FABRICATION AND ELECTRICAL CHARACTERIZATION OF CARBON-BASED
MOLECULAR ELECTRONIC JUNCTIONS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy in the
Graduate School of The Ohio State University

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* * * *

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Contact mode atomic force microscopy (AFM) was used to intentionally scratch a monolayer deposited on a pyrolyzed photoresist film (PPF). The force was set to completely remove the monolayer but not to damage the underlying PPF surface. A line profile determined across the scratch with tapping mode AFM permitted determination of the monolayer thickness from the depth of the scratch. A statistical process was devised to avoid user bias in determining the monolayer thickness, and was used to determine the thickness as a function of derivatization parameters. PPF surfaces modified by reduction of diazonium ions of stilbene, biphenyl, nitrobiphenyl, terphenyl, and nitroazobenzene (NAB) were scratched, and their modification layer thicknesses determined. For single scan derivatizations of 1 mM diazonium ions to –0.6 V vs. Ag⁺/Ag, monolayers exhibited thicknesses close to those expected for true monolayers. However, more extensive derivatization resulted in multilayers up to 6.3 nm thick for the case of NAB. Such multilayers imply that electrons are transmitted through the growing film during diazonium reduction, despite the fact that electron tunneling would not be expected to be operative over such long distances. The results are consistent with a conductance increase in the growing film, which yields a partially conductive layer that can support further diazonium ion reduction and additional layer growth.

Carbon/molecule/metal molecular junctions were fabricated by metal deposition of titanium or copper onto monolayers of biphenyl (BP), and nitrobiphenyl (NBP), and multilayers of NBP covalently bonded to sp² carbon substrates. The electronic behavior
of Ti junctions was extremely dependent on residual gas pressure during e-beam deposition, due to the formation of a disordered Ti oxyhydroxide deposit. Junction resistance decreased with decreasing residual gas pressure, and the hysteresis and rectification observed previously for relatively high deposition pressure was absent for pressures below 5 x 10^{-7} torr. Deletion of the molecular layer resulted in low resistance junctions for both high and low deposition pressures. Ti junctions made at low residual gas pressure had resistances and current/voltage characteristics similar to those of junctions with Cu top contacts, with the latter exhibiting high yield and good reproducibility. The current/voltage characteristics of both the Ti and Cu junctions fabricated with low residual gas pressure were nonlinear, and showed a strong dependence on the thickness of the molecular layer. The hysteresis and rectification previously observed for junctions fabricated at relatively high residual gas pressure depend on the combination of the BP layer and the semiconducting TiO\textsubscript{x} film, with the conductivity of the TiO\textsubscript{x} layer depending strongly on formation conditions. Hysteresis in BP/TiO\textsubscript{x} junctions may result from either redox reactions of the BP and TiO\textsubscript{x} layers, or from electron injection into the conduction band of Ti oxide.

Carbon/molecule/Cu molecular electronic junctions were fabricated by metal deposition of copper onto films of various thicknesses of fluorene (FL), biphenyl (BP) and nitrobiphenyl (NBP) covalently bonded to flat, graphitic carbon. A “crossed wire” junction configuration provided high device yield and good junction reproducibility. Current/voltage characteristics were investigated for 72 junctions with various molecular structures and thicknesses, and at several temperatures. The strong effects of molecular structure and thickness on junction conductance and current density indicate molecular
control of electronic properties. The current/voltage curves for all cases studied were nearly symmetric, scan rate independent, repeatable at least thousands of cycles, and exhibited negligible hysteresis. For junctions made with BP, FL, and NBP monolayers, the conductance varied by a factor of 40 at low voltage. Junctions made with NBP showed a decrease in conductivity of a factor of 1300 when the molecular layer thicknesses increased from 1.6 to 4.5 nm. The slope of ln(i) vs layer thickness for both BP and NBP was weakly dependent on applied voltage, and ranged from 0.16 to 0.24 Å⁻¹. These attenuation factors are similar to those observed for similar molecular layers on modified electrodes used to discern electrochemical kinetics. Plots of ln(i) vs V¹/² were linear above ± 0.01V and over 2 to 4 orders of magnitude of the current. All junctions studied showed weak temperature dependence in the range of approximately 325 to 214 K, implying activation barriers in the range of 0.06 to 0.08 eV. The carbon/molecule/copper junction structure provides a robust, reproducible platform for investigations of the dependence of electron transport in molecular junctions on both molecular structure and temperature.
Dedicated to:

Daisy H. Bardales  Mother
Santos G. Anariba  Father
Darwin V. Anariba  Brother
Kenia Y. Anariba   Sister

And to my nieces and nephews

Alejandra, Alberoni, Michelle, Nicole, Samantha and Javier (J.J)
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CHAPTER 1

INTRODUCTION

The term *molecular electronics* refers to the replacement of functions in electronic circuitry currently performed by semiconductor technology by a single molecule or an array of molecules. Electronic devices constructed from molecules and performing molecular functions such as diodes, switches, and memory, could be two orders of magnitude smaller than their silicon counterparts. The field of molecular electronics studies molecular switches, molecular rectifiers, molecular memory and molecular junctions. Sandwiching organic molecules in parallel between two metallic electrodes fabricates a *molecular junction*, and its main purpose is to understand electron transport through molecules.

The purpose of this introductory chapter is to offer the reader sufficient background information pertaining to the subject of molecular electronics and to provide a context for the investigation presented in this dissertation. Chapter 1 commences with a discussion on classical junction platforms, such as self-assembled monolayers and Langmuir-Blodgett films. After that, it presents a brief commentary on the features of carbon-based molecular junctions studied prior to the work described in this dissertation.
It ensues with a brief discussion of past investigations of vapor metal depositions, followed by an outline of some of the physical properties of pyrolyzed photoresist film (PPF). It subsequently addresses the electrochemical characteristics of PPF material with emphasis on current efforts to characterize films formed by diazonium ion reduction, especially the formation of multilayers. Finally, chapter 1 ends with an outline of the research objectives for the current investigation.

1.1 Self-assembled Monolayers and Langmuir-Blodgett Junctions

The promise of incorporating molecules into microelectronic devices has stimulated a variety of approaches to making metal/molecule/metal electronic junctions. To date the vast majority of molecular junctions are based on self-assembled monolayers (SAM) \(^1, 2\) and Langmuir-Blodgett (L-B) \(^3-6\) structures in which the bonding between a metallic contact and a molecular monolayer is either a Au-S or an electrostatic bond. For example, SAM junctions have been investigated by making contact to a monolayer on a metal with mercury drops \(^7-12\), by depositing metals through low temperature evaporation \(^1, 13, 14\), electroless \(^15\) or electrochemical deposition \(^16, 17\), and by employing scanning probe microscopy tips as the metal top contact \(^18-25\). Top metal contacts for L-B junctions include Al or Al oxide \(^26-29\), titanium \(^3, 5, 30-33\), and Au metal \(^27\). Figure 1.1A displays a sketch of a typical metal/SAMs/metal molecular junction. The contacts can be either metals or metal oxides. Figure 1.1B shows metal/SAMs/STM tip junctions; usually employed to probe single molecules. And finally, Figure 1.2 exhibits a schematic of a Langmuir-Blodgett film molecular junction. The strengths of both platforms stems from
the ability to form ordered monolayers with known molecular length and orientation on
the surface of the bottom electrode.

Figure 1.1: Sketch of self-assembled monolayer molecular junctions between (A) two
metal contacts and (B) metal and scanning tunneling microscopy (STM) tip.

Figure 1.1: Sketch of self-assembled monolayer molecular junctions between (A) two
metal contacts and (B) metal and scanning tunneling microscopy (STM) tip.
Results for molecular junctions fabricated by incorporating Langmuir-Blodgett films and self-assembled monolayer between metals can be seen in Figures 1.3 –1.5 below. Figure 1.3 displays current-voltage curves for three molecular switch tunnel junction devices, based on L-B rotaxane structures. The structure of the molecules utilized and a sketch of the proposed graphical representations can be seen in Figure 1.4. The hysteresis observed has been attributed to molecular rearrangement during the voltage excursion. Figure 1.5 portrays i/V and dI/dV–V traces for a biphenyldithiol device sandwiched between two Au metals and modulated by AlOx/Al gate electrode.
Figure 1.3: Current-voltage traces of the three molecular switch tunnel junction devices: (a) the $^{35}$ catenane $1^{4+}$, (b) the $^{35}$ rotaxane $3^{4+}$, and (c) the $^{35}$ pseudorotaxane $2 \cdot$ CBPQT$^{4+}$. Adapted from ref$^3$. 
Figure 1.4: Molecular structures and graphical representations of the $^{35}$ catenane $1^{4+}$, the two station $^{35}$ pseudorotaxane $2\cdot$CBPQT$^{4+}$, and the single-station $^{35}$ rotaxane $3^{4+}$. Adapted from ref$^3$. 
However, a more recent approach to fabricating molecular junctions involves modification of graphitic surfaces by the electroreduction of a variety of diazonium ions. A more complete review on this junction fabrication strategy is provided below.
1.2 Carbon-based Molecular Junctions

The carbon-based approach to making molecular junctions offers several distinct features that permit fabrication of reproducible molecular junctions via vapor deposition of a metal or metal oxide top contact on a molecular layer bonded to a graphitic carbon substrate. First, the C–C bond between the substrate and the organic layer forms irreversibly, and is symmetric and strong (~100 Kcal/mol) compared to Au-S (40 Kcal/mole) and LB films (< 10 Kcal/mole). The pyrolyzed photoresist film (PPF) substrate is structurally and electronically similar to glassy carbon, with a very flat surface (< 0.5 nm rms roughness) and a resistivity of 0.005 Ω-cm\(^{37-40}\). Second, diazonium reduction on carbon surfaces has been shown by X-ray photoelectron spectroscopy, Raman spectroscopy, FT–infrared spectroscopy, atomic force microscopy and scanning tunneling microscopy to result in high coverage of covalently bonded organic molecules, with very low pinhole density\(^{41-60}\). Since possible pinholes are sites for phenyl radical formation, they are actively “patched” by the newly formed radical. Third, carbon based molecular junctions are amenable to in-situ Raman spectroscopy through a partially transparent metal top contact, permitting verification of structure and observation of bias-induced structural changes\(^{61,62}\). Finally, the monolayer is robust enough that metal deposition can be accomplished without apparent monolayer damage or the formation of metal filaments\(^{63,64}\). A comparison of monolayers formed by diazonium reduction on carbon substrates to other monolayer types is shown in Figure 1.6.

Carbon-based molecular electronic junctions have previously been prepared by lowering a Hg drop onto the modified PPF surface\(^{65-67}\), similar to a technique pioneered
by Majda \(^7, 11, 68\) and Whitesides \(^8, 10, 12\). The results indicated a strong correlation between molecular structure, film thickness and conductivity. Junctions fabricated with alkanes molecules, such as methylphenyl, tert-butyl phenyl, and \(n\)-butyl phenyl, showed that as the length of the molecules increases, the conductivity decreases.

Figure 1.6: comparison between several surface modification procedures employed to fabricate molecular junctions.
On the other hand, a conjugated molecule such as stilbene displayed a higher conductivity by a factor of 50 than the aforementioned alkane structures, even though stilbene is a longer molecule. In a follow up investigation of conjugated systems, the dependence of conductivity on molecular length was examined with the phenylene series of phenyl, biphenyl and terphenyl. It was found that conduction is strongly dependent on molecular length, as shown in Figure 1.7 (top). Furthermore, structural, voltage, and temperature studies suggested that the dominant electron transport mechanism in action was tunneling for phenyl and biphenyl junctions, while tunneling was observed at temperatures lower than 10 °C in the case of terphenyl junctions, followed by an activated process at higher temperatures. Similar results were observed for nitroazobenzene junctions, as illustrated in Figure 1.7 (bottom). More recently, carbon-based molecular junctions capped with Ti/Au as the top contact have been reported. Interesting junction behavior has been encountered including rectification and hysteresis with strong dependence on metal identity and deposition conditions. Figure 1.8 displays the behavior of a PPF/NAB/Ti/Au junction, with Ti deposited at 8 x 10⁻⁶ torr. A schematic depicting a carbon-based molecular junction with a biphenyl monolayer can be found in Figure 1.9A and an optical image of 14 fabricated junctions as prepared are shown in Figure 1.9B.
Figure 1.7: (Top) I/V curves for the phenylene series of phenyl, biphenyl and terphenyl in PPF/molecule/Hg junctions. (Bottom) Arrhenius plots for phenylene series and NAB junctions.
In order to make carbon-based junctions, it is necessary to have considerable understanding over the pyrolyzed photoresist film (PPF) properties, both physical characteristics and electrochemical behavior. In addition, substantial control over metal deposition and monolayer formation is required to successfully fabricate carbon-based molecular junction. The abovementioned topics are addressed in more detail in the following sections.
Figure 1.9: (A) Schematic depicting a carbon-based molecular junction using a biphenyl monolayer. (B) Optical photograph of 14 carbon/biphenyl/Ti/Au molecular junctions made by vapor deposition of Ti and Au onto chemically modified PPF on silicon.
1.3 Pyrolyzed Photoresist Film (PPF) Physical Properties

A procedure that is common to all junctions investigated here, and distinct from alternative approaches to junction fabrication, is the bonding of organic molecules to a flat, graphitic carbon substrate. Pyrolyzed photoresist film (PPF) is obtained after pyrolysis at 1100 °C of a positive novolac photoresist (AZ 4330) in a reducing atmosphere of 95% N₂ + 5% H₂. There is an initial 11% weigh loss between 150 and 250 °C, followed by another 49% weigh loss between 250 and 500 °C, and finally a gradual 9% weight loss between 500 and 1100 °C. There is a total weigh loss of 69% after the pyrolysis process, presumably due to loss of H₂O, CO, and CO₂ at low temperatures. It is believe that aromatization is in effect at higher temperatures. After pyrolysis, the carbon film herein called pyrolyzed photoresist film (PPF) shows a sheet resistance of 51.2 Ω/cm², corresponding to a resistivity of 0.0051 Ω-cm. PPF resistivity is comparable to that of glassy carbon of (4.5 –5.0) x 10⁻³ Ω-cm. In order to assess the development of the film structure, the carbon sp² Raman bands at ~1360 (D band) and ~1600 cm⁻¹ (E₂g band) have been studied and their peak ratio have been correlated with disorder in the sp² carbon matrix. The large D/E₂g peak ratio obtained is an indication of smaller crystallite size domain in the carbon matrix, similar in disorder to glassy carbon (GC).

