. This explain why the odd-even effect in tunneling has larger magnitude on Ag than on Au, which is contrary to the SAMs wetting data where the odd-even oscillation in SAMs contact angle on Ag is significantly weaker than on Au.

iii) **The phase change of SAM exists and affects the tunneling behaviors.** As previously demonstrated with wetting, we observed an analogous molecular chain-length dependent limit to the odd-even effect in charge transport. As with the wetting studies where odd-even oscillation in contact angles disappears at C₈/₉, a similar vanishing of the odd-even effect in charge transport behavior was observed in this study. This further confirms that a likely phase transition occurs at this chain length leading to stochastic distribution of the orientation of the terminal moiety in n-alkanethiolate based SAM.

**References**


47. Thijssen, J. M.; Van der Zant, H. S. Charge transport and single-electron effects in nanoscale systems. physica status solidi (b) 2008, 245 (8), 1455-1470.


Delineating the role of dipoles in large area junctions that are based on self-assembled monolayers (SAMs) is challenging due to molecular tilt, surface defects, inter-chain coupling among other features. To mitigate SAM-based effects in study of dipoles, we investigated tunneling rates across carboranes—isostructural molecules that orient along the surface normal on Au (but bear different dipole moments) without changing the thickness, packing density, or morphology of the SAM. In a more complex system, molecules with multiple isolated dipoles (variation in dipoles moments without Fermi level pinning), the chain length (barrier width) dominates the tunneling current from first moment statistical analysis. Analysis of higher statistical moments, however, indicates that the isolated dipoles affect the nature of the distributions even though they do no manifest in the average current densities.

5.1 Introduction

The simplified Simmons equation (Eq. 5.1) is commonly used to describe the rate of charge transport and highlights the need for a constant barrier width in a comparative study of electronic properties of the SAM;

\[ J = J_0 e^{-\beta d} \]  

(5.1)

Where \( J \) (A/cm\(^2\)) is the current density, \( J_0 \) is the injection current, \( \beta \) is the decay constant, and \( d \) is the barrier width. This interdependence has led to some ambiguities, especially across different platforms or groups. For example; several recent reports show an odd-even effect (in terms of non-H atoms
in the SAM) on the rate of charge transport through monolayers\textsuperscript{1-3} or organic field-effect transistors (OFETs)\textsuperscript{1-4} while others do not.\textsuperscript{2,5} Jiang et al.\textsuperscript{1} recently reported the origin of odd-even effect in tunneling rates across n-alkanethiolate SAMs, observing that the contact resistance is different between odds and evens. This variance indicates that the orientation of the top moiety affects the charge transport rate, to a small extent. Others, however, have indicated that a “small” perturbation to the electronic nature of the “saturated” molecules, such as H-bonding and polarity of the head group,\textsuperscript{5-7} anchoring group,\textsuperscript{8-9} and backbone,\textsuperscript{10} has little or no observable effect on the rate of charge transport. These two sets of studies do not resolve the role of a moiety’s dipole in charge tunneling, the latter being complicated by associated changes in the SAM with changes in molecule-structure.

Dipole moments have, however, been implicated in modifying the charge transport properties of SAMs manifesting in effects like rectification, quantum confinement or perturbing the overall rate of charge transport or associated mechanisms.\textsuperscript{11-13} Some of these phenomena is associated with the potential for molecular dipoles to significantly tilt the barrier allowing transition from direct tunneling to Fowler-Nordheim tunneling (Figure 5.1) and this bias-dependent behavior can be captured through transition voltage spectroscopy (TVS) as the transition voltage ($V_T$) as shown below (Figure 5.1)
Figure 5.1 Illustration of the transition from direct tunnelling to Fowler-Nordheim tunnelling at transition voltage.

Charge transport across molecules is usually fitted to the simplified Simon’s model \(a\) (Eq. 5.1), and, in most case, the decay constant, \(\beta\), is associated with barrier height \(\phi\), as in Eq. 5.2:

\[
\beta = 2 \sqrt{\frac{2m\alpha (\phi - \frac{qV}{2})}{\hbar^2}}
\]  

(5.2)

Where \(m\) is the effective mass of an electron (0.9\(m_e\); kg), \(\alpha\) is a unitless fitting parameter for non-rectangular barrier compensation, \(\hbar\) is Plank’s constant divided by 2\(\pi\) (J·s), \(\phi\) is the barrier height, \(qV\) is the energy level change due applied field.

From this relation, we can infer that, at least under positive bias, \(\beta\) decreases as \((\phi - \frac{qV}{2})\)—since the magnitude of the effective energy barrier for charge injection at the metal-molecule interface decreases. This dependence is largely due to metallic orbitals and molecular orbitals coming into resonance. At the metal/molecule interface, significant band bending occurs due to Fermi-level pinning/ Charge Neutrality Level (CNL) alignment for weakly physisorbed molecule/metal interface.\(^{14-17}\) The case for chemisorbed interface is much more complicated, due to particle charge transfer across the bond, resultant surface dipoles, \(\sigma - \sigma^*\)
hyperconjugation, and delocalization of orbitals between metal and molecules. It is therefore important to compare current densities from equivalent positive and negative biases, or deploy isomorphic SAMs (no structural differences) where the decay parameter is not a necessary variable to consider as there are no height changes.

Differences in tunneling rate can also be due to changes in total work function (surface potential), $\Delta \Phi_{\text{total}}$, at the metal surface, which can be induced by chemical bond formation ($\Delta \Phi_{\text{chem}}$), metal surface dipole/work function exchange ($\Delta \Phi_{\text{m,dipole}}$) and molecular dipole ($\Delta \Phi_{\text{mol,dipole}}$), as shown in Eq. 5.3:

$$\Delta \Phi_{\text{total}} = \Delta \Phi_{\text{chem}} + \Delta \Phi_{\text{m,dipole}} + \Delta \Phi_{\text{mol,dipole}}$$

Recent theoretical work reported by Mete et al. shows that the work function change of Au surface upon M1 deposition (a carboranethiol monolayer deposition) is negligible (an increase of 0.05eV), while the change of work function with M9 deposition is much more significant (a decrease of 0.70eV). Based on this observation, we can anticipate that there will be significant differences in charge tunneling when the junction symmetry plays a significant role or this change in the work function significantly tilts the barrier towards a change into classical physics based transport as opposed to direct tunneling where only the nature of the barrier plays a significant role. This difference in work function may also lead to differences in contact resistance or charge injection into the metal.