Of critical importance in the fabrication of molecular junctions are the surface characteristics of the substrate. X-ray photoelectron spectroscopy of PPF films shows an O/C atomic ratio of 1.2% even after exposure to air for 4 days. On another XPS study it was found that the O/C ratio can be as high as 2.3%. The low O/C ratio implies that the majority of the PPF surface is homogeneous and hydrogen terminated. Another important characteristic of PPF films cured at 1100 °C is the resulting surface
smoothness. AFM line profiles along a 10 µm line display a root-mean-square (rms) roughness in the Z (height) direction on the line of < 0.5 nm $^{39}$.

1.4 Pyrolyzed Photoresist Film (PPF) Electrochemical Characteristics

Given the novelty of PPF, a comparison to other graphitic electrode surfaces is appropriate. The capacitance of PPF was obtained from background voltammograms in 1M KCl (20 V/s) at 0.3 V. On average, the capacitance values was 9.2 µF/cm², a factor of two less than the capacitance of heat-treated GC, and less than 4 times the capacitance of polished GC sonicated in activated carbon/isopropyl alcohol (AC/IPA). The apparent low capacitance of a PPF surface can be partially attributed to its flatness. Surface adsorption to PPF has been examined in a 10-µM solution of methylene blue (MB) with the adsorption coverage monitored by cyclic voltammetry. It was found that adsorption of MB followed the same trend of capacitance, with high-temperature glassy carbon (HT-GC) showing the highest adsorption and PPF the lowest, presumably due to its hydrogen-terminated surface.

Electron transfer kinetics of various redox systems were studied on PPF surfaces and compared to HT-GC. The results indicate that for outer-sphere systems, where electron transfer is insensitive to surface chemistry or adsorbed monolayers, such as Ru(NH$_3$)$_6^{3+/2+}$ and Fe(CN)$_6^{3-/4-}$ and Chlorpromazine$^{73}$, the difference in rate constant between PPF and HT-GC is less than a factor of 2. On the other hand, for systems whose electron transfer is catalyzed by surface carbonyl groups, such as Fe$^{3+/2+}$ $^{73}$, electron transfer on PPF is much slower than on HT-GC, by as much as a factor of 32. The disparity in electrochemical response can be ascribed to differences in the surface oxygen...
functionalities. Dopamine is a redox system known to involve reactant adsorption to the surface and the kinetics are significantly decreased if such adsorption is restricted. Dopamine kinetics on PPF are consistent with a weaker adsorption ability as exemplified by MB adsorption.

PPF is similar in several ways to heat-treated glassy carbon (HT-GC), especially in its bulk properties. PPF has a resistivity comparable to that of glassy carbon and is mostly comprised of a sp\(^2\) hybridized disordered carbon structure. However, there are significant differences that have substantial electroanalytical consequences. First, PPF has much less oxygen-containing functionalities than GC, with an XPS O/C ratio of 2% even after exposure to ambient conditions. Second, PPF has a smooth surface with an rms roughness of < 0.5 nm, about 3 to 10 times lower roughness than polished glassy carbon. Third, since PPF is made from commercial photoresist, it is amenable to photolithography on the scale of 10 to 20 \(\mu\)m. Fourth, capacitance and background currents are lower for PPF than glassy carbon, mainly due to a low roughness factor. Fifth, physisorption is much weaker on PPF than on glassy carbon. Sixth, electron transfer (ET) is slower by a factor of < 2 for outer-sphere redox systems on PPF, but much slower for systems catalyzed by surface oxides or adsorption. Finally, PPF has a significant internal resistance as a thin film.

1.5 Characterization of Diazonium Multilayer Formation

Monolayer formation of diazonium ions is extensively addressed in the following chapter, where it is shown that by carefully choosing the proper modification parameters, diazonium film formation at monolayer thickness is possible. Diazonium
reduction has been extensively studied for monolayer formation, but in some cases multilayers have been reported. Since this is an important issue to making junctions, a review of past film formation findings is appropriate. The first report of multilayer formation by diazonium reduction was put forth by McDermott et al. The authors probed the effect of diethylaniline (DEA) film growth on the blocking of Fe(CN)$_6^{3/-4-}$ voltammetry as a function of deposition cycle. In addition, they monitored DEA film growth by scanning force microscopy (SFM). Surface modification by DEA diazonium ion in a high concentration (~ 5 mM) on a HOPG (Highly Ordered Pyrolytic Graphite) electrode led the investigators to conclude that aryl radicals initially attached at defect sites on the HOPG surface. Scanning force microscopy provided strong evidence of multilayer formation during diazonium reduction. First, topographical information displayed heights ranging from 0.7 to 2.5 nm for DEA films made by electroreduction of DEA diazonium ion. Since a single DEA molecule has a length of ~ 0.8 nm, the observed heights imply that the films are likely comprised of more than one DEA molecule. Second, multilayer formation is localized at nucleation sites. The gradual increase in the height of these structures as a function of deposition time suggests continued deposition of DEA. Subsequent infrared reflectance absorption spectroscopy (IRRAS) studies on glassy carbon electrodes modified by DEA diazonium ion also provided support for the formation of multilayers. First, a band at ~2300 cm$^{-1}$ due to the N≡N stretch of the diazonium salt is absent in all spectra, suggesting multilayer formation by a radical attachment mechanism. Second, the absorbance of each band increases with deposition time, an observation consistent with gradual multilayer formation. Third, a band due to aromatic C–H stretching is observed at 3016 cm$^{-1}$ for
films formed for short periods of time, presumably due to monolayer formation only. However, films formed for extensive periods of time (e.g., 30 min) lost the peak at 3016 cm\(^{-1}\). The disappearance of this peak is consistent with the replacement of these C–H bonds by phenyl–phenyl bonds during multilayer formation. Finally, for films formed for longer periods of time (20 or 30 min), the spectra contain several weak bands (1890, 1800, and 1730 cm\(^{-1}\)), which are consistent with combination and the overtone bands expected for multisubstituted aromatic rings\(^{79}\). A question arises regarding the electron transport mechanism capable of transport through a film several molecules thick.

McDermott et al. proposed an alternative electron transport pathway through substrate defects\(^{79}\). Prolonged film growth is indicative of continuous aryl radical generation. If the radical were generated at defect sites, it would be surprising that the defects continue to provide radicals over a period of 30 min. Therefore, the authors speculate that the defect sites may be efficient ET locations for radical production but may not be sites favorable for binding and that more favorable attachment sites can be found at the film terminus. Figure 1.10 illustrates a multilayer structure proposed by McDermott and coworkers.

Belanger and coworker studied the grafting and stability of 4-carboxyphenyl, 4-nitrophenyl, 4-diethylaniline (DEA) and 4-bromophenyl via diazonium reduction onto glassy carbon electrode surfaces by cyclic voltammetry, electrochemical impedance spectroscopy, and X-ray photoelectron spectroscopy\(^{80}\). Thick films of the aforementioned diazonium ions were generated and then subjected to electrode polarization. The authors found that a significant portion of the thick diazonium film is removed upon polarization. Their results seem to suggest that the polymerization type
reaction between a tethered monolayer and the electrognerated free radicals, to yield a relatively thick layer of substituted phenyl species, appears unlikely unless cleavage of the C–C bond between two phenyl rings can occur during polarization of the modified electrode after the grafting process. According to Belanger, this mechanism is operative for a few molecular layers. The authors contends that the remainder of the film could be the result of adsorption of reaction products emanating from the electrognerated aryl radical and these species could be a mixture of dimers and oligomers.

Figure 1.10: Schematic illustration of the predicted mode of multilayer formation of nitrophenyl diazonium ion proposed by McDermott et al. Adopted from ref 79.
In a recent study, Cu surfaces and polished aluminum alloy 2024 T3 substrates were modified at open-circuit potential (OCP) with aryl diazonium salts in both aprotic and aqueous media and studied by X-ray photoelectron spectroscopy. The study revealed evidence of Cu–O–C and Cu–C bonding between the diazonium ion and the substrate. In addition, the XPS results suggest the formation of multilayers as shown by the gradual loss of signal from Cu 2p electrons from samples modified with increasing dipping times. The reduction of the diazonium ions is apparently driven by electrons provided by the metallic substrate, which are conducted through the conjugated π system. Furthermore, derivatized bare Cu and native oxide Cu surfaces contain azo groups present as indicated by the XPS – 400 eV N 1s peak. Based on XPS data it was calculated that the modified film on bare Cu contains 1 azo group for every 5.9 phenyl rings, while the modified film on native oxide Cu contains 1 azo group in 17.4 phenyl rings. It is apparent that the nature of the initial monolayer–substrate bond could account for the difference, by affecting electron transfer through the initial monolayer. Figure 1.11 shows a schematic of the final structure proposed by Hurley, et al. The azo group is present inside the polymeric chain, resulting from a *para* attack on the tethered phenyl chain.

Downard and coworkers have investigated the formation of thick diazonium films on PPF by electrochemistry and atomic force microscopy (AFM). The authors found a linear relationship between surface coverage of nitrophenyl as estimated by electrochemical methods and the AFM “scratching” technique, suggesting that on average the films are uniformly structure. While patterning PPF surfaces in a nanoscale level by AFM and electrochemistry, Downard et al. discovered that film
passivation is more prominent after the films reach > 2 nm thick. However, provided
enough derivatization time, the films can grow as much as ~7 nm thick. As a result, the
authors contend that the surface–phenyl ring and phenyl–phenyl ring reaction pathways
are competitive when modifying graphitic surfaces.\textsuperscript{82}

Figure 1.11: Multilayer formation of phenyl diazonium salt on a copper substrate as
proposed by Hurley, et al. Adopted from ref\textsuperscript{81}. 

Copper
In contrast, Vautrin-Ul et al. found a discrepancy between electrochemical surface coverage of nitrophenyl and atomic force microscopy (AFM) measured film thickness. Although both techniques support the formation of multilayers on various metallic surfaces, the thickness calculated from voltammetry were equivalent to 2–6 monolayers, whereas AFM measurements indicated coverage in the order of 8–15 monolayers. The authors proposed several theories to explain the difference. First, the loss of the nitro group due to aryl substitution during film growth and therefore a smaller number of nitro group remain in the layer, providing an underestimation of surface coverage by electrochemistry. Second, crowding in the layer could push most of the nitro group out of planarity and would render them most difficult to reduce and hence render them electroinactive. Finally, growth of further layers by physisorption of nitrophenyl groups on the initial layer could impede electrochemical reduction.

Combellas et al recently examined diazonium film formation on glassy carbon by time-of-flight secondary ion mass spectroscopy (TOF SIMS). Their findings provide direct evidence for the formation of covalent C–C bonds responsible for the strong attachment of these layers onto the carbon substrate. In addition, they found inconclusive but recurrent evidence for the presence of azo groups in the layers as demonstrated by peaks of m/z ~ 14 and 28 associated with N and N2, and m/z ~ 409 and 423 associated with \{N–C6H4C6F13\}+ and \{N=N–C6H4C6F14\}+. In an effort to account for the electrochemical and AFM film layer thickness discrepancy, a mechanism for multilayer formation is proposed by the authors. Although grafting occurs spontaneously without electrochemical induction, it is more efficient when the substrate is biased at the reduction potential of the diazonium reagent. Furthermore, cyclohexadienyl radicals
are attacked by oxygen or metal ions\textsuperscript{85-87} and the layer growth is impeded by molecular oxygen\textsuperscript{30}. In the authors’ scheme, biasing the electrode forms an initial covalent monolayer. Subsequent layer growth occurs via an electrochemically catalyzed hemolytic aromatic substitution. It is argued that the chain terminating reaction is likely to be a hydrogen atom transfer from the solvent to a phenyl radical or a cyclohexadienyl radical. Moreover, a disproportionation between two cyclohexadienyl radicals would also terminate the radical chain reaction, imbedding a cyclohexadiene in the polymeric chain. The presence of cyclohexadienyl groups in the layer can account for the low surface coverage estimation on nitrophenyl layers studied by cyclic voltammetry, mainly because such nitro groups in cyclohexadienyl rings have lost their aromaticity and are not reduced at the potential of the nitrophenyl groups. The final product of the diazonium structure is displayed in Figure 1.12. It is worth mentioning that in all of the aforementioned proposed diazonium film formation mechanisms, an initial monolayer step is needed. The experimental conditions allowing film formation at monolayer thickness is described in chapter 2. Control over the thickness of the electroreduced film is accomplished by manipulating the modification deposition time and voltage applied.
A pivotal aspect in fabricating molecular junctions is the manner in which metals are deposited onto thin films. Chemical interactions play an essential role in the formation of metal/SAM/metal junctions. Evaporation of metal atoms on thin films is believed to proceed by four main reactivity paths: (1) metal/organic functional group (OFG) reactions at the interface; (2) formation of non-bonded metal clusters when the metal/OFG reactivity is weaker; (3) penetration through the organic layer followed by a reaction with the underlying substrate, and (4) destruction of the organic thin film. Of
particular interest in this dissertation is the interaction of Ti and Cu metals with the organic monolayer. Reed and coworkers deposited Ti by low temperature evaporation on Au/4-thiobiphenyl layers, and the junction showed a rectifying behavior with maximum currents observed when electrons were injected from the Ti to the monolayer \(^1\).