Understanding charge transport through uni-molecular systems bears an inherent fabrication challenge, but, the so-called large area junctions have emerged as one of the more reliable platforms in terms of yield of working device, data reproducibility, and stability. Fundamental relations between molecular properties and charge transport behavior, however, need to be delineated for functional uni-molecular devices to be realized. Among these,
decoupling stereo-structural effects (e.g. barrier width, conformations, phase-evolution) from electronic (e.g. dipoles, band broadening, interfacial coupling, barrier height) molecular properties is vital. Adoption of self-assembled monolayers (SAMs) in large area junctions, viewed as a series of resistors (Figure 1a), for example, fails to decouple molecular dipoles from steric orientation of the molecules making up the SAM.

The uncoupled effect of molecular dipole on charge transport remains unresolved, in part, due to challenges inherent in pinning a vector quantity on a dynamic (rotating/vibrating) and/or canted SAM system(s). In single molecule junctions, it has been shown that direction of embedded dipoles significantly affects rates of charge transport.\textsuperscript{25-28} As expected, current across junctions with parallel dipole moments, relative to electron flow, are much larger than across analogous junctions with anti-parallel dipole moments (Figure 1b).\textsuperscript{25} These observations can be attributed to molecular dipoles enhancing polarity at the electrodes through associated mirror charges and/or inductive effects. In SAM-based studies, however, such direct correlations have been a challenge. Thuo et al.\textsuperscript{29}, and later Yoon et al.,\textsuperscript{6,30} for example, reported that introduction of amides and/or aromatic moieties—with associated polarity (dipole) changes, in n-alkanethiol-based SAMs does not significantly affect tunneling rates. Kovalchuk et al.\textsuperscript{11} also reported that molecules with dipoles oriented in different directions comparable similar tunneling rates in conflict to the single molecule junction studies. Discrepancy between SAM-based junctions and the single molecule junctions, calls for further evaluation for clarity. From simple coulombic interactions, however, dipole moments should be influenced by an applied field and vice versa. Transition voltage, \(V_T\), —a transition point from direct tunneling to Fowler-Nordheim tunneling due to barrier tilting (Figure 5.1)\textsuperscript{11,31-32} can, however, be used to delineate any changes due to field-driven dipole-dependent band alignments. As such,
studies on role of dipoles in charge transport necessitates determination of $V_T$. Besides $V_T$, an experimental caveat in the above studies is that SAM structural and electronic properties were not decoupled, hence the inferences can be limited by lack of a detailed understanding of the nature of the SAM structure.  

5.2 Effect of molecular dipole on tunneling

We desired to decouple stereo-electronic (dipole moment) and steric (SAM tilt angle and packing density) effects on the rate of charge transport across SAMs and, hence, demonstrate the singular (isolated) effect of the dipole moment on charge transport behavior. We address this challenge by: i) designing SAMs that do not tilt upon forming a SAM, i.e. molecules that orient along the surface normal, ii) fabricating SAMs from isomeric molecules (structural isomers) with differences in both magnitude and direction of their dipole moments—due to atomic arrangement, but forming isomorphic SAMs (similar packing density, binding strength, thickness or top interface structure). We chose molecules whose direction and magnitude of dipole can be tuned without significantly altering the stereo-structural properties of the molecule, iii) Addressing changes in barrier height by using a class of isostructural/isomorphic molecules where the elemental composition, dipole moment or localization of frontier orbitals is not significantly perturbed from one structure to the other.

Carboranethiols, which are primarily boron-based molecules with a few carbons atoms interspersed between the boron atoms, are the candidates for this study. We choose three commercially available molecules, meta-1-carboranethiol (M1), meta-9-carboranethiol (M9), and 1,2-o-carboranethiol (1O2) (Figure 5.2c-e). Monolayers derived from M1 and M9 on Au are well studied, giving well-ordered SAMs with similar coverage, thickness, and surface properties (i.e. they are Isomorphic). Weiss and co-workers have shown that when these
carboranethiols are attached to a surface (Au or Ag), the work function of the surface can be tuned, which is believed to be caused by the molecular dipole moment.\textsuperscript{34-36} 1O2 forms SAMs with similar coverage and thickness as M1 and M9, albeit with a different bottom interfaces where the molecule is anchored via two thiols.\textsuperscript{36} The dipole moments between M9 and 1O2 SAMs are anti-parallel, while M1 is oriented orthogonal to the surface normal upon forming SAMs (Figure 5.2e).\textsuperscript{37}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.2.png}
\caption{a) Calculated electrostatic potential (ESP) of M1 (i), M9 (ii) and 1O2 (iii), respectively. b) Estimated dipole moment and direction of M1, M9 and 1O2 molecules. c) Dipole direction of M1 SAM, M9 SAM and 1O2 SAM.}
\end{figure}
5.2.1 Carboranethiol SAMs and interface

The electrostatic potential (ESP) maps were calculated using the Gaussian software package\(^{38}\) and the corresponding minimized structural energies (Figure 5.2a). The geometries of the 3 isomers were optimized using density functional theory at the B3LYP level with the 6-311++g(2d,p) basis set. For comparison purposes, the complete basis set method (QBS-QB3) was also used and the dipole moments evaluated. Mulliken charges used for the electrostatic potential mapping were computed from the single point structures of the CBS-QB3 geometry at the Hartre-Fock level with the 6-31+G(d) basis set.