Furthermore, the fabrication and electrical properties of a successful Ni/SAM/Ni junction has been recently reported \(^88\). It has been shown by X-ray photoelectron (XPS) analysis that vapor deposited Ti reacts with alkanethiols to form Ti carbide compounds \(^89\). During the early stages of growth (<10 Å) Ti tends to form clusters around the functional groups, which serve as nucleation sites. As a result, the stronger the functional group-Ti reactivity, the smaller the clusters. From a SIMS study of the alkenethiols/Ti interface, it was concluded that Ti contacts are highly problematic for the formation of reproducible devices because Ti aggressively reacts with the film to form progressively thicker carbide layers, eventually degrading the molecules \(^89\). Infrared spectroscopy has been used to probe Ti reactivity toward a self-assembled monolayer comprised of backbone naphthalene and an alkane tail. The investigators concluded that Ti degrades the alkane chain, but had a small effect on the naphthalene back bone \(^90\).

Undesired features such as the strong reactivity of Ti toward molecular layers and oxide formation has led some researchers to replace Ti with Cu as the top electrode in junctions. The percolation of Cu atoms onto self-assembled monolayers ranges from low to moderate depending on the deposition conditions and functional group on the monolayer. Metal adhesion to polymers with oxygen functionalities can be more effective due to the oxygen–metal reactivity than on films lacking oxygen groups \(^91\). Suppressed Cu penetration into self-assembled monolayers has been achieved by
evaporating at low temperatures (< 220 K) \(^{92}\), and in contrast to Ti, Cu oxidizes slowly in conditions where moisture is present \(^{93}\).

### 1.7 Research Objectives

The first important reason for assembling molecular junctions is for investigating how molecular structure affects electron flow, and the possibility of affecting current/voltage behavior by controlling structural changes in the molecule. Molecules possess a wide range of molecular orbital arrangements, much greater than the number of different band gaps of silicon-based materials. Consequently, molecules can potentially exhibit a significantly greater number of current/voltage properties. A second reason for studying molecular junctions is elucidation of electron transport mechanisms driving electron flow in molecular junctions.

To date, a wide range of molecular electronic junctions have been reported in the literature. Currently, the state of molecular electronics is unclear due to (1) poor junction yield, (2) lack of junction reproducibility and (3) a variety of electronic effects observed for junctions of identical design. As a result, the main research objective is to establish a junction platform possessing the following attributes: (1) high junction yield, (2) good junction reproducibility, and (3) robust junctions that (4) allow for the investigation of the effects of molecular structure on electronic behavior.

The diazonium salts studied include nitroazobenzene (NAB) and stilbene (SB) in the AFM studies only, nitrobiphenyl (NBP), biphenyl (BP) and fluorene (FL) in the junctions. Figure 1.13 illustrates the structures of the aforementioned diazonium ions.
Chapter 2 provides a detail analysis on the development of the AFM “scratching”
technique that permits direct determination of the film thickness without knowledge
about the dielectric constant of the film. Moreover, a correlation between various
thicknesses (monolayer vs. multilayer) with derivatization conditions is clearly
established, and an explanation describing multilayer formation is put forth. Chapter 3
addresses the difficulties associated with fabricating and characterizing
carbon/molecule/metal junctions; especially vapor deposition of Ti and Cu metals as
differences in top metal contacts provide different junction properties. Finally, chapter 4
describes how conductivity is affected by both molecular structure and film thickness on
carbon/molecule/copper molecular electronic junctions.

Figure 1.13: Sketch of the molecular structure of the diazonium reagents studied, all of
which have a fluoroborate anion, BF$_4^-$.
CHAPTER 2

CHARACTERIZATION BY ATOMIC FORCE MICROSCOPY OF MONOLAYER AND MULTILAYER FORMATION BY DIAZONIUM ELECTROREDUCTION ON GRAPHITIC SURFACES

Chapter 2 provides brief background information on atomic force microscopy as a technique for the structural analysis of the films. It also discusses in a brief manner previous characterization efforts on diazonium chemistry. In summary, chapter 2 addresses in detail the surface modification procedure by diazonium ions and the efforts to characterize the ensuing films, and lays out the foundation for the fabrication of molecular electronic junctions.

Atomic Force Microscopy

Atomic force microscopy (AFM) was first introduced in 1986\textsuperscript{94}, soon after its predecessor, scanning tunneling microscopy. The technique is capable of individual atom resolution on both conducting and insulating surfaces. The AFM procedure employs a force-sensitive cantilever stylus that is scanned in a raster pattern over the sample surface. The force interacting between the sample surface and the cantilever
causes minute deflection of the cantilever, which can be detected by an optical detection system, as shown in Figure 2.1. In the most common configuration, a laser beam is reflected off a spot on the back of the cantilever to a partitioned photodiode that detects the probe motion. Figure 2.2 below displays a common AFM instrumental arrangement whereby the x, y, z tip motion is achieved by the tip holder fabricated out of a piezoelectric material. The signal from the laser beam detector is fed back into the holder piezoelectric transducer, which causes the cantilever/tip assembly to move up and down to maintain a constant force between the tip and the sample surface.  

![Figure 2.1: Lateral view of an AFM optical detection system. Adapted from ref 95](image-url)
The performance of an atomic force microscopy instrument is critically dependent on the physical features of the cantilever and tip. Both are remarkably small and delicate and are mass-produced by etching entire cantilever/tip assemblies out of silicon, silicon oxide or silicon nitride. Typically, cantilevers vary in dimensions depending on the mode of operation. For instance, contact mode cantilever/tip assemblies vary in length from 85-350 µm, with a frequency range of 7–120 kHz, and force constant \( k \) of 0.01 –1.0 N/m. On the other hand, tapping mode probes can be longer, with a range of 85 –450 µm, with a higher frequency in the order of 200–400 kHz, but most importantly its force constant usually varies from 20 to 80 N/m.

Figure 2.2: Current atomic force microscope design. Adapted from ref\(^ {95} \).
While in *contact* mode, the tip is in contact with the sample material at a constant force, providing topographical information while the tip is being scanned in a raster pattern. During such a process, several forces can be present: (1) attractive Van der Waals forces originating from fluctuating dipole moments, (2) coulomb repulsion of the electron clouds of the sample and the tip, (3) electrostatic forces between tip and sample interface, and finally (4) magnetic interaction if both tip and sample have magnetic moments. A disadvantage of the *contact* mode scanning is that it is possible for the downward force to be strong enough to drag along the sample, causing sample damage, especially when working with soft materials, such as polymers and biological substrates.

During *tapping* mode, the cantilever is oscillated at its natural frequency and is positioned so that the tip touches the substrate surface only at the bottom of each cycle. When the tip is far away from the sample surface, in such a way as to avoid any interaction between tip and sample, the spring constant of the cantilever is designated as $K_0$. As the cantilever approaches the surface, the spring constant changes due to the tip/sample interaction and becomes:

$$ K = K_0 + \frac{dF}{dz} $$ \hspace{1cm} \text{Equation 2.1}

Where $K_0$ is the original cantilever spring constant and $dF/dz$ is the instantaneous variation of the force with tip–sample distance. The interaction results in a change of the natural resonant frequency of the cantilever, which alters the amplitude and phase of the oscillation. A feedback loop mechanism is in place to stabilize both the amplitude and oscillation phase. 

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**Diazonium Surface Modification**

Covalent bonding of a variety of molecules to carbon electrode surfaces via phenyl diazonium ion reduction is a relatively recent addition to the arsenal of methods for modifying electrode surfaces. Electrochemical reduction of diazonium ion reagents in water or acetonitrile produces free N₂, and a reactive phenyl radical, which irreversibly binds to carbon surfaces, particularly glassy carbon and carbon fibers. The high reactivity of phenyl radicals produces densely packed monolayers on carbon, which often exhibit negligible observable pinholes. The strong, covalent C–C bond is stable, and a wide variety of diazonium reagents are either available commercially or via a one-step synthesis from an aromatic amine. Applications of carbon electrodes modified via diazonium reduction include electrode kinetic investigations, adhesion promotion in carbon fiber composites, and improvements in electroanalytical selectivity and electrocatalysis. Examples of the electrochemical effects of diazonium modification include enhanced activity for dopamine oxidation with an anthraquinone monolayer, minor inhibition of electron transfer to methyl viologen, and complete inhibition of dopamine oxidation. The structure of the diazonium reagent is easily varied by substitution of the phenyl ring, permitting a wide range of modified electrode surface structure and behavior.

Although the strong bonding and dense packing of monolayers produced by diazonium reduction are well established, there is uncertainty about the modification layer thickness. Kariuki and McDermott used scanning probe microscopy to demonstrate that reduction of diethylamino phenyl diazonium ion can produce multilayers with thicknesses of ~ 20 nm under certain conditions, particularly high diazonium ion
concentration and long reduction times\textsuperscript{78}. They also provided FTIR evidence for the attack of the initial monolayer by a second layer of electrogenerated radical. A related paper demonstrated that diazonium reduction on highly ordered pyrolytic graphite nucleated at defects, then grew into multilayer “mushrooms” by continued radical generation\textsuperscript{79}. McCreery et al. have reported multilayers produced by nitroazobenzene diazonium ion reduction, with substantial effects on molecular junctions compared to those made from monolayers\textsuperscript{66,67}. Since most applications of surface modification are critically dependent on layer thickness, it is usually essential to be aware of possible multilayer formation. On a more general note, multilayers on modified electrodes have been studied by a variety of techniques, including profilometry\textsuperscript{101,102}, FTIR\textsuperscript{103}, ellipsometry\textsuperscript{102}, and AFM\textsuperscript{104,105}. In some cases, an intentional “scratch” was made in the modification layer with an AFM tip in order to assess the layer thickness\textsuperscript{104-108}.

The current experiments were directed toward three objectives bearing on the issue of multilayer formation from diazonium ion reduction. First, an atomic force microscopy (AFM) method was sought which yielded a direct measure of layer thickness. Second, the conditions that result in monolayer and multilayer formation were determined for several diazonium reagents. Third, the perplexing question of how thick (> 40 Å) multilayers can form by electrochemical reduction was addressed. Since electron tunneling should be very slow over such distances, it is not obvious how diazonium ion reduction can occur once a ~ 40 Å layer is present. An AFM approach based on intentional “scratching” of the surface followed by non-contact AFM similar to that of Frankel, et al.\textsuperscript{106-108}, and Bradley, et al.\textsuperscript{104}, was exploited to address these questions about diazonium ion modification of carbon surfaces.
2.1 Experimental

The procedure for preparing pyrolyzed photoresist films (PPF) has been described previously \(^{39,71}\). Briefly, positive photoresist AZ P4330-RS (AZ Electronic Materials (formerly Clariant Corp), Somerville, NJ) was spin-coated onto clean silicon at 6000 rpm on a spin coater (PWM101, Headway Research Inc., Garland, TX) for 30 seconds. Three coatings were applied, with a final film thickness of 5–6 µm. The spin-coated samples were then soft baked at 90 ºC for 20 minutes, and pyrolysis took place in a tube furnace (Lindberg Blue M) fitted with a 1-inch diameter quartz tube. The tube was flushed by a continuous flow of forming gas (95% N\(_2\) + 5% H\(_2\)) at approximately 100 sccm during pyrolysis and cooling; samples were heated at 20 ºC/min to 1100 ºC, held at 1100 ºC for 60 minutes, then allowed to cool to room temperature while gas remained flowing.

Electrochemical experiments were performed with a BAS 100W potentiostat (Bioanalytical Systems, West Lafayette, IN). An Ag\(^+\)/Ag (0.01 M) (Bioanalytical Systems) reference electrode calibrated to the \(E_{1/2}\) of ferrocene was used for derivatization. An observed \(E_{1/2}\) for Ferrocene of 89 mV vs. Ag\(^+\)/Ag established the Ag\(^+\)/Ag potential to be +0.22 V vs. aqueous SCE, based on a Ferrocene \(E^0\) of +0.31 V vs. aqueous SCE \(^{109}\). Contact to the PPF substrate was made with an alligator clip to one end of the PPF sample, which had dimension of 3.0 cm by 1.5 cm.

Derivatization of PPF surfaces was performed by the reduction of the corresponding diazonium salt in acetonitrile (Aldrich) with n-tetrabutylammonium tetrafluoroborate (TBABF\(_4\), 0.1 M; Aldrich) as the supporting electrolyte. Tetrafluoroborate diazonium salts of 4-nitroazobenzene-4’- (NAB), stilbene (SB), biphenyl (BP), nitrobiphenyl (NBP), and terphenyl (TP) were prepared according to
previously established procedures\textsuperscript{59,110}. It was essential to ensure the diazonium salt solutions were freshly prepared, degassed thoroughly with argon and had low water content before derivatization. The concentration of the diazonium salt solution was 1 mM and derivatization scans were from +0.4 V to -0.6 V and back to +0.4 V vs. Ag\textsuperscript{+}/Ag at 0.2 V/s except where noted. After derivatization, PPF samples were immediately rinsed with 30 mL of acetonitrile, dried with an argon stream, rinsed thoroughly with isopropyl alcohol (IPA, Mallinkrodt, Inc), then argon-dried, and finally rinsed with acetonitrile and dried with argon gas again. The samples were kept in a glass vial containing clean acetonitrile until ready for analysis. The diazonium ion post-modification procedure is addressed in more detail in appendix A.

Atomic force microscopy measurements were carried out in air with a Nanoscope IIIa Multimode instrument (Digital Instruments, Santa Barbara, CA). Rotated tapping mode etched silicon probes (RTESP) with resonant frequencies of ~300 kHz were purchased from Veeco (Sunnyvale, CA). The AFM tip was replaced after several “scratches,” and its resonant frequency was checked frequently to test for tip damage or possible residue adhering to the tip. The z-axis of the AFM was calibrated with a standard grid provided by Digital Instruments. The force used for scratching was determined empirically as described in the Results section, but was approximately 1 µN, corresponding to 0.25 V as the deflection setpoint. Height measurements were made in tapping mode and scratches were made in contact mode. The images were acquired with a scan rate of either 0.5 or 1.0 Hz, and were flattened with a first-order polynomial before analysis. The apparent “ripple” with a period of ~ 0.2 µm is due to electronic or mechanical interference, and its period depends on the scan rate.
Table 2.1: Physical characteristics of a typical rotated tapping mode etched silicon probes (RTESP).

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Force (or Spring) Constant:</td>
<td>20 - 80 N/m</td>
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<tr>
<td>Resonant Frequency:</td>
<td>200 - 400kHz</td>
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<tr>
<td>Nominal Tip Radius of Curvature:</td>
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</tr>
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<td>Tip height:</td>
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<tr>
<td>Cone Half Angle:</td>
<td>17.5 on each side, 15.0 front, 25.0 back</td>
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</tbody>
</table>

The inability to reproduce the position of the “ripples” on repetitive scans indicates they do not represent real variations in sample height. Filtering was adjusted on the AFM to reduce interference as much as possible without seriously degrading resolution.

Theoretical thicknesses for monolayers were calculated using Gaussian 98 \(^{111}\) with density functional theory (B3LYP/6-31G(d)). Thickness was defined as the length of the molecule bonded perpendicularly to the PPF surface, including the Van der Waal radius of the terminal atom and a C–C single bond length between the surface and the phenyl ring carbon atom bonded to the surface.
Table 2.2: Typical AFM parameters used during the film “scratching” procedure.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Tapping</th>
<th>Contact</th>
<th>Tapping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filename</td>
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<td>NBP1_S2_002</td>
<td>NBP1_S2_003</td>
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<tr>
<td>Scan Size</td>
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<td>5 x 5 µm</td>
</tr>
<tr>
<td>Scan Rate</td>
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<td>1.000 Hz</td>
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<td>0.500</td>
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<td>1.444 V</td>
</tr>
<tr>
<td>Deflection Setpoint</td>
<td>-----</td>
<td>0.2500 V</td>
<td>-----</td>
</tr>
<tr>
<td>Driving Frequency</td>
<td>382.668 KHz</td>
<td>-----</td>
<td>382.672 KHz</td>
</tr>
</tbody>
</table>

2.2 Results

The term “AFM scratching” is used here to describe intentional damage to a modification layer on a relatively hard substrate. If the applied force is sufficient to disrupt the monolayer but not to damage the substrate, it is possible to “carve out” a rectangular trench in the monolayer. The pyrolyzed photoresist film (PPF) substrate used here is similar to glassy carbon, and is quite hard. A set-point voltage of 0.05 V in contact mode was initially used to scratch a stilbene monolayer. However, it was found that the depths of the trenches varied with scratch and scan area, an indication that the
force being applied could be easily offset by tip-sample interactions. The set-point voltage was increased until trenches with flat bottoms and consistent depths were observed. The depth of the scratches did not change between set-point voltages of 0.20 and 0.25 V, and minimal variation in trench depth was observed at these voltages. A set-point voltage value of 0.25 V provided even-bottomed scratches with minimal variation in roughness (root-mean-square, rms) inside and outside the scratch region. The independence of observed trench depth on set-point voltage implies that the monolayer was completely removed. However, a set-point voltage of 0.25 V proved weak enough to scratch the unmodified PPF surface (see Figure 2.3 below). As a consequence, a set-point voltage force of 0.25 V was applied to all contact mode “scratching” experiments because it was found suitable for removing covalently bonded mono- or multilayer without affecting bare PPF. Moreover, the applied set-point voltage of 0.25 V was suitable for all silicon probes used (RTESP) without prior force calibration.

Figure 2.3 shows sample AFM images of PPF (right) and PPF modified by reduction of terphenyl (TP) diazonium ion (left). For both the TP/PPF surface and unmodified PPF, a 500 nm x 500 nm scratch was made by rastering the tip in contact mode with a setpoint voltage value of 0.25 V. The images shown were acquired in tapping mode after “scratching”, and line profiles through each scratch are also shown in Figure 2.3. The image and line profile for the unmodified PPF surface show some debris around the scratch, but no discernible damage to the PPF surface. The observed rms roughness for PPF is < 5 Å, as reported previously, and observable defects were quite rare. For instance, the observed rms roughness for an unmodified PPF sample was 0.409 nm, but the observed roughness for a NBP monolayer was 0.597 nm and for a NBP
multilayer it increased to 0.830 nm. The flatness and high quality of the PPF surface is presumably due to high temperature curing in an H₂ containing atmosphere and the lack of any polishing after curing.^{39}

Figure 2.3: Upper left: tapping mode AFM image of a terphenyl monolayer showing a 500 x 500 nm trench in the monolayer formed with contact mode AFM. Lower left: line profile across the trench in upper image. Upper right: tapping mode image of bare PPF, with the white box framing a 500 x 500 nm scratch made in contact mode. Lower right: line profile through the image in the upper right.
Three line profiles drawn at random positions in the TP/PPF scratch are shown in Figure 2.4. Since the height axis is magnified significantly relative to the x and y axes, the ridges of debris around the scratch are not as tall as they appear relative to the scratch width. Although all three profiles show a clear trench indicative of the TP layer thickness, there is variation in the apparent trench depth within a given profile and between different profiles. To avoid possible bias by the observer, a statistical procedure was devised to average the trench depth over a large fraction of the scratch area.

Figure 2.4: Three random single line profiles through a scratch in a terphenyl monolayer, along the lines shown in the images.
As shown in Figure 2.5, a rectangle was defined on the image, which included both scratched and unscratched regions. Lines were defined across this rectangle arbitrarily, one inside the scratch and one outside. The AFM software calculated the average height along each line, and then the trench depth was determined by calculating the difference between the mean heights along the lines inside and outside of the scratch. This difference is designated as “line 1” in Table 2.3, and represents the average layer thickness between the lines shown in Figure 2.5. “Line 2” was determined in the same fashion after incrementing the two lines laterally (to the right in Figure 2.5) by 100 nm. Such increments were repeated through the entire rectangle to generate 5-12 “lines” within each rectangle. The mean and standard deviation of the height difference of these “lines” provide the trench depth, and therefore film thickness, averaged over a large fraction of the rectangle. The “ripple” apparent in the images contributes slightly to the observed rms roughness, but these contributions are largely averaged out by the statistical procedure. Figure 2.5 shows an averaged depth profile obtained from the TP/PPF image obtained from the average height along each line. This averaged profile is less noisy than those in Figure 2.4 because each point is an average across the short axis of the rectangle. In some cases, the increment size was larger than 100 nm in order to cover a larger area. For most scratches, a second rectangle was drawn perpendicular to the first, and the same height analysis was performed.

Table 2.3 compares film thickness variation for three independent samples of PPF derivatized with four voltammetric scans to –0.6 V vs. Ag+/Ag in 1 mM NAB diazonium ion solution (referred to herein as “NAB-4”). Each sample was scratched, and 7-8 “lines”
were analyzed for each scratch as previously described. For a given rectangle, the relative standard deviation of the scratch depth varied from 4 to 8%, while the rsd for all

Figure 2.5: Schematic of statistical method used to determine film thickness. A pair of lines was chosen randomly, one line inside and one outside the scratch. The depth was calculated as the difference in the average height of each line in a pair. Upper right trace shows the profile of the average height through the scratch.
<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Rectangle 1</th>
<th>Rectangle 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line 1</td>
<td>4.114 (^b)</td>
<td>4.225</td>
</tr>
<tr>
<td>Line 2</td>
<td>3.982</td>
<td>4.436</td>
</tr>
<tr>
<td>Line 3</td>
<td>4.136</td>
<td>4.767</td>
</tr>
<tr>
<td>Line 4</td>
<td>4.268</td>
<td>4.667</td>
</tr>
<tr>
<td>Line 5</td>
<td>4.321</td>
<td>4.805</td>
</tr>
<tr>
<td>Line 6</td>
<td>4.619</td>
<td>4.570</td>
</tr>
<tr>
<td>Line 7</td>
<td>4.399</td>
<td>4.370</td>
</tr>
<tr>
<td>Line 8</td>
<td>4.351</td>
<td>4.443</td>
</tr>
</tbody>
</table>

Mean: 4.274 | 4.535
Standard deviation: 0.185 | 0.202

Sample 2

| Line 1   | 4.463       | 3.567       |
| Line 2   | 4.600       | 3.848       |
| Line 3   | 4.305       | 4.036       |
| Line 4   | 4.074       | 3.942       |
| Line 5   | 4.500       | 4.036       |
| Line 6   | 4.093       |             |
| Line 7   | 4.411       |             |
| Line 8   |             | 4.693       |

Mean: 4.388 | 4.078
Standard deviation: 0.205 | 0.343

Sample 3

| Line 1   | 4.465       | 5.724       |
| Line 2   | 5.082       | 5.851       |
| Line 3   | 5.132       | 5.732       |
| Line 4   | 4.565       | 5.579       |
| Line 5   | 4.920       | 5.686       |
| Line 6   | 4.988       | 5.835       |
| Line 7   | 4.880       | 5.621       |

Mean: 4.862 | 5.782
Standard deviation: 0.254 | 0.101

Mean for 43 lines on 3 samples: 4.64
Standard deviation: 0.58

---
a. Four derivatization scans to –0.6 V vs. Ag⁺/Ag
b. Each value is the difference between the average heights of a line pair with each rectangle, one inside and one outside of the trench.

Table 2.3: Observed film thickness (nm) for NAB-4\(^a\) films.
43 lines on three samples was 12%. The average scratch depths for three completely independent samples were 4.40, 4.23, and 5.28 nm, implying some variation in layer thickness for separate NAB derivatizations. Note also that the observed mean scratch depth of 4.28–5.28 nm significantly exceeds that expected for a true monolayer. Based on Gaussian 98 calculations and including the Van der Waal radius of the terminal oxygen atom, a true NAB monolayer should have a thickness of 1.43 nm, relative to the PPF surface.

The results shown in Figures 2.3–2.5 and Table 2.3 indicate that AFM scratching provides a direct and reasonably reproducible measure of modification layer thickness, but they do not provide a calibration of the accuracy of the scratch depth. In fact, the observed layer thickness of ~ 4.5 nm for NAB4 is itself surprising, since it corresponds to a film thickness of three or more NAB molecules attached end to end. In order to verify the accuracy of the scratch depth, a variety of monolayers was examined, some of which have thicknesses predictable from molecular geometry. Figure 2.6 shows mean profiles through scratches made using deposition conditions expected to yield true monolayers for PPF modified with stilbene, biphenyl, nitrobiphenyl, and terphenyl diazonium reagents. In each case, one voltammetric cycle between +0.4 and –0.6 V vs. Ag⁺/Ag and back to +0.4 V in 1 mM diazonium ion solution was used for derivatization.

The mean layer thicknesses determined in the same fashion as that illustrated for NAB-4 are listed in Table 2.4 for all modified PPF surfaces studied. In addition, the rms roughness over relatively large areas was determined, and is listed in Table 2.5. The areas used for determining the rms roughness varied for different modified surfaces, but in all cases were larger than the size of both a single molecule and a typical trench. The
one-scan films such as nitrobiphenyl (NBP-1) and terphenyl (TP-1) have rms roughness values slightly higher than the PPF substrate.

Figure 2.6: Mean line profiles for stilbene (SB-1), biphenyl (BP-1), nitrobiphenyl (NBP-1), and terphenyl (TP-1) monolayers, each obtained with one derivatization scan to -0.6 V vs. Ag⁺/Ag.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Calc nm&lt;sup&gt;a&lt;/sup&gt;</th>
<th>AFM mean nm</th>
<th>AFM Std. dev nm</th>
<th>% Std. dev</th>
<th># Of samples&lt;sup&gt;b&lt;/sup&gt;</th>
<th># Of scratches</th>
<th># Of areas</th>
<th>Total Lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare PPF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.375</td>
<td>0.155</td>
<td>41</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>SB1&lt;sup&gt;d&lt;/sup&gt; (-0.6 V)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1.34</td>
<td>1.336</td>
<td>0.162</td>
<td>12.1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>BP-1 (-0.0 V)</td>
<td>0.738</td>
<td>0.318</td>
<td>43.1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>BP-1 (-0.2 V)</td>
<td>0.932</td>
<td>0.164</td>
<td>17.6</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>BP-1 (-0.4 V)</td>
<td>0.968</td>
<td>0.329</td>
<td>34.0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>BP-1 (-0.6 V)</td>
<td>1.11</td>
<td>1.507</td>
<td>0.236</td>
<td>15.7</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>23</td>
</tr>
<tr>
<td>BP-4 (-0.6 V)</td>
<td>1.712</td>
<td>0.152</td>
<td>8.9</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>BP-10 (-0.6 V)</td>
<td>2.325</td>
<td>0.956</td>
<td>41.1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>TP-1 (-0.6 V)</td>
<td>1.523</td>
<td>1.809</td>
<td>0.154</td>
<td>8.5</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>TP-4 (-0.6 V)</td>
<td>2.123</td>
<td>0.153</td>
<td>7.2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>28</td>
</tr>
<tr>
<td>TP-10 (-0.6 V)</td>
<td>4.416</td>
<td>0.734</td>
<td>16.6</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>27</td>
</tr>
<tr>
<td>NBP-1 (0.0 V)</td>
<td>0.271</td>
<td>0.150</td>
<td>55.3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>NBP-1 (-0.2 V)</td>
<td>0.644</td>
<td>0.333</td>
<td>51.8</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>33</td>
</tr>
<tr>
<td>NBP-1 (-0.4 V)</td>
<td>1.208</td>
<td>1.708</td>
<td>0.210</td>
<td>12.3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>14</td>
</tr>
<tr>
<td>NBP-1 (-0.6 V)</td>
<td>2.118</td>
<td>0.504</td>
<td>23.7</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td>NBP-4 (-0.6 V)</td>
<td>2.526</td>
<td>0.531</td>
<td>21.0</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>31</td>
</tr>
<tr>
<td>NBP-10 (-0.6 V)</td>
<td>4.229</td>
<td>0.219</td>
<td>5.2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>19</td>
</tr>
<tr>
<td>NAB-1 (0.0 V)</td>
<td>0.998</td>
<td>0.227</td>
<td>22.8</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>23</td>
</tr>
<tr>
<td>NAB-1 (-0.2 V)</td>
<td>1.43</td>
<td>1.884</td>
<td>0.143</td>
<td>7.6</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>NAB-1 (-0.3 V)</td>
<td>2.065</td>
<td>0.163</td>
<td>7.9</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>NAB-1 (-0.4 V)</td>
<td>2.334</td>
<td>0.093</td>
<td>4.0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>NAB-1 (-0.6 V)</td>
<td>2.623</td>
<td>0.293</td>
<td>11.2</td>
<td>3</td>
<td>2</td>
<td>6</td>
<td>3</td>
<td>37</td>
</tr>
<tr>
<td>NAB-2 (-0.6 V)</td>
<td>3.245</td>
<td>0.347</td>
<td>10.7</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>26</td>
</tr>
<tr>
<td>NAB-4 (-0.6 V)</td>
<td>4.508</td>
<td>0.682</td>
<td>12.5</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>43</td>
</tr>
<tr>
<td>NAB-10 (-0.6 V)</td>
<td>6.357</td>
<td>0.508</td>
<td>8.0</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>32</td>
</tr>
</tbody>
</table>

a. From Gaussian98, B3LYP/6-31G(d), plus Van der Waals radius of terminal atom.
b. “Samples” refers to independently prepared PPF surfaces and monolayers
c. Control sample, prepared and scratched same as monolayer samples
d. Number indicates number of derivatization scans
e. Negative potential limit for derivatization scan, stated vs. Ag<sup>+</sup> (0.01 M)/Ag