The magnitude of the associated molecular dipoles is given alongside the molecule while the direction is illustrated by an arrow (Figure 5.2b). The calculated values are comparable to those in literature.\(^{36}\) The dipoles slightly change upon chemisorption onto the substrate, with M1 aligning along the substrate surface (orthogonal to surface normal) while in M9 and 1O2 the dipoles align with the surface normal albeit in opposite directions.\(^{36}\) The three carboranes have also been shown to structurally orient along the surface normal while retaining the same packing structure and density.\(^{36}\) In this article, we deploy these isostructural molecules to form isomorphic SAMs in order to delineate the effect of molecular dipole on charge transport across EGaIn-based large area junctions, Au-SAM//Ga\(_2\)O\(_3\)-EGaIn junction (where ‘//’ = physisorption, ‘-’ = chemisorption, and EGaIn is eutectic gallium-indium). The M1 and M9 have the same structure at the molecule//Ga\(_2\)O\(_3\) interface, but the 1O2//Ga\(_2\)O\(_3\) is slightly different and is only included solely to probe the role of dipole directionality. Despite the slight differences, we infer that 1O2 can be used to support inferences drawn from M1 and M9 if deployed in a comparative manner and not as an equal.

Template-stripped gold (Au\(^{TS}\), roughness root-mean-square \(R_{RMS} = 0.38 \pm 0.04\) nm) was used as substrate for device fabrication since; i) carboranethiols oriented along the surface normal
when bonded to Au,\textsuperscript{36-37} ii) has low surface roughness (Figure 5.3a), iii) Au\textsuperscript{TS} surface is uniformly faceted along the (111) direction.\textsuperscript{39} Upon deposition of carboranethiol SAMs, the grain boundaries become less distinguishable from a AFM image and its $R_{RMS}$ is statistically smaller than Au\textsuperscript{TS} ($p<0.002$), indicating a slight modification in the substrates morphology ($R_{RMS}$, power spectrum density and bearing volume) due to presence of the cage molecules. The X-ray analysis confirms that our surfaces are (111) orientation dominated Au surface with or without a SAM (Figure 5.3c).

\textbf{Figure 5.3} Surface characterizations of substrates and the SAM. a) Atomic force microscopies of bare template-stripped gold, Au\textsuperscript{TS} and b) Au\textsuperscript{TS} surface bearing a SAM of carboranethiol, showing a difference in RMS roughness ($R_{RMS}$), power spectrum density (PSD) and bearing volume (BV). c) Wide angle X-ray diffraction pattern on Au\textsuperscript{TS} and that with a SAM of carborane thiol showing that the metal is (111) oriented and that the faceting does not change upon deposition of the SAM.

\textbf{5.2.2 Charge transport behavior across the junctions}

All charge transport data were collected using a previously reported method.\textsuperscript{3,10,30} The raw data were then analyzed by \textit{LAJA},\textsuperscript{40} and data summarized into heat-maps (Figure 5.4a). We observed significant differences between charge transport properties across these molecules.
despite being of same barrier width.\textsuperscript{36} Carborane M9 showed narrowest distribution in $\log|J|$, with the distribution widths following the order; M9<M1<<102. Peak broadening and significant outliers in the data obtained from M1 and 102 molecules (Figure 5.4a) necessitated investigation of auto-correlation through lag plots, to help identify the outliers (random non-correlated data points). The outliers shown in the lag plots were removed from consideration (Figure 5.5), and the main portion of the data shows a strong autocorrelation (linear narrow distribution), as shown in Figure 3b, suggesting a non-random series of data. Gaussian mean values and standard deviations were also calculated before and after removing the outliers giving statistically indistinguishable values. These results confirm that previously used approach of fitting a Gaussian over tunneling data\textsuperscript{1, 3, 10, 29, 40-41} does not skew with outliers (Figure 5.6), and can be reliably deployed in analyzing charge tunneling characteristics as described in the LAJA method.\textsuperscript{29}
Figure 5.4 Tunneling current across carboranethiolate junctions. a) The tunneling data across all three molecules was demonstrated via heat maps. b) Lag plot for tunneling rates across M1 at -0.5V, to show the effect of outliers. c) Calculated mean value for tunneling rates across the three molecules.
Figure 5.5. The lag plots showing the current density at -0.5V for all junctions of M1. The outliers can be easily distinguished from the main part of the data.

Figure 5.6. The heap-map of charge transport data across M1 junctions before removing and after removing the outliers. The Gaussian mean values calculated from raw data and “purified” data show no significant differences.
Figure 5.4c summarizes the charge transport data obtained from the three carboranethiols. The average current densities obtained from M9 and 1O2 at ±0.5 V are comparable while M1 has a significantly higher current density. We observe that the distribution of the data correlates well with the charge density at the vertex of the molecule with low-electron density at the vertex leading to significant broadening (1O2) in the distribution of J (A/cm²). Junctions derived from 1O2 were also observed to create ‘sticky’ contacts which could be due to a stronger contact analogous to so-called ‘hard’ contacts. Strong physi-sorption, however, does not necessary imply stronger electrical coupling since the less ‘sticky’ M9 gave comparable average current densities.

5.2.3 Effect of molecular dipoles on tunneling rates

Figure 5.4a compares the magnitude of the dipole moments of the three molecules with current density at +0.5V and -0.5V. The molecule with a lower magnitude dipole moment (1.1 D), M1, gave the highest average current density while the higher dipole, M9 and 1O2 (4.1 D for both) gave statistically indistinguishable average current densities that were lower than observed with M1. Dipoles moments, however, are characterized by both magnitude and direction. Considering direction of the dipole moments, higher current is observed for the dipole oriented orthogonal to the surface normal. With flat substrates and well-ordered SAMs, the surface normal aligns with the direction of charge injection in carboranethilate SAMs. Molecule, M1, has a dipole moment orthogonal to the surface normal while M9 and 1O2 have dipole moments oriented along the direction of electron flow although in an anti-parallel direction. The directions of the dipole moments relative to the flow of electrons are given as inserts above each value of obtained current density in Figure 4a. From these data, and assuming no significant field effects, we can deduce that the effect of magnitude of dipole...
moments on the rate of charge transport in these SAMs is $\Delta \log |J| \approx 0.4$ per Debye, a value that is critical in comparative studies of structurally varying molecules.