Table 2.4: Observed thickness for films formed by diazonium reduction. PPF average trench depth has not been subtracted.
One would expect the rms roughness of an undisturbed monolayer (Table 2.4) to be comparable to or smaller than the standard deviation of the trench depth (Table 2.5, third data column). Since trench depth is the difference between the substrate and monolayer heights, the standard deviation of the depth should be approximately 1.4 times the rms roughness of substrate or monolayer. The observed standard deviations for trench depth are generally smaller than this estimate (e.g., TP-1 (-0.6 V)), possibly because the procedure used to measure trench depth corrects for long-range variation in PPF flatness, and the areas used for Table 2.5 are larger than those for Table 2.4. It is clear from Table 2.4 that the use of multiple derivatization scans results in greater film thickness, indicating the formation of multilayers. Figure 2.7 shows a plot of the film thickness resulting from multiple modifications scans for biphenyl, terphenyl, nitrobiphenyl, and nitroazobenzene. For biphenyl, the observed thickness increases slowly with additional derivatization scans, while the NAB thickness rapidly exceeds the 1.43 nm calculated for a true monolayer. Biphenyl, nitrobiphenyl and NAB were examined more closely by using less negative derivatization scans to 0.0, -0.2 and –0.4 V vs. Ag⁺/Ag.
<table>
<thead>
<tr>
<th></th>
<th>Area, µm x µm</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPF alone a</td>
<td>3.9 x 2.3</td>
<td>0.643</td>
<td>0.409</td>
<td>0.526</td>
</tr>
<tr>
<td>SB-1</td>
<td>1.4 x 0.8</td>
<td>0.465</td>
<td>0.461</td>
<td>0.463</td>
</tr>
<tr>
<td>BP-1</td>
<td>0.8 x 0.6</td>
<td>0.818</td>
<td></td>
<td>0.818</td>
</tr>
<tr>
<td>BP-4</td>
<td>4.0 x 4.0</td>
<td>0.710</td>
<td>0.907</td>
<td>0.809</td>
</tr>
<tr>
<td>BP-10</td>
<td>3.6 x 4.1</td>
<td>0.732</td>
<td>0.745</td>
<td>0.739</td>
</tr>
<tr>
<td>TP-1</td>
<td>1.2 x 1.0</td>
<td>0.683</td>
<td>0.239</td>
<td>0.461</td>
</tr>
<tr>
<td>TP-10</td>
<td>3.3 x 2.8</td>
<td>1.020</td>
<td>0.668</td>
<td>0.844</td>
</tr>
<tr>
<td>NBP-1</td>
<td>2.8 x 3.5</td>
<td>0.509</td>
<td>0.597</td>
<td>0.553</td>
</tr>
<tr>
<td>NBP-10</td>
<td>2.1 x 1.6</td>
<td>0.810</td>
<td>0.830</td>
<td>0.820</td>
</tr>
<tr>
<td>NAB-1</td>
<td>4.0 x 4.0</td>
<td>1.081</td>
<td>0.443</td>
<td>0.762</td>
</tr>
<tr>
<td>NAB-2</td>
<td>3.2 x 1.4</td>
<td>0.518</td>
<td>0.497</td>
<td>0.508</td>
</tr>
<tr>
<td>NAB-4</td>
<td>0.7 x 0.8</td>
<td>0.365</td>
<td>0.389</td>
<td>0.377</td>
</tr>
<tr>
<td>NAB-10</td>
<td>3.8 x 3.9</td>
<td>0.551</td>
<td></td>
<td>0.551</td>
</tr>
</tbody>
</table>

a. Unmodified PPF carried through all cleaning and processing steps, except for reduction in diazonium ion solution.

Table 2.5: Roughness of bare and modified PPF
Figure 2.7: Plot of AFM film thickness versus number of derivatization scans to -0.6 V vs. Ag+/Ag. Error bars indicate ± one standard deviation unit of the layer thickness.

Figure 2.8 shows AFM images of four biphenyl samples scratched after derivatization with scans to 0.0, -0.2, -0.4 and -0.6V vs. Ag+/Ag. Also shown in Figure 2.8 and Table 2.4 are the means and relative standard deviations (rsd) obtained from the procedure illustrated in Figure 2.5. The -0.6 V image appears smooth and has the lowest relative standard deviation of the four, with a mean thickness a few angstroms larger than
that predicted for a true BP monolayer. The images of samples derivatized with less
negative scans have high relative standard deviations, and apparent “high spots” are
observed. These height irregularities are likely to be due to incomplete coverage of the
PPF until the -0.6 V negative limit is reached. The situation is different for nitrobiphenyl,
as shown in Figure 2.9 and Table 2.4. The -0.6 V film has a mean thickness (2.2 nm)
almost twice that predicted geometrically (1.21 nm), and shows “spots” similar to those
on incompletely derivatized biphenyl. For NBP, the -0.4 V image appears smooth, and
less negative potentials yield apparent submonolayer coverage. An obvious possibility
for nitrobiphenyl is that multilayer formation starts when the derivatization scan
progresses negative of -0.4 V vs. Ag⁺/Ag, and the “spots” in the -0.6 V image are due to a
partial second layer of NBP attached to the initial monolayer.

Table 2.6 shows the AFM thicknesses of modifier molecules obtained when
modification occurs on 0.5 mm thick PPF stripes. Since PPF has a resistivity of ~ 0.005
Ω-cm², the modifier thickness varies along the length of the PPF stripes mainly due to
ohmic losses. Of relevance here is the lengthening of the applied potential in order to
compensate for PPF ohmic losses. More information on the PPF stripes design and
fabrication can be found in chapter 4 where the topic is addressed in full detail.
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and 0.6 V vs. Ag/Ag\(^+\) were used to modify the PPF surface, as indicated. Also shown are the mean thickness and relative standard deviation determined statistically as described in the text.

Figure 2.8: Tapping mode images for a biphenyl-modified PPF surface following a contact mode scratch. Single derivatization scans from +0.4 V to 0 V, -0.2 V, -0.4 V, and -0.6 V vs. Ag/Ag\(^+\) were used to modify the PPF surface, as indicated. Also shown are the mean thickness and relative standard deviation determined statistically as described in the text.
Figure 2.9: Tapping mode images for a nitrobiphenyl modified PPF surface following a contact mode scratch. Single derivatization scans from +0.4 V to 0 V, -0.2 V, -0.4 V, and -0.6 V vs. Ag⁺/Ag were used to modify the PPF surface, as indicated. Also shown are the mean thickness and relative standard deviation determined statistically as described in the text.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sample</th>
<th>Line</th>
<th>AFM, mean thickness, nm</th>
<th>AFM, std dev, nm</th>
<th>% Std dev</th>
<th>Surface roughness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP-2^(-1.0 V)</td>
<td>1</td>
<td>1^d</td>
<td>1.540</td>
<td>0.253</td>
<td>16.5</td>
<td>0.901</td>
</tr>
<tr>
<td>BP-2 (-1.0 V)</td>
<td>1</td>
<td>2</td>
<td>1.856</td>
<td>0.330</td>
<td>17.8</td>
<td>0.426</td>
</tr>
<tr>
<td>BP-2 (-1.0 V)</td>
<td>2</td>
<td>1</td>
<td>1.815</td>
<td>0.320</td>
<td>17.6</td>
<td>0.629</td>
</tr>
<tr>
<td>BP-2 (-1.0 V)</td>
<td>2</td>
<td>2</td>
<td>2.872</td>
<td>0.294</td>
<td>10.2</td>
<td>0.307</td>
</tr>
<tr>
<td>BP-2 (-1.0 V)</td>
<td>3</td>
<td>1</td>
<td>1.603</td>
<td>0.183</td>
<td>11.4</td>
<td>0.365</td>
</tr>
<tr>
<td>BP-2 (-1.0 V)</td>
<td>3</td>
<td>2</td>
<td>1.847</td>
<td>0.167</td>
<td>9.0</td>
<td>0.410</td>
</tr>
<tr>
<td>FL-1 (-0.8 V)</td>
<td>1</td>
<td>1</td>
<td>2.170</td>
<td>0.283</td>
<td>13.0</td>
<td>0.416</td>
</tr>
<tr>
<td>FL-1 (-0.8 V)</td>
<td>1</td>
<td>2</td>
<td>1.713</td>
<td>0.272</td>
<td>15.9</td>
<td>0.436</td>
</tr>
<tr>
<td>FL-1 (-0.8 V)</td>
<td>2</td>
<td>1</td>
<td>1.797</td>
<td>0.215</td>
<td>11.9</td>
<td>0.486</td>
</tr>
<tr>
<td>FL-1 (-0.8 V)</td>
<td>2</td>
<td>2</td>
<td>1.743</td>
<td>0.171</td>
<td>9.8</td>
<td>0.451</td>
</tr>
<tr>
<td>NBP-1 (-0.6 V)</td>
<td>1</td>
<td>1</td>
<td>2.068</td>
<td>0.259</td>
<td>12.5</td>
<td>0.465</td>
</tr>
<tr>
<td>NBP-1 (-0.6 V)</td>
<td>1</td>
<td>2</td>
<td>1.665</td>
<td>0.089</td>
<td>5.3</td>
<td>0.290</td>
</tr>
<tr>
<td>NBP-1 (-0.6 V)</td>
<td>2</td>
<td>1</td>
<td>1.780</td>
<td>0.188</td>
<td>10.6</td>
<td>0.637</td>
</tr>
<tr>
<td>NBP-1 (-0.6 V)</td>
<td>2</td>
<td>2</td>
<td>1.659</td>
<td>0.137</td>
<td>8.3</td>
<td>0.455</td>
</tr>
<tr>
<td>NBP-4 (-0.9 V)</td>
<td>1</td>
<td>1</td>
<td>2.805</td>
<td>0.309</td>
<td>11.0</td>
<td>0.422</td>
</tr>
<tr>
<td>NBP-10 (-0.9 V)</td>
<td>1</td>
<td>1</td>
<td>3.774</td>
<td>0.172</td>
<td>6.3</td>
<td>0.445</td>
</tr>
<tr>
<td>NBP-20 (-0.9 V)</td>
<td>1</td>
<td>1</td>
<td>4.511</td>
<td>0.437</td>
<td>9.7</td>
<td>0.518</td>
</tr>
<tr>
<td>NBP-20 (-0.9 V)</td>
<td>2</td>
<td>1</td>
<td>4.331</td>
<td>0.175</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

a. Number indicates number of derivatization scans.
b. Negative potential limit for derivatization scan, stated vs. Ag^+(0.01M)/Ag.
c. “Sample” refers to independently prepared film surfaces.
d. “Line” refers to an arbitrarily position within the PPF stripe surfaces where junctions were fabricated. Due to PPF non-negligible resistivity, a thickness gradient formed along the length of the PPF stripe surfaces. (Refer to chapter 4). All mean, standard deviation, and % standard deviation measurements based on 1 scratch, 2 rectangles, and 10 total numbers of lines.

Table 2.6: Observed film thicknesses for modified 0.5 mm lithographically prepared PPF stripes. See chapter 4 for more details.
2.3 Discussion

Before considering any quantitative measures of monolayer thickness, it is necessary to consider the most basic issue of whether the model of a “scratched” film as a well-defined rectangular trench is, in fact, accurate. The upper right image of Figure 2.3 shows no visible damage to bare PPF from the same force used to dig a trench in a modified surface, as expected for the hard, glassy structure of PPF. Furthermore, the statistical procedure described in Table 2.3 and Figure 2.5 yielded a “depth” of a scratch in unmodified PPF of 0.37 ± 0.13 nm, much shallower than the scratches in any of the modified surfaces examined. So intentional AFM scratching of unmodified PPF causes little or no observable disruption of the PPF surface, except for the small amount of debris apparent in Figure 2.3. The possibility that a residue of the monolayer remains in the bottom of the trench after scratching is unlikely, given the apparent flatness of the trench bottom. None of the scratches had significant observable deposits of debris inside the scratch, and in all cases, the observed debris at the scratch edges are much thicker than any height variations inside the scratch. In addition, the cantilever forces applied here have been shown to be sufficient to completely remove a 5-nm oxide layer on an aluminum alloy that has been submerged in water 107, 108. Furthermore, Downard and coworkers examined film formation via electrochemical reduction of NP and NAB on PPF by AFM. Utilizing a similar “scratching” technique to the one described in this chapter, but employing two AFM cantilevers with different lengths located on one device, the authors concluded that meaningful film thicknesses can be determined and that there is negligible film degradation during the film analysis 112. In a subsequent investigation, PPF was patterned through the assembly of a continuous surface film, such
as methylpheny (MP), by removal of selected geometric areas of the modified surface using the AFM “scratching” technique, and subsequently filling in of the exposed PPF area with a second modifier (e.g., NAB) \(^ {82}\). It was shown that diazonium ion graphitic modified surfaces could be nanopatterned. As a result, it can be said with certainty that the “scratching” technique described here completely removes the molecular layer in a uniform manner.