To fully quantify the effect of the dipole, however, the dot product of the two vector quantitates, $I \cdot \hat{p}$ (where $I =$ current and $\hat{p} =$ effective dipole moment along the surface normal), should be considered. In this case therefore, M1 has an effective charge vector oriented at angle relative to the surface normal, while M9 and IO$_2$ are aligned with direction of electron flow, hence can be assumed to have an additive or resistive effect on the injection of charge into the molecules. A parameter that can capture the effect of dipole on tunneling rate is, therefore, the coupling between the electrode and the molecule. Considering molecule-electrode coupling, the rate of charge tunneling, expressed in current density, can be expressed as (Eq. 5.4),

$$J(V) \sim \frac{2q}{\pi \hbar} \Gamma_1 \Gamma_2$$  \hspace{1cm} (5.4)

Where $\Gamma$ is the coupling strength, $q$ is the electronic charge and $\hbar$ is the Planck constant. Here, we focus on the coupling at the chemisorbed interface, since the chemisorbed termini is expected to be in the strong coupling regime.$^{19}$

If the molecules have significant polarizability and cooperativity, an intramolecular charge redistribution with the metal substrate will occur.$^{44}$ As shown (Figure 1c), the electrostatic potential differences within the molecule is significantly larger for M9 and IO$_2$, and thus, in SAMs, a pseudo-2D layer of oriented dipoles forms on the substrate (Figure 5.1e and 5.7b (left)). This dipole layer is metastable and tends to partially transfer charge from/to substrate to energetically reduce the field within the molecules (Figure 5.7b right). A partial electrostatic potential is then formed and locked at the molecule/metal interface. As a result, the delocalized combined orbitals between the metal and the molecules are thus disentangled to some degree, hence, decreasing interfacial coupling strength ($\Gamma$). The resulting broadened bandgap leads to
narrowing of HOMO and LUMO states (Figure 5.7b), leading to a more “resistive” path across the molecule due to a decrease in energetically accessible/coupled conduction states. The energy gain, $\Delta E$, per molecule to disentangle the delocalized orbitals is proportional to the potential drop, $\Delta \Phi$, (Eq. 5.5), which is proportional to the effective molecular dipole along the surface normal, (Eq. 5.6):

$$\Delta E = q \cdot \Delta \Phi / 2 \quad (5.5)$$

$$\Delta \Phi = \sum_i \int_0^{\pi} N_i(\theta) P_i(\theta) \cos \theta \frac{\varepsilon_r \varepsilon_0}{\varepsilon_r - \varepsilon_0} d\theta \quad (5.6)$$

Where $P$ is the dipole moment, $N$ is the density of the dipole, $\theta$ is the angle between dipole orientation and the surface normal, and $\varepsilon_r\varepsilon_0$ is the molecule permittivity. For M1, $\Delta E \sim 0$ because the dipole direction is orthogonal to the surface normal ($\cos \theta \approx 0$); while for M9 and 1O2, energy change is significantly larger. From this expression, therefore, we predict and empirically show that tunneling rates for M9 and 1O2 are significantly lower than M1. We also demonstrate that the difference in tunneling rates is not just dependent on the magnitude of the dipole moment, but also on its orientation relative to the surface normal. Kovalchuk et. al. further supports our inference that SAMs with larger effective molecular dipoles promote disentanglement of mixed orbitals, hence reduced tunneling rates. From the higher current density and the theoretical work that M1 does not significantly affect the work function (see supporting information for details), we can infer that a molecule with a dipole moment orthogonal to the surface normal is akin to one without a dipole moment since there is no effect on the SAM-electrode coupling (i.e. $\Delta \Phi = 0$).

### 5.2.4 Fermi level pinning

For more detailed understanding of the molecule/electrode coupling, Fermi level pinning/depinning theory is used to explain the phenomenon that M9 significantly changes...
the electronic properties, while M1 has minimal electronic perturbations due to the interface dipole coupling effects. Figure 4c shows a schematic of the energy level diagram for the prepared molecular junctions (without pinning), based on molecular energy levels derived from simulation and UPS studies.\textsuperscript{20, 34} According to Liu et al.,\textsuperscript{14} there should be a potential drop at the Au/M9 interface due to the dipole but no analogous drop at Au/M1 interface due to negligible effective dipole moment—we believe there is Fermi level pinning only at Au/M9 interface but not at Au/M1 interface. As a result, M9 junctions have larger barrier height than M1 due to dipole induced energy band shift.\textsuperscript{14} The Fermi level depinning within M1 SAMs has also been demonstrated in carboranethiol SAMs modified organic semiconductor device,\textsuperscript{34} where M1 modified device show significantly improved performance than M9. This is because M1 serves as a depinning insulating layer that reduces the injection barrier (hence the contact resistance).\textsuperscript{14}
Figure 5.7 Charge transport rate across carboranethiolate SAMs and the effect of dipole. a) The charge transport rate at -0.5V and +0.5V for all three molecules. The dipole moment of the adsorbates are collected from [36] b) The charge reorganization at the molecule/substrate interface and the resulting HOMO/LUMO shrinkage. c) The energy level diagram (before contact without pinning and band bending) at 0 bias and ±1V, respectively. d) The rectification for all three molecules was irrelevant to dipole (moment and direction). e) The transition voltage spectroscopies (TVS) for all three molecules at both positive bias (solid symbol) and negative bias (open symbol).
5.2.4 Transition voltage analysis

To further support inferences drawn so far, transition voltage spectroscopy (TVS) was performed. A transition voltage ($V_T$) was observed for all three molecules (Figure 4e). Compared to previously reported molecules with aromatic groups, the transition voltage for carboranes are diffuse (broad).\textsuperscript{11, 32} This broadening of the $V_T$ is possibly due to the pseudo-aromatic cages having empty non-bonding boron p-orbitals, which result in a large number of field tunable states hence a ‘diffuse’ field-driven tilting of the non-frontier energy level bands. The transition voltage ($V_T$) when the top-electrode bears a positive bias was calculated from TVS (Figure 5.8 and Table 5.1) to be; $V_T$ (M1)=0.49±0.02V, $V_T$ (M9)= 0.43±0.01V and $V_T$ 1O2 =0.40±0.02V. Considering the broadened transition, we infer that the $V_T$ for M9 and 1O2 are not statistically significantly different but M1 is significantly different ($\Delta V_T\approx 0.07$). Since by definition $V_T$ is associated with position of molecular levels, this result indicates that M1 has more accessible band(s) than M9, a result that concurs with reported theoretical work\textsuperscript{20} and agrees well with our inference on Fermi level pinning.
Figure 5.8 The F-N plots for three molecules for forward and reverse bias. There is distinct transition at forward bias at certain transition voltage ($V_T$) for all molecules. For reverse bias, no distinct transition was observed from direct tunneling to F-N tunneling.