The statistical method for determining average scratch depth was devised to objectively average surface roughness and instrumental noise, but also to correct for long-range (>100 nm) variation in PPF flatness or tilt. By averaging the difference between two members of a line pair (as shown in Figure 2.5), a gradual slope of the PPF or monolayer height is ignored. In effect, the approach corrects for sample tilt and height variations over a lateral distance, which is large, compared to the scratch dimensions. In addition, the method prevents biasing the results by user choice of particular spots on the monolayer surface or inside the scratch. Since many points are averaged on each of several pairs of lines, an average that objectively represents the sample depth is obtained.

With the exception of stilbene (SB-1), the observed monolayer thicknesses shown in Figure 2.5 and listed in Tables 2.4 and 2.6 for stilbene, biphenyl, terphenyl, nitroazobenzene, and nitrobiphenyl are slightly higher than the thicknesses calculated from Gaussian 98, assuming the molecules stand perpendicular to the PPF surface. Several factors can account for this discrepancy. First, the single scan cases in Table 2.4 (SB-1, BP-1, NBP-1, NAB-1, and TP-1) and Table 2.6 (BP-2, FL-1, NBP-1) used derivatization conditions normally employed for monolayer formation. The AFM observed values were high and one reason could be the effect of the depth of the trench
made on bare PPF. On Table 2.7 shown below, the AFM thicknesses have been adjusted by subtracting the average depth of the trench on bare PPF, thus bringing the calculated –
to –experimental values more in accordance. Second, the remaining calculated-to-
experimental monolayer deviation may be due to a layer of adsorbed water or hydrocarbon. Third, the remaining discrepancy could also be attributed to sporadic addition of as second derivatization layer, for it has been shown that there is a clear
danger that higher diazonium ion concentrations or more extensive electrolysis during derivatization can lead to unintended multilayers. Fourth, the accuracy of the measurements is limited by the resolution of the AFM instrument. The resolution of the instrument in the x-y plane (defined as the surface plane of the PPF) is limited by the radius of tip curvature, and the mechanical path of the cantilever coupled with vibrational and acoustical contributions. It has been previously calculated that AFM lateral resolution is limited to ~ 10 nm and the height dimension (z-axis) accuracy is in the range of ± 0.2 nm 112. It is not surprising then to find a percent relative standard deviation varying from +20.7% (+0.23 nm) for FL-1 monolayer to −5.3% (-0.08 nm) for a TP-1 monolayer, with SB-1 showing submonolayer coverage in this analysis. Finally, even if this apparent overestimate of thickness were considered a systematic error, the method would still be adequate for detecting widespread multilayer formation 78-84, 112, 113. For example, the continued growth of a nitroazobenzene film with additional derivatization scans (Figure 2.7) clearly demonstrates multilayer formation, since the thickness increases monotonically to 6.3 nm for ten derivatization scans. This result indicates an NAB film, which is about 4.4 times that calculated for a monolayer of NAB molecules.
<table>
<thead>
<tr>
<th>Monolayer</th>
<th>a Calculated thickness, nm</th>
<th>AFM thickness nm</th>
<th>Difference nm</th>
<th>% Error</th>
<th>c after PPF trench subtraction</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB-1</td>
<td>1.34</td>
<td>1.34</td>
<td>0</td>
<td>0</td>
<td>0.97</td>
<td>-27.6</td>
</tr>
<tr>
<td>BP-1</td>
<td>1.11</td>
<td>1.51</td>
<td>0.40</td>
<td>36.0</td>
<td>1.13</td>
<td>+1.8</td>
</tr>
<tr>
<td>BP-2b</td>
<td>1.11</td>
<td>1.54</td>
<td>0.43</td>
<td>38.7</td>
<td>1.17</td>
<td>+5.4</td>
</tr>
<tr>
<td>NBP-1</td>
<td>1.21</td>
<td>1.71</td>
<td>0.50</td>
<td>41.3</td>
<td>1.34</td>
<td>+10.7</td>
</tr>
<tr>
<td>NBP-1b</td>
<td>1.21</td>
<td>1.66</td>
<td>0.45</td>
<td>37.2</td>
<td>1.29</td>
<td>+6.6</td>
</tr>
<tr>
<td>FL-1b</td>
<td>1.11</td>
<td>1.71</td>
<td>0.60</td>
<td>54.1</td>
<td>1.34</td>
<td>+20.7</td>
</tr>
<tr>
<td>TP-1</td>
<td>1.52</td>
<td>1.81</td>
<td>0.29</td>
<td>19.1</td>
<td>1.44</td>
<td>-5.3</td>
</tr>
<tr>
<td>NAB</td>
<td>1.43</td>
<td>1.88</td>
<td>0.45</td>
<td>31.5</td>
<td>1.51</td>
<td>+5.6</td>
</tr>
</tbody>
</table>

a. From Gaussian98, B3LYP/6-31G(d), plus Van der Waals radius of terminal atom.
b. Modified under different conditions as described in text and table 2.6.
c. AFM thickness minus average PPF trench depth of 0.375 nm as listed in table 2.4.

Table 2.7: Observed AFM monolayer thicknesses after PPF scratch adjustment.

Figure 2.7 and Tables 2.4 and 2.6 all show that multilayers are formed for BP, FL, NBP, NAB and TP with certain scan conditions. Since monolayers are often considered “blocking” toward electron transfer, an obvious question arises of how multilayers can form. In order to reduce diazonium ions in solution after the first monolayer is deposited, electrons must be transported from the PPF substrate through the monolayer. Tunneling may be effective over distances of ~ 2.0 nm or less, but tunneling should be very slow over larger distances. How can a diazonium reagent be reduced to its reactive radical form through organic films with > 4.0 nm thickness? A likely explanation is “conductance switching” reported for biphenyl, NBP, and NAB monolayers, in which
electron injection into the monolayer results in a partially conductive film\textsuperscript{19,31}. For the case of NAB, this electron injection was monitored spectroscopically\textsuperscript{8}, and it was proposed that the resulting NAB layer had a significantly lower barrier for electron tunneling\textsuperscript{19,31}. Loosely speaking, the organic layer was switched “ON” electrochemically to a more conductive state, permitting relatively fast electron transfer to species in solution.

If such a switching mechanism were operative during derivatization of the PPF surface, it is possible that an initial monolayer of NAB or BP, for instance, could become sufficiently conductive to reduce further diazonium ions in solution. The resulting radical could then attack the existing monolayer to form a multilayer. Similar monolayers have been shown to support outer sphere electron transfer to solution redox couples following negative potential excursions\textsuperscript{31}, and even a slow electron transfer through a growing film would be sufficient to continue film growth. Since this mechanism should be able to continue beyond a second layer, the NAB film grew to at least 6.3 nm, and NBP to 4.2 nm with repeated derivatization scans. Furthermore, Kariuki and McDermott observed multilayers with > 20 nm thickness during reduction of diethyaminophenyl diazonium ion\textsuperscript{79}, a result which is very difficult to explain by simple tunneling. For the reagents studied here, the order of reduction potential for the parent molecules is NAB > NBP > TP > BP, meaning that free nitroazobenzene reduces at a more positive potential than nitrobiphenyl, etc. The correlation between the ease of reduction and the film thickness listed in Table 2.4 is consistent with a model based on multilayer formation through conductance switching of the initial monolayer.
Figures 2.8 and 2.9 show that deposition potential for even a single derivatization scan affects the resulting layer thickness. A concern arises of whether a true monolayer can form at all, in which coverage is complete, but initiation of a second layer has not occurred. The images of Figures 2.8 and 2.9 indicate that smooth monolayers of biphenyl and nitrobiphenyl are indeed formed for single scans to -0.6 and -0.4 V scans, respectively, for the conditions employed (1 mM diazonium reagent, 0.2 V/s scan rate). In addition, there are mechanistic grounds to expect a true monolayer to form before the initiation of a second layer. The initial reduction of diazonium reagent occurs at a bare PPF surface, and the maximum density of attachment sites is present. For the second modification layer to form, an electron must transfer through 1–1.5 nm of organic monolayer, and an electrogenerated radical must react with a phenyl ring, presumably involving H atom abstraction or attack of an aromatic double bond. We expect electron transfer to be significantly slower through >10 Å of monolayer and the reaction of the radical with a phenyl ring should be no faster than that with the PPF surface. Unless electron transfer through the initial monolayer is unexpectedly fast, or the PPF layer is much less reactive than expected, there should be a window during derivatization in which a low-defect true monolayer is formed.

That said, it is clear that derivatization conditions are critical to producing a monolayer without progressing to multilayer films. The low reagent concentrations (≤ 1 mM) and relatively short electrolysis times used by many investigators are generally suitable for monolayer formation on glassy carbon. However, Kariuki and McDermott noted that high diazonium concentrations or extensive electrolysis can result in thick
multilayers, and the results reported here demonstrate formation of multilayers of NBP, BP, FL, TP and NAB with supposedly gentle conditions.

Finally, the formation of monolayers by diazonium ion reduction can be compared to the widely studied thiol adsorption to metal surfaces to yield self-assembled monolayers (SAMs). Since SAM formation requires a metal-thiol bond, covalent multilayers are not possible unless the thiol reagent is specifically designed to form additional layers. SAM formation is an equilibrium process, with desorption and readsorption resulting in annealing of the SAM to produce an ordered monolayer. The bonding of a radical produced by diazonium reduction is irreversible, and annealing is unlikely. However, pinholes in an incomplete monolayer facilitate electron transfer to diazonium reagent, thus patching the pinhole.

2.4 Conclusion

The AFM scratching experiment described here is an objective measure of layer thickness, which does not require any assumptions about electron transfer through a monolayer. The technique allows for the differentiation of monolayer and multilayer formation of diazonium ions on graphitic PPF. Wherever possible, we strongly recommend verification of monolayer formation when testing new reagents or conditions. We plan to continue to use AFM to evaluate layer thickness for monolayers on PPF, and the activity of a modified surface toward dopamine oxidation as a test for pinholes.

Provided the initial reduction and radical attack to the carbon surface are significantly faster than formation of the second layer, an irreversibly attached, low-pinhole monolayer results. The aggressive, irreversible binding of radicals
electrogenerated from diazonium reagents yields a robust monolayer which is prone to multilayer formation, but monolayer formation is achievable with the aid of a direct measure of layer thickness to define derivatization conditions.
CHAPTER 3

FABRICATION AND CHARACTERIZATION OF
CARBON/MOLECULE/METAL MOLECULAR JUNCTIONS WITH TITANIUM
AND COPPER TOP METALS

A great deal of research has been focused in molecular electronics on the prospects of incorporating molecular properties into microelectronic devices. Of particular interest is a better understanding of electron transport through molecules and how it is affected by molecular structure. For such purposes, several of metal/molecule/metal platforms have been established. Among the most widely studied techniques are self-assembled monolayers (SAMs) and Langmuir-Blodgett films (L-B), and extensive characterization of metal/SAMs/metal \(^8,13,16,116-121\) and metal/L-B/metal structures \(^117,118,3,119\) have been carried out. In addition, metal/polymer/metal junctions \(^120\), carbon nanotube cross-arrays \(^121,122\), metal/carbon nanotubes/metal architecture \(^123\) and carbon/molecule/metal molecular junctions \(^66,65,124,125,126,69\) have recently been reported. See Figures 3.1 and 3.2 below.

Several approaches have been used to deposit metals onto molecules. In the majority of cases, physical vapor deposition has been the technique of choice. Physical
vapor deposition (PVD) is the process by which a condensable vapor is produced by physical means and subsequent deposition of a thin film from this vapor occurs \cite{127,128,129}. Film deposition can be accomplished by evaporative deposition such as e-beam, reactive vapor deposition (PVD) is the process by which a condensable vapor is produced by physical means and subsequent deposition of a thin film from this vapor occurs \cite{127,128,129}. Film deposition can be accomplished by evaporative deposition such as e-beam, reactive

![Diagram of molecular junctions fabricated with Langmuir-Blodgett films (L-B) and Self-assembled monolayers (SAMs).](image)

Figure 3.1: Diagram of molecular junctions fabricated with Langmuir-Blodgett films (L-B) and Self-assembled monolayers (SAMs).
evaporation and ion plating or by sputtering, either by a plasma or by a beam of ions \(^{130}\). In order to successfully deposit a thin metal layer onto a monolayer, metal atoms need to impact the molecules with such low kinetic energy as to avoid penetration into the monolayer. E-beam evaporation is favored because the electron beam (electron gun) is directed to the metal, reducing heating and cross-contamination \(^{131}\) of the sample. Unlike ion-cluster sputtering, e-beam evaporation requires moderate to ultrahigh vacuums (\(10^{-6} – 10^{-9}\) torr), further minimizing contamination from residual gases.

In an effort to better understand metal/molecule interfaces, the interaction of transition and some rare earth metals with polymers and self-assembled monolayers has
been investigated. For example, the dependence of metal-C$_{60}$ bonding was examined by XPS for Ti, Cr, Au, La and In metals. The interaction of metal/SAMs has been critically summarized and recently revisited in a secondary ion mass spectrometry (SIMS) study. Moreover, the importance and reactivity of functionalized monolayers as in the Au-S bond has also been documented.

Chemical interactions play a pivotal role in the formation of meta/SAMs interfaces. Evaporation of metal atoms on thin films is believed to proceed by four main reactivity paths: metal/organic functional group (OFG) reactions at the interface, formation of non-bonded metal clusters when the metal/OFG reactivity is weaker, penetration through the organic layer followed by a reaction with the underlying substrate, and destruction of the organic thin film. Of particular interest in this chapter is the interaction of Ti and the organic monolayer. Reed and coworkers deposited Ti by low temperature evaporation on Au/4-thiobiphenyl layers. The junction showed a rectifying behavior with maximum currents observed when electrons were injected from the Ti to the monolayer. Furthermore, the fabrication and electrical properties of a successful Ni/SAMs/Ni junction has been recently reported. It has been shown by XPS analysis that vapor deposited Ti reacts with alkanethiols to form Ti carbide compounds. During the early stages of growth (<10 Å) Ti tends to form clusters around the functional groups, which serve as nucleation sites. As a result, the stronger the functional group-Ti reactivity, the smaller the clusters. Ti reacts strongly with functional groups in the following order: COOH$_3$ ≈ CN < OH < CH$_3$. From a SIMS study of the Ti/alkenethiol interface, it was concluded that Ti contacts are highly problematic for the formation of reproducible devices because Ti aggressively reacts with the film to form progressively
thicker carbidic layers, eventually degrading the molecules \(^\text{89}\). Infrared spectroscopy has been used to probe Ti reactivity toward a SAM comprised of backbone naphthalene molecule and an alkane tail. The authors conclude that, Ti degrades the alkane chain, but had a small effect on the naphthalene backbone \(^\text{90}\).