Table 5.1 Transition voltage of three molecules estimated at positive bias and negative bias.

<table>
<thead>
<tr>
<th>Transition voltage</th>
<th>At positive bias $[Vt(+)]$</th>
<th>At negative bias $[Vt(-)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0.50</td>
<td>0.93</td>
</tr>
<tr>
<td>M9</td>
<td>0.43</td>
<td>0.74</td>
</tr>
<tr>
<td>IO2</td>
<td>0.41</td>
<td>0.71</td>
</tr>
</tbody>
</table>

From the above studies, we inferred that a change from direct tunneling to Fowler-Nordheim tunneling regime at 0.4-0.49 V should result in an increase in the rate of tunneling across these barriers. Based on Schottky–Mott rule, the difference in work function of M1 and M9 lead to different degree of band bending, which can be associated with rectification- especially with sweeps larger than the $V_T$ due, in part, to mixed transport mechanism. In these carboranethiol junctions, despite inherent junction asymmetric due to different electrode materials (Figure 5.7c), rectification was observed for all molecules when we expanded the sweep width from
±0.5V to ±1V. With increased voltage, we observed slight current rectification for all 
molecules in the order; M1>M9>1O2 (Figure 5.7d, and Table 5.2). We observe that although 
the standard deviations for current density are comparable (σ\text{log}|j|\sim±0.4) for the three molecules 
at ±0.5V applied bias, the rectification ratios (RR) follow the general trend σ\text{RR-M1}=4.8>σ\text{RR-M9}=3.3>σ\text{RR-1O2}=2.1 which changes to σ\text{RR-M1}=14>σ\text{RR-M9}=9>σ\text{RR-1O2}=6 at 1V sweep (see 
supporting information Figure S7). We infer that the variance in the distributions may be due 
to differences in the degree of barrier tilting above the V_T and, potentially, the perturbation of 
this process by the molecular dipole. More importantly, the trend in RR is similar to the V_T 
(see supporting information, Figure S7). The change of work-function through M1/M9 
monolayer gives Schottky barrier induced rectification in those junctions. We infer that 
differences in barrier height between M1 and M9, as deduced from V_T, mostly arise from the 
Schottky-type behavior rather than structural differences in the molecules (size, packing 
density, surface-bond strength). This is likely affecting the coupling between the electrode and 
the molecule, hence M1 with a larger transition voltage shows higher tunneling rate.

| Table 5.2 | The measured rectification ratio (RR) of current at +1V to that at -1V. |
|------------|--------------|--------------|
| Gaussian mean | Average | Gaussian mean | Average |
| M1 | 13.0x10^(±0.406) | 13.7 ± 4.8 | 10.3x10^(±0.397) | 9.4 ± 3.3 |
| M9 | 6.4x10^(±0.337) | 6.4 ± 2.1 |

We estimated the ratio by comparing the Gaussian mean values of current density at +1V and 
at -1V. RR= log|J(+1V)/log|J(-1V) We also estimated this through averaging the rectification 
ratio between +1V and -1V of each measurement traces. RR= Ave[J(+1V)/J(-1V)]. Those 
two method gives very similar average values, though the errors from these two methods are 
much more different.
In this section, we have shown that carboranethiols—oriented perpendicular to the Au substrate (along the surface normal), are ideal for the study of effect of molecular dipoles on charge transport behavior. The cage structures in the two (M1 and M9) carboranes used in this study are structurally isomorphic (structure, empirical formula, barrier width, pseudo-aromaticity, SAM structures and packing density), but distinct in magnitude and orientation of their molecular dipoles which was verified through literature and calculated electrostatic potential maps. To further support our inferences, a structurally slightly different analog of M9 carborane, 1O2 was also investigated realizing that although the SAMs are isomorphic, the latter has two anchoring units which may lead to differences in metal-molecule orbital mixing, hence slight differences in stereo-electronic properties of the surface-bound molecules. SAMs derived from carboranes on Au align along the surface normal (no canting), with comparable packing density and effective thickness, and are therefore ideal for delineating the role of surface dipoles on charge transport since structural variabilities are not a concern. From this study, we demonstrate that dipole moments oriented orthogonal to the surface normal do affect the charge transport behavior across these molecules as much as that oriented along the surface normal. When the dipole moments is oriented parallel to the surface current densities comparable to tridecanethiol (C_{13}) are observed. When the dipoles are oriented along the surface normal, however, the current densities are comparable to those of pentadecanethiol (C_{17}). This shows that when two similar (isomorphic) SAMs have differences in magnitude and direction of the dipoles, then a difference in current density equivalent to 4 C-C bonds is observed. By isolating stereo-structure SAM effects from the dipole, we deduce that the effect of dipole moments in charge transport to be $\Delta \log|J| \approx 0.4$ per Debye, a value that is critical in interpreting effect of dipoles in charge tunneling through large-area junctions especially in
SAMs where the cant angle and packing density are a concern. By evaluating extent of electrode-SAM coupling, we infer that the dipole moment is likely manifesting significantly during the charge injection step and, as such, effect of dipoles can be expressed as a dot product (two vectors oriented at an angle) where the charge potential and dipole moment affect injection of the charge into the molecular orbitals, hence the degree of interference (decay) between the charge (moving wave) and the molecule (standing wave). We can therefore infer that the dipoles affect the potential drop across the metal-molecule interface, hence, effect of dipoles mainly manifests as differences in the coupling strength, $\Gamma$.

5.3 Effect of complex multi-dipole on tunneling

Contrary to single molecules, a self-assembled monolayer (SAM) is a collection of molecules aliened on the substrate surface. In SAMs, molecules are chemisorbed onto metal substrate surface and form a close-packed well-ordered monolayer due to intermolecular interactions. As a result, the collective effect in SAMs makes the effect of dipole on tunneling different from that of single molecule junction. For example, the conformational change of a molecule with increase in bias is more significant in single molecule junctions than in large-area junctions (SAM based) due to the high fields at the tip of a nanoprobe and strong coupling between the often needed chemisorbed contacts. The intermolecular interaction significantly affect the effect of dipole. With the vast amount of work done in molecular junctions, comprehensive understanding of molecular behavior and their effects on junctions is riddled with discrepancies. The lack of empirically validated insight into molecular level or nanoscale features in molecular junctions is mainly causing the disagreements, especially between theoretical and experimental work, or between different experimental platforms. One example is the effect of dipole or polarity of the molecules on charge transport.
Referring to the simplified Simmon’s equation, which is widely used to model tunneling rate across molecular junctions, the effect of the embedded dipoles are not readily deciphered. However, a number of studies have shown that the dipoles affect the tunneling rates. Results on carboranethiol based junctions, as discussed in previous section, have indicated that dipoles will affect the coupling between the electrodes and the molecules, hence the overall tunneling rate. Chiechi et al.\textsuperscript{11} recently reported that for EGaIn based large area molecular junction, tunneling rates were affected by embedded dipoles, which depends on the relative direction of the dipoles with respect to applied electrical field. This relation was shown to be capable of inducing asymmetric charge transport which manifests as rectification. Recent reports have, however, implied that changing the polarity of the terminal group of the molecules in SAMs does not significantly affect the tunneling rates. We hypothesized that relying only on the average values and standard deviations (first and second moment statistics) does not lead to a complete or accurate understanding of effect of molecular dipoles in charge transport behavior in large area tunnel junctions. We inferred that, based on the Simmons equation, first and second moment statistics would only reveal distance (barrier width) dependent properties.

As a result, to analyze the subtle changes that has been buried by the collective effect from the SAMs, a good statistical tool/parameter need to be employed. We deployed recently developed method (3D data visualization- chapter 3\textsuperscript{40}) to extract more useful information from subtle molecular perturbations in tunneling and coupled this with third and fourth moment statistical parameters for quantitative analysis.

Three substituted $N$-alkylamides, alongside corresponding control molecules, were used in this study. As shown in Figure 5.9a, the structure of the three molecules are similar, molecule (i) has a toluene (methylbenzene, $MB$) as top moiety, while molecules ii and iii have 2-
methylpyridine (2MP) and 4-methylpyridine (4MP) as terminal group, respectively. For brevity and clarity, we abbreviate the molecules as MB, 2MP and 4MP respectively. The amide group, buried in the backbone, provides a stabilizing hydrogen bonding network in the assembled molecules and a strong dipole that is used as an isolated, common, stereo-electronic tensor perturbing the barrier width and abets in investigating dipole cross-talk under applied bias. The dipoles and ESP are calculated using the same method that is discussed in the previous section (section 5.2.1). The amide group has a calculated dipole of 3.9 Debye while the terminal group has varying magnitude and direction of the dipole moment (Figure 5.9a).

**Figure 5.9** a) Structure of molecules with indicated dipoles. b) Electro-static potential maps of the four molecules. c) The average value of tunneling rate at the voltage of -0.5V across all molecules, indicating a statistical insignificance.

SAMs of all molecular were formed on template-stripped silver substrate, whose surface faceting is dominated by the (111) orientation. An EGaIn conical tip was used as a top electrode
to form an Ag\textsuperscript{TS}/SAM//Ga\textsubscript{2}O\textsubscript{3}/EGaIn junction (‘/’ denotes a chemisorbed interface while ‘//’ denotes a physisorbed interface). Measurements were taken from all these fabricated junctions.

5.3.1 Average tunneling rate is insensitive in complex systems.

From the measurements, the Gaussian mean current density were obtained, indicating that for all molecules, the current densities at -0.5V/+0.5V are statistically indistinguishable. A 95% confidence band was drawn with SC\textsubscript{12} as a control (Figure 5.9c), showing that there is no statistically significant differences in the average current density for all the molecule. Obtained charge tunneling data were further analyzed using previously developed method, LAJA, (Chapter 3) to investigate the nature of data distribution.\textsuperscript{40} In Figure 5.9, the heat maps and histograms (at -0.5V) present the distribution of current density across the junctions. The distribution of all molecule are mostly symmetric with small amount of outliers. Based on the heat-maps and histograms (all based on first and second moment statistics), no insight into the details of the dipole induced perturbations to the tunneling current can be deduced.
A different metal/SAM contact interface usually affect the coupling, for example, the electronegativity of nitrogen can affect the extent of interfacial coupling between the SAM and the electrode.\textsuperscript{49} From Figures 5.9c and 5.10, it has been suggested that the effect of the coupling is buried in the collective information from the SAMs that is dominated by the chain length, where all amide molecules with different terminal group show similar charge transport behavior as the control SC\textsubscript{12} alkanethiolate SAMs.

\textbf{5.3.2 Dynamic systems}

According to a discussion of Simmons model by Vilan,\textsuperscript{50} it can be inferred that the tunneling barrier width across molecular junctions is not static under applied bias due to change
in the shape of the barrier. A shape factor, $\rho$, is used to determine the shape of the barrier, which is however, also bias dependent (Equation 5.7).

$$\rho(V) = \alpha(V)\rho(0)$$  \hspace{1cm} (5.7)

Where $\alpha$ is the barrier width ratio and $\rho(0)$ is the shape factor at equilibrium state ($V=0$). Field driven variance in band width, $\alpha(V)$, can lead to perturbation to the overall tunneling current, as shown in Eq. 3;

$$I = \frac{2G_0\phi_0}{\alpha(V)^2(\rho\phi_0-2)} \left\{ \left( 1 - \frac{V}{2\phi_0} \right) \times \exp \left[ \rho\phi_0 \left( 1 - \alpha(V) \sqrt{1 - \frac{V}{2\phi_0}} \right) \right] \right\} \left\{ \left( 1 + \frac{V}{2\phi_0} \right) \times \exp \left[ \rho\phi_0 \left( 1 - \alpha(V) \sqrt{1 + \frac{V}{2\phi_0}} \right) \right] \right\}$$  \hspace{1cm} (5.8)