Techniques for the deposition of TiO\(_2\) films on SAMs have been previously described \(^\text{72}\). Opila and coworkers investigated Ti deposition on thick polymer films at base pressures ranging from \(5 \times 10^{-8}\) torr to \(3 \times 10^{-9}\) torr. The primary component was found to be TiO\(_2\), and presumably the source of the oxygen was water or/and molecular oxygen dissolved in the polymer film \(^\text{137}\). It has been recently demonstrated that the composition of Ti deposited onto monolayers is strongly dependent on residual gas pressure \(^\text{69}\) and a reduction/oxidation mechanism based on i/V characteristics and Raman observations has been proposed \(^\text{69} \text{138}\).

Undesired features such as the strong reactivity of Ti towards molecular layers and oxide formation has led some researchers to replace Ti with Cu as the top electrode in junctions. The percolation of Cu atoms onto SAMs ranges from low to moderate depending on the paradigm and functional group. Metal adhesion to polymers with oxygen functionalities can be improved by as much as an order of magnitude than on films lacking oxygen groups, as judged by percolation studies \(^\text{91}\). Suppressed Cu penetration into self-assembled monolayers can be achieved by evaporating at low temperatures (< 220 K) \(^\text{92}\), and in contrast to Ti, Cu oxidizes slowly in moist ambient conditions \(^\text{93}\).

An alternative approach to self-assembled monolayers and Langmuir-Blodgett structures is carbon–based molecular junctions. In this novel approach the C–C bond
substitutes for the Au-S bond in SAMs or the electrostatic forces in L-B films. This chapter describes the electrical properties of carbon/molecule/metal molecular junctions using a “spot” configuration, rather than the “crossed” arrangement described in detail in chapter 4. Monolayers and multilayers of biphenyl, fluorene and nitrobiphenyl were attached to a carbon surface, before Ti and Cu were used as the top contacts. Fluorene is similar to biphenyl but lacks ring rotation while nitrobiphenyl contains a nitro head group. Ti was used for its reactivity and very low percolation ability while Cu was employed for its resilience to ambient oxidation and low penetration into monolayers. The two types of metal contacts were compared regarding their suitability for carbon/molecule/metal junctions.

3.1 Experimental

The procedure for preparing pyrolyzed photoresist films (PPF) has been described on previous works 71. Positive photoresist AZ-P4330-RS (AZ Electronic Materials (formerly Clariant Corp), Somerville, NJ) was spin-coated onto clean polished silicon substrates at 6000 rpm on a spin coater for 30 seconds. The silicon substrate was boron doped and showed a resistivity of 1 Ω-cm, but the electronic properties of the silicon did not appear to be significant. Since the resistivity of the PPF is ~ 0.005 Ω-cm, the bulk of the conductivity is carried by the PPF and Si acts merely as a flat, relatively insulating substrate. The silicon pieces (1.5 cm x 3.0 cm x 1mm thick) were cut and then sonicated in nanopure water (18 MΩ) for 5 min and dried with an argon stream. Several (1-3) applications of photoresist film were applied to yield a total thickness of 5-7 µm. Spin-coated samples were soft baked at 90 °C for 20 minutes before pyrolysis took place in a
furnace (Lindberg Blue M) fitted with 1-inch diameter quartz tube. The tube was flushed by a continuous flow of forming gas (95% N$_2$ + 5% H$_2$) at ~100 sccm during pyrolysis and cooling. Samples were heated at 20 °C/min to 1100 °C, held at 1100 °C for 60 minutes, and then allowed to cool to room temperature while the gas remained flowing. The final PPF film thickness after pyrolysis was between 1-2 µm. Prior to surface derivatization, the pyrolyzed samples were rinsed with and immersed in acetonitrile (Sigma-Aldrich, 99.5+ %) for 5 minutes before drying with an Ar gas stream.

Electrochemical derivatization was performed with a BAS 100-W Potentiostat (Bioanalytical Systems, West Lafayette, IN). A Bioanalytical Systems (BAS) Ag/Ag$^+$ (0.01M AgNO$_3$ in 0.1M $n$-tetrabutylammonium tetrafluoroborate) reference electrode calibrated to the $E_{1/2}$ of ferrocene was used for derivatization. An observed ferrocene $E_{1/2}$ of 89 mV versus Ag$^+$/Ag established the Ag$^+$/Ag potential to be +0.22 V versus aqueous SCE, based on a ferrocene $E^\circ$ of +0.31V versus aqueous SCE. 109.

Modification of PPF surfaces was carried out by the reduction of the corresponding diazonium salt in 0.1M $n$-tetrabutylammonium tetrafluoroborate (TBATFB, Sigma-Aldrich) in acetonitrile (Sigma-Aldrich, 99.5+ %) as the supporting electrolyte. Diazonium salt solutions of biphenyl (BP), fluorene (FL), and nitrobiphenyl (NBP) were freshly prepared as previously described elsewhere. 42, 50, 59, 99 It was paramount to ensure the diazonium salt solutions (0.1M) were freshly prepared, degassed thoroughly with Ar gas for 30 minutes, and had low water content before electro-reduction. Monolayers of biphenyl and fluorene were achieved by applying a single cycle scan at 0.2 V/s from +0.4V to –0.8V and back to +0.4V vs Ag$^+$/Ag. Deposition conditions were chosen such that various thicknesses of NBP were prepared. A single potential cycle ($\nu = 0.2$ V/s)
from +0.4V to –0.4V and back to +0.4V vs Ag+/Ag provided monolayer coverage, while 4, 10 and 20 cyclic scans from +0.4V to –0.6V and back to +0.4V vs Ag+/Ag allowed for the preparation of films of various thicknesses. The above-mentioned conditions produced BP, FL and NBP layers covalently bonded to the PPF and confirmed with AFM by measuring the depth in tapping mode of an intentional scratch in the various films in contact mode (with a tapping mode nanoprobe) as described in more detail in chapter 2. The film thicknesses, also listed in Table 1, are as follows: 1.507 ± 0.236 nm for BP; 1.337 ± 0.351 nm for FL; 1.708 ± 0.152 nm for NBP (1 scan); 2.526 ± 0.531 nm for NBP (4 scans); 4.229 ± 0.219 nm for NBP (10 scans); and 4.510 ± 0.239 nm for NBP (20 scans).

Following surface modification all samples were immediately immersed in clean acetonitrile (Sigma-Aldrich, 99.5+ %) for 60 seconds to remove residual diazonium salt physisorbed on the substrate, followed by rinsing in acetonitrile and drying with an Ar stream. Afterwards, samples were rinsed with isopropyl alcohol (Sigma-Aldrich), dried with Ar gas stream, rinsed with acetonitrile and finally Ar-dried. Immediately after rinsing, the modified samples were placed behind a contact mask consisting of ~0.5 mm diameter holes in a 1/32-inch thick transparent polystyrene sheet. The mask and samples were positioned on a rotating holder in the top part of an electron beam vapor deposition chamber. The samples were facing down ~50 cm from the crucible containing metallic Ti, Cu and Au. An automated e-beam instrument (Telemark, Freemont, CA) vaporized Ti, Cu and Au from the crucible with the beam current operating near the threshold for evaporation.
In summary, three different metal deposition programs were used. For the “high pressure” Ti case the current was controlled to yield a Ti deposition rate of 0.03 nm/s to reach a thickness of 3 nm, then the deposition was paused for 5 minutes to reduce local heating. Afterwards, 10 nm of Ti were deposited at a rate of 0.1 nm/s with an additional 40 nm of Ti added at a rate of 1.0 nm/s. Following Ti deposition and without breaking the vacuum, Au was deposited through the same mask at 1.0 nm/s for Au thickness of 100 nm. The gold layer yielded good electrical contact and offer protection to the junction structure. The vacuum was cryopumped to $6 \times 10^{-6}$ torr during deposition, and the chamber temperature gradually increased from 15 to 25 °C due to heating by the e-beam crucible. For the samples designated as “medium pressure,” the e-beam evaporation chamber pressure was decreased to $< 4 \times 10^{-7}$ torr instead of the previous 6 x 10^{-6} torr. Initially 10 nm of Ti were deposited at a rate of 0.1 nm/s followed by 40 nm of Ti at 1 nm/s (note there is no 5 min waiting time). Finally and without breaking the vacuum 100 nm of Au were deposited at a rate of 1 nm/s. For the samples termed “low pressure” Ti and for Cu samples, during the deposition the residual gas pressure was maintained at $< 2.7 \times 10^{-7}$ torr. Initially 10 nm of Ti or Cu were deposited at 0.03–0.07 nm/s (first ~2 nm deposited at 0.03 nm/s), followed by another 20 nm at 0.5–0.7 nm/s, and finally 10 nm of Au were deposited at 1.0 nm/s.

All junctions were 0.5–0.6 mm in diameter ($A = 0.00196$ cm$^2$ to $A = 0.00283$ cm$^2$, corresponding to $\sim 10^{10}$ molecules in parallel for the monolayer case), with 7-14 junctions per sample as displayed in Figure 3.3. Spot junctions were contacted individually using a ~ 120-μm diameter Pt wire positioned with a 3-axis micro positioner and macro camera. Contact with the PPF was achieved by piercing the
various films with a ~ 220-µm diameter metal spike at a position 2-5 mm away from the junction. All voltammetric experiments and reported values for all junctions were carried out at room temperature and within 1 day from fabrication unless otherwise specified.

Initial electronic testing was conducted with a 2-point probe and a Labview-based system using a National Instruments 6120 data acquisition board. As shown in Figure 3.4A, the Au top contact was connected to a current amplifier (Keithley, model 428). $V_{\text{drive}}$ and the current amplifier output were monitored simultaneously by the two channels of the acquisition board controlled by Labview (National Instruments). To partially compensate for ohmic losses to the PPF substrate, a 3-wire configuration was used where indicated. The voltage was applied at $V_{\text{drive}}$ (shown in Figure 3.4B), but the junction voltage was monitored at point $V_{\text{sense}}$. Assuming that Ti/Au lead remained at virtual ground, $V_{\text{sense}}$ represents the iR corrected junction voltage. $V_{\text{drive}}$, $V_{\text{sense}}$ and current amplifier outputs were connected to the National Instruments 6120 data acquisition board controlled by Labview. It is important to mention that the 3-wire configuration does not completely compensate for PPF ohmic loss, as it will be noted in the discussion section. Moreover, the 3-wire arrangement fails to correct for the metal lead contact resistance, but this error is negligible in the order of < 3Ω.
Figure 3.3: Schematic of PPF/molecule/Ti/Au molecular junction sample.
3.2 Results

The effect of residual gas pressure on the current/voltage response of PPF/BP(1.5)/Ti/Au molecular junctions is shown in Figure 3.5, with the ordinate expressed as current density (A/cm²). The curve for the “high pressure” Ti junction (6 x 10⁻⁶ torr, lower right inset) shows hysteresis for both positive and negative voltage and a
large resistance at low voltage (7.7 ± 6.9 MΩ). For lower Ti deposition pressures, the low voltage resistance (LVR) decreases to 3.0 ± 2.6 MΩ for 4 x 10⁻⁷ torr and 6.5 ± 3.2 KΩ for 2.7 x 10⁻⁷ torr. All curves were acquired at room temperature and at a scan rate of 1 V/s. In comparison, the “medium” and “lower pressure” Ti junctions displayed two orders of magnitude higher currents, with little or no observable hysteresis.

Figure 3.5: I/V curves for PPF/BP(1.5 nm)/Ti/Au junctions, with Ti deposited at varying residual gas pressures. Scan rate set at 1 V/s in all cases and the deposition pressure is indicated in torr units for each curve.
Based on the simple formula that the time required (in seconds) for a monolayer of collisions between a trace gas and a surface approximates $2.5 \times 10^{-6} / P \text{ (torr)}$, and that every collision of Ti with H$_2$O or O$_2$ is reactive, a significant fraction of the deposited Ti layer will be oxide or hydroxide. The presence of Ti oxide has been confirmed with XPS depth profiling of a PPF/azobenzene/Ti/Au junction. Metal deposition conditions were identical to those for BP, FL and NBP, although the junction was much larger than 0.5 mm to permit XPS analysis. Upon insertion into the XPS chamber, the metal layers were sputtered with Ar$^+$ ions and XPS spectra were periodically acquired. Figure 3.6 displays high resolution XPS spectra of the Ti (2p) region obtained near the azobenzene layer for pressures of $2.1 \times 10^{-7}$ torr, $8 \times 10^{-6}$ torr and a junction exposed to air for 1 year. Various Ti oxides were observable, including TiO (454.8 eV), Ti$_2$O$_3$ (456.1 eV) and a small amount of TiO$_2$ (458.8 eV). It is evident that the $2.1 \times 10^{-7}$ torr base pressure of the e-beam system was not sufficiently low to yield a Ti metal deposit free of oxides. The small TiO$_2$ peak apparent in the sample deposited at high pressure increased with time after deposition, with TiO$_2$ becoming the dominant species after 1-year exposure to air.

After metal deposition, the molecular junctions were periodically tested for electronic behavior. Figure 3.7 shows low voltage resistance ($\pm 0.2$ V) values for BP normalized to junction area versus time after metal deposition (in days). The largest aging effects in ambient conditions were observed for Ti junctions deposited at the “medium” pressure of $4 \times 10^{-7}$ torr, while Cu junctions exhibited significant aging effects only after 3 months.
Figure 3.6: XPS spectra of PPF/azobenzene/Ti/Au junctions prepared with a deposition pressure (a) $2.1 \times 10^{-7}$ torr, (b) $8 \times 10^{-6}$ torr, following Ar$^+$ sputtering of the junction for 1500 sec. Lower spectrum (c) $P = 8 \times 10^{-6}$ torr is a Ti junction after exposure to lab air for about 1 year. Figure obtained from ref$^{69}$
The low bias resistance of Ti “medium pressure” (4 x 10^{-7} torr) junctions increased by a factor of 15,000 during the 6-day period after metal deposition. The changes in resistance are less evident for lower pressure. As shown in the inset, “low pressure” Ti junction’s resistance increased by only a factor of 31 during the five days after deposition. As noted earlier, the lowest backpressure employed (2.1 x 10^{-7} torr) yielded a Ti deposit containing significant oxides, making it difficult to evaluate junctions containing only metallic Ti. To circumvent this problem, Ti was replaced with Cu to reduce the tendency of the top electrode to oxidize during metal deposition and
subsequent exposure to air. The aging behavior of Cu junctions is described in Figure 3.7, with the low voltage resistance decreasing by only a factor of 3 in a 90-day period.

A complete list of the junction yield and film thickness as determined by AFM is shown in Table 3.1. Junctions were rejected if the low voltage resistance was significantly lower than the average value or if the second current/voltage curve greatly differed from the first. Higher junction yields were obtained with BP and FL (100%), while the lowest yield corresponded to NBP (4.2), at 50%.

<table>
<thead>
<tr>
<th>Junction Type</th>
<th>AFM mean thickness, nm</th>
<th>AFM, std dev, nm</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP-2 (-0.8 V)</td>
<td>1.507</td>
<td>0.236</td>
<td>28/28</td>
</tr>
<tr>
<td>FL-1 (-0.8 V)</td>
<td>1.337</td>
<td>0.351</td>
<td>28/28</td>
</tr>
<tr>
<td>NBP-1 (-0.4 V)</td>
<td>1.708</td>
<td>0.152</td>
<td>25/28</td>
</tr>
<tr>
<td>NBP-4 (-0.6 V)</td>
<td>2.526</td>
<td>0.531</td>
<td>26/28</td>
</tr>
<tr>
<td>NBP-10 (-0.6 V)</td>
<td>4.229</td>
<td>0.219</td>
<td>14/28</td>
</tr>
<tr>
<td>NBP-20 (-0.6 V)</td>
<td>4.510</td>
<td>0.239</td>
<td>25/28</td>
</tr>
</tbody>
</table>

a. Pressure during Ti deposition was 4x10^{-7} torr.
b. More details in chapter 2.
c. Junctions were rejected if low voltage resistance was significantly lower or if second i/V curve greatly differed from first.
d. Number of derivatization scans, starting at +0.4 V vs Ag/Ag+ to the negative potential indicated and back to +0.4 V. v = 0.2 V/s.
e. Negative potential limit for modification scan, stated vs Ag/Ag+ (0.01M).

Table 3.1: Observed film thickness and yield for Ti/Au junctions

Ti deposition backpressure substantially influenced J-V characteristics of Ti molecular junctions. Figure 3.8 exhibits J-V curves for PPF/BP/Ti/Au junctions. For
“medium pressure” Ti junctions, a strong dependence on scan rate accompanied by hysteresis at low scan rates is observed. For instance, at 1000 V/s the J/V trace shows higher currents and displays no hysteresis, as shown in Figure 3.8A. As the scan rate is decreased to 10 V/s, the J/V curve exhibits a pronounced hysteresis at negative voltage. A less visible hysteresis effect is observable at positive bias. When the scan rate is slowed to 1 V/s, the current magnitudes at both positive and negative voltages decreases to the minimum observed. Figure 3.8B shows that “low pressure” (2.7 x 10^{-7} torr) Ti junctions lack both scan rate dependence and hysteresis.

![J-V characteristics of BP junctions for different Ti deposition conditions; (A) 4 x 10^{-7}torr and (B) 2.7 x 10^{-7} torr.](image)

Figure 3.8: J-V characteristics of BP junctions for different Ti deposition conditions; (A) 4 x 10^{-7}torr and (B) 2.7 x 10^{-7} torr.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sample</th>
<th>Yield</th>
<th>Mean Resistance (±0.2V), Ω</th>
<th>Mean J&lt;sup&gt;+&lt;/sup&gt;+2V A/cm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Mean J&lt;sup&gt;-&lt;/sup&gt;-2V A/cm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Mean J&lt;sup&gt;+&lt;/sup&gt;/J&lt;sup&gt;-2&lt;/sup&gt;</th>
<th>RR</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP(1.5)</td>
<td>1</td>
<td>13/14</td>
<td>6.46 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>2.697</td>
<td>2.615</td>
<td>1.034</td>
<td></td>
</tr>
<tr>
<td>FL(1.3)</td>
<td>1</td>
<td>14/14</td>
<td>2.33 x 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>3.899</td>
<td>3.887</td>
<td>1.003</td>
<td></td>
</tr>
<tr>
<td>FL(1.3)</td>
<td>2</td>
<td>14/14</td>
<td>1.58 x 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>4.885</td>
<td>4.864</td>
<td>1.004</td>
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</tr>
<tr>
<td>NBP(1.7)</td>
<td>1</td>
<td>14/14</td>
<td>2.14 x 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>4.506</td>
<td>4.423</td>
<td>1.020</td>
<td></td>
</tr>
<tr>
<td>NBP(1.7)</td>
<td>2</td>
<td>14/14</td>
<td>1.62 x 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>4.997</td>
<td>4.938</td>
<td>1.012</td>
<td></td>
</tr>
<tr>
<td>NBP(4.2)</td>
<td>1</td>
<td>11/14</td>
<td>1.75 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>2.299</td>
<td>1.743</td>
<td>1.294</td>
<td></td>
</tr>
<tr>
<td>NBP(4.2)</td>
<td>2</td>
<td>14/14</td>
<td>1.70 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>2.349</td>
<td>1.750</td>
<td>1.343</td>
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</tr>
<tr>
<td>NBP(4.5)</td>
<td>1</td>
<td>14/14</td>
<td>4.42 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.965</td>
<td>1.427</td>
<td>1.378</td>
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</tr>
<tr>
<td>NBP(4.5)</td>
<td>2</td>
<td>14/14</td>
<td>3.44 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>2.058</td>
<td>1.521</td>
<td>1.356</td>
<td></td>
</tr>
</tbody>
</table>

- **Table 3.2: PPF/molecule/Ti/Au Junction Results**

a. Ti deposition pressure was 4 x 10<sup>-7</sup> torr ("medium pressure").
b. Inverse slope of i/V (dV/di) for V = ± 50 mV.
c. Percent relative standard deviation in parentheses.
d. Number in parentheses refers to thickness of molecular layer in nm.
e. “Sample” refers to independently prepared junctions.
f. Junctions were rejected if low voltage resistance was significantly lower or if second i/V curve greatly differed from first.
g. Scan rate of current/voltage curves was 1000 V/s
“Medium pressure” Ti junctions had higher resistance values than “low pressure” (2.7 x 10^{-7} torr) Ti junctions at low bias, even though the J/V curve shapes were similar at 1000 V/s. Table 3.2 includes low voltage resistance values, current densities at ± 2V, and rectification ratios obtained for several “medium pressure” (4 x 10^{-7} torr) PPF/molecule/Ti/Au junctions, including standard deviations for multiple junctions on two separate samples. The largest standard deviations were found in the resistance values, followed by current densities, rectification ratio and capacitance. The low bias resistance was calculated from the average of a series of scan rates ranging from 0.2 V/s to 100 V/s. Current densities were recorded from i/V curves sampled at 1000 V/s.

Figure 3.9: Reproducibility of J-V characteristics for seven PPF/BP(1.5)/Ti/Au junctions obtained from 2 different samples. Ti deposition pressure was 2.7 x 10^{-7} torr and \( \nu = 1000 \) V/s.
LVR reproducibility varied from 7.9% for NBP (4.5) to 47.9% for NBP (4.2), while standard deviation of J(+2V) ranges from 4.5% for NBP (2.5) to 24.8% for NBP (4.2). “Medium pressure” (4 x 10^{-7} torr) PPF/BP(1.5)/Ti/Au junction reproducibility is shown in Figure 3.9.

Current density versus voltage curves for monolayer junctions of NBP, FL and BP are shown in Figure 3.10. Each of the J-V traces is the average of four independent junctions. In an effort to avoid dielectric breakdown due to local heating, the scan rate

![Figure 3.10: J-V traces for nitrobiphenyl, fluorene and biphenyl taken at room temperature with a scan rate of 1000 V/s. Top contact and residual gas pressure indicated.](image-url)
was generally kept above 1 V/s and the junction current limited to <10 mA. The potential range for NBP and FL i/V curves was ± 2V, with rectification ratios of \((J^+/J^-)\) 0.95 and 1.02 respectively. Similarly BP had a rectification ratio of 0.93. Strong differences can be observed for low bias resistance values. For a total of 25 junctions tested the average NBP resistance was 978 Ω. The fluorene monolayer showed an average low voltage resistance of 5770 Ω, while a BP monolayer slightly thicker than FL displayed an average resistance of 3.0 x 10⁶ Ω. Current densities, however, exhibited a weaker contrast between the monolayers. For example, at +2V NBP had a current density of 2.59 A/cm² while at –2V the current density was 2.54 A/cm². FL showed current densities of 2.36 A/cm² at +2V and 2.51 A/cm², while BP displayed J values of 1.09 A/cm² at +2V and 1.51 A/cm² at –2V. In the absence of a molecule layer, J-V curves are much more conductive and display ohmic conduction.

The current density–voltage behavior for a series of NBP junctions of different thickness is displayed in Figure 3.10. The measured NBP film thicknesses were 1.7 nm, 2.5 nm, 4.2 nm and 4.5 nm as determined by AFM. Figure 3.11 clearly shows that junction conductivity is strongly dependent on film thickness. For example, the low voltage resistance varied from 978 Ω for NBP(1.7), 7741 Ω for NBP(2.5 nm), 1.8 x 10⁶ Ω for NBP(4.2) to 9.6 x 10⁶ Ω for NBP(4.5). That is, a decrease in thickness by a factor of 2.8 caused a decrease in resistance by a factor of 9.8 x 10⁵. Current densities for NBP (1.7) were 2.59 A/cm² at +2V and 2.54 A/cm² at –2V. For NBP (4.2) J values were 1.32 A/cm² at +2V and 1.24 A/cm² at –2V, while for NBP (4.5) J values observed were 0.32 A/cm² at +2V and 0.34 A/cm² at –2V. The rectification ratios varied from 1.02 for NBP (1.7), 2.17 for NBP (4.2) to 1.39 for NBP (4.5).
Junctions with a Ti top contact deposited at $2.7 \times 10^{-7}$ torr exhibited higher conductivity than the “medium pressure” ($4 \times 10^{-7}$ torr) Ti junctions. Low bias resistance values, current densities and rectification ratios for all molecules studied are summarized in Table 3.3. As mentioned earlier, conductivity increased significantly for all molecules when Ti was deposited at lower pressure. For example, average low voltage resistance values were 188 $\Omega$ for NBP junctions, 196 $\Omega$ for FL and 6456 $\Omega$ for BP. In the absent of molecules the resistance was 150 $\Omega$. Figure 3.12 exhibits J–V plots for monolayers of NBP, FL and BP. For NBP junctions the current densities were 4.8 A/cm$^2$ at +2V and 4.7 A/cm$^2$ at −2V, with a rectification ratio of 1.02. FL junctions were slightly less
conductive with J (+2V) of 4.39 A/cm² and J (-2V) of 4.38 A/cm², with a rectification ratio of 1. Consistent with trends observed at higher pressures, BP junctions remained the least conductive of the monolayers studied with current densities of 2.70 A/cm² at +2V and 2.62 A/cm² at -2V.

Table 3.3: PPF/molecule/Ti/Au Junction Results

<table>
<thead>
<tr>
<th>a Molecule</th>
<th>c Sample</th>
<th>f Yield</th>
<th>b Mean Resistance (±0.2V), Ω</th>
<th>Mean J⁺ +2V A/cm²</th>
<th>Mean J⁻ -2V A/cm²</th>
<th>Mean RR J(+2)/J(-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP (1.5) d</td>
<td>1</td>
<td>13/14</td>
<td>6.46 x 10² (51.1%) c</td>
<td>2.70</td>
<td>2.62</td>
<td>1.03</td>
</tr>
<tr>
<td>FL (1.3)</td>
<td>1</td>
<td>14/14</td>
<td>2.33 x 10² (22.2%)</td>
<td>3.90</td>
<td>3.89</td>
<td>1.00</td>
</tr>
<tr>
<td>FL (1.3)</td>
<td>2</td>
<td>14/14</td>
<td>1.58 x 10² (6.4%)</td>
<td>4.89</td>
<td>4.86</td>
<td>1.00</td>
</tr>
<tr>
<td>NBP (1.7)</td>
<td>1</td>
<td>14/14</td>
<td>2.14 x 10² (32.5%)</td>
<td>4.51</td>
<td>4.42</td>
<td>1.02</td>
</tr>
<tr>
<td>NBP (1.7)</td>
<td>2</td>
<td>14/14</td>
<td>1.62 x 10² (6.0%)</td>
<td>4.99</td>
<td>4.94</td>
<td>1.01</td>
</tr>
<tr>
<td>NBP (4.2)</td>
<td>1</td>
<td>11/14</td>
<td>1.75 x 10⁴ (30.1%)</td>
<td>2.30</td>
<td>1.74</td>
<td>1.294</td>
</tr>
<tr>
<td>NBP (4.2)</td>
<td>2</td>
<td>14/14</td>
<td>1.70 x 10⁴ (40.1%)</td>
<td>2.35</td>
<td>1.75</td>
<td>1.34</td>
</tr>
<tr>
<td>NBP (4.5)</td>
<td>1</td>
<td>14/14</td>
<td>4.42 x 10⁴ (20.1%)</td>
<td>1.97</td>
<td>1.43</td>
<td>1.38</td>
</tr>
<tr