The hypothesis is then that the conformation change in the molecules will lead to perturbation in the barrier shape and hence the tunneling rate. Previous study has shown that the dipoles can align themselves within internal field at low temperature (4k), the molecular dipoles are not static but rather mobile, and at ambient temperature dipoles can rotate upon excitation by an external stimuli such as applied fields. Based on this premise, we can infer that a molecular junctions subject to a sweeping bias is not static but a dynamic system where the overall structure (steric or electronic – herein referred to as stereo-electronics) of the SAMs and hence the tunneling currents across the junctions should be dependent on the applied field. Since this is a secondary effect, i.e. it follows the onset of low-bias tunneling, first and second moment statistics may fail to reveal such effects, hence the need for high moment statistical parameters.

Dipoles in an electric field tends to align to external fields in accordance to their magnitude and directions and hence an applied electric field can induce localized force field within the molecules that can introduce angular-dependent conformational changes. This has been discussed in single molecule junction. These possible conformational change lead to a
change in the number (density) of states along the tunneling pathway, which should be reflected in the distribution of the tunneling rates. A bias dependence on the nature of the current density distributions is, therefore, expected since the strength of the applied voltage influence the torque of the molecular dipoles in the field. Distance dependent responses to such an applied electric field is expected since a highly localized field- as on the tip used in molecular junctions, rapid decays with distance. It is therefore expected that in the molecules used in this study, the dipole moment closest to the electrode will respond faster that one distal to the electrode. To visualize such changes of bias dependent current density distribution, the fitted Gaussian curves at different bias were plotted using LAJA, as shown in Figure 5.11, for MB, 2MP and 4MP.

A bias dependent change of shape of the Gaussian curves is observed, the extent of which depends on the head group. A separated curve plots for MB and 4MP in Figure 5.11 show the different types of bias dependence Gaussian fits with peakedness either increasing or decreasing due to convergence or divergence of tunneling probability along the first moment (Gaussian mean). To fully understand the meaning of curve shape change and to investigate the role of dipoles in these junction, a better statistical analysis rather than Gaussian averaging is needed.
Figure 5.11 The Gaussian curves fitted from measurement results. The shape of the curves are dependent on the voltage and there is observable differences for different molecules, such as MB and 4MP.

5.3.3 Kurtosis and skewness analysis

Kurtosis and skewness are introduced to analyze the obtained data, and quantitatively evaluation the evolution in the Gaussian fit at each voltage. This analysis is critical in deciphering the correlation between bias dependent Gaussian curve shape and molecular dipoles. Kurtosis is an indicator of peakedness of a distribution and can thus quantify convergence or divergence of the number of states in tunneling path along the mean. A larger kurtosis typically refers to a narrower distribution and hence fewer number of states-band narrowing. Skewness of the distribution, on the other hand, captures the tilting of the barrier-
hence the band structure, towards more or less conductive with the changes in symmetry with bias indicating either band narrowing of interface band bending that can be correlated to band structures in ceramic based semi-conductor systems. The larger positive value typically means a larger right tail in the distribution of the population, while a larger negative value indicates a larger left tail. In this case, a larger positive skewness correlates to more “conductive” tunneling pathways while a larger negative suggests more “resistive” tunneling pathways. The skewness and kurtosis analysis was estimated using LAJA and are plotted in Figure 5.12. The absolute value of skewness and kurtosis may be indicative of new phenomena, but they are heavily dependent on precise of the measurements. We chose not to over interpret the results by avoiding discussion of absolute value of skewness and kurtosis, but focus on bias-dependent trends.

It can be noted that both kurtosis and skewness for 3MP show a non-continuous trend with bias. This unexpected trend, we believe, comes from challenges in forming quality junctions, whose origin is unclear to us at this stage. Further studies to delineate the origin of this effect is beyond the scope of this thesis and will be reported elsewhere. As a result, the interpretations of the results from 3MP is not elaborated in this section.

As mentioned above and based on literature, we anticipated that alignment of dipoles would occur when an external electric field was applied, hence decreases the states of conformation as the field increase. For SC_{12}, whose dipole is significantly smaller (0.5 D) compared to the other 4 molecules, no significant change in kurtosis with bias was observed (Figure 5.12). For molecules with significant (>1 D) dipole moments and varying directions, the change of kurtosis with bias was significantly different and varied with the nature of the dipole (Figure 5.12). The kurtosis decreases, as expected, for MB that has 1 dipole moment, in part due to
potential alignment with the applied field. While for 2MP and 3MP with two dipoles that aligned nearly parallel to the dipole of the amide, the decrease in kurtosis from the amide group was compensated by the increase of kurtosis from the terminal group (slight variance in orientation leads to change of number of states, as analogous to two tensor case in materials). While the dipole are aligned almost perpendicular to each other, the number of state was increased drastically to the different orientation of the dipole alignments. And hence, as in Figure 5.11, the change of kurtosis for 4MP was increased with bias.

As has been demonstrated in various work that the direction of the molecular dipole can affect the tunneling rates,\textsuperscript{25-27, 52} The dipoles are aligned to the electric fields, but antiparallel to the electron flow, which leads to lower charge transport.\textsuperscript{25-26, 52} In addition, an enhanced alignment of dipoles lead to more resistive junctions. It has been shown in Figure 5.11 that the skewness for MB, 2MP, 4MP and even SC12 were decreasing with voltage, indicating an increase in the number of resistive tunneling pathways. A decreasing skewness suggests an enlarged left tail in the distribution (lower current density), indicating a larger population of more resistive tunneling paths.

We also observed a variance in decrease rate in skewness with forward bias and reverse bias, which is partially due to different rate of dipole alignment as described before (kurtosis). This field-direction related bias effect can be the explanation for some rectification in molecular junctions, in which the cooperativity is large enough to have variance in statistical mean values rather than just the skewness.\textsuperscript{53}
Figure 5.12 The fitted Gaussian curves of current density across molecular junctions, from which the kurtosis and skewness were derived. a) Gaussian curves of distribution of current density at different bias for junctions made of the three molecules. The calculated c) kurtosis and d) skewness for junctions of different molecules. *Solid symbol: at reverse bias; open symbol: at forward bias.

5.4 Summary

The effect of molecular dipoles on tunneling junction has been a challenge to investigate. To isolate the effect of dipole in tunneling without changing other parameters, such as molecular structure, intermolecular interactions and more. This thesis has demonstrated that using carboranethiolate SAMs, the monolayer of the molecules on Au substrate share similar packing density, orientation, bonding strength and barrier width, but bear different charge transport characteristics which we infer is due to the only difference between these molecules, magnitude and direction of dipole moments. Using carboranethiol as a platform, therefore, we are able to delineate effect dipoles on tunneling rates across molecular junctions.

It has been discovered that the orientation of the dipoles in the molecules affect the tunneling rate in a way that is not similar to single molecule junction. The dipoles in the molecules that are chemisorbed onto the substrate will affect the level alignment between the metal electrode and the molecules. A Fermi level pinning occurs when partial charge transfer happens between
the molecule and the metal substrate, which can be a consequence of metal induced gap states. Molecules with a significant fraction of the dipole normal to the substrate tend to transfer charges to the substrate to form a more stabilized charge state. For this reason, the orientation of the molecules affect the tunneling rates across the junctions.

For a more complex molecules that have two isolated dipoles, changes in tunneling characteristics due to dipoles are not easily decoupled. We used hydrocarbon-based molecules with different terminal moieties to investigate the effect of two uncoupled dipoles. Saturated carbons between the two dipole-bearing moieties enables us to isolate the terminal groups from the substrate and the internal amide so that there will be Fermi level pining between the terminal group and the substrate. As expected, the average tunneling current is not significantly affected by the dipoles of the terminal groups. Using a statistical analysis of the distribution of the measurements, it enables to delineate subtle changes in the tunneling behaviors across the junctions, which as believed, is caused by the variation in the dipoles in the molecules.

References


CHAPTER 6 CONCLUSIONS

Recent developments in molecular electronics are fruitful. Molecular rectifiers have been realized with large rectification ratio in simple hydro-carbon based ferrocene molecules. Both experimental and theoretical work has been done to understand more about the charge transport across molecules or molecular junctions.

For the stability and reproducibility of junction, EGaIn based large area junctions have recently gained attention. This type of junctions, though widely studied, still face challenges such as understanding the role of interfaces. In this thesis, fundamental studies have been conducted to understand the structure of molecular junction (including the interfaces and other associated properties) and the effect of molecular dipoles on charge tunneling across SAMs. From these studies, one can conclude that:

1. The SAMs open interface is affected by SAMs structure, which is heavily dependent on substrate roughness. Increasing substrate roughness induces disorder of molecules in the SAMs and hence produce poorly defined interfaces, which can be captured in wetting, spectroscopies and tunneling properties.

2. Odd-even effect is observed in charge tunneling, wetting and interface-sensitive spectroscopy for n-alkanethiolate SAMs fabricated on flat surfaces. It is, therefore, deduced that the odd-even effect is an inherent property of n-alkanethiolate SAMs and, by extension, of other related SAMs structures.

3. Morphology of the top electrode significantly affects tunneling characteristics of a junction. Reducing the oxide thickness through a wet chemistry etching can achieve higher tunneling sensitivity to reveal subtle junction properties like the odd-even effect, and other interface effects analogous to wetting studies. We can therefore infer that
charge tunneling characteristics closely mirror the properties of the SAM and are representative of the quality of the SAM.

4. Simple statistical analysis and data representation can be used to reveal the quality of the junction, hence, the junction is self-reporting if all collected data are reported in one forum. The use of Gaussian fits to deduce first or second moment statistical variables (mean and variance respectively) is not significantly influenced by the outliers in the measurements. For junctions with noisy measurements (significant amount of outliers), Gaussian mean value is a good choice for analysis. When such junctions bear isolated dipole moments, however, only higher moment statistics can reveal effect of these vector properties.

5. The molecular dipoles affect the tunneling behaviors. For isomorphic substrate-coupled SAMs, like the pseudo-aromatic carboranethiolate monolayers, the molecular dipoles affect the coupling between electrodes and the molecules through a Fermi level pinning (bottom electrode) or strong interfacial coupling (top electrode). These effects significantly perturbed the tunneling rates across the junctions at about \( \log|J(V)| \sim 1.7/\text{debye} \). In a more complex junction structure where the molecules have multiple dipoles, because of Fermi depinning from the backbone, the effect of dipole is subtle. Perturbations in the distribution of measurement, derived from higher moment statistical analysis, such as kurtosis and skewness, help to delineate the effect of dipoles in these complex system.

**Perspectives**

In addition to the fundamental research on understanding and engineering the charge transport behaviors across junction, another major area about molecular electronics is the
integration of molecular junctions into functional devices. The premise of molecular electronics is to use molecules as active and functional electronic parts in complex integrated circuits. There are, however, several factors that need to be considered and addressed before realizing molecular based circuits, viz; the stability of the junctions in integrated circuits and ii) the controllable performance of molecular electronics.

1. The stability of the junction in the circuits: As has been acknowledged, organic molecular layers are less stable than inorganic device due to physical and chemical susceptibility of underlying bonds. Although labile, the transient nature could be used as a programmable variable in design of next generation tunneling-based electronic devices.

2. Controlled/tunable tunneling current. For molecular electronics, wide distribution in average tunneling currents across the junctions is a major hindrance to their utility even as sensors. But with improved molecular design and better quality SAMs, narrowing the distribution of tunneling current across the junction will serve as a significant improvement in the device performance.

Once these are achieve, molecular electronics is close to being adopted for electronics industries.
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APPENDIX PUBLICATION LIST

A. Peer-reviewed journal articles


**B. Book chapters**


**C. Peer-reviewed Conference proceedings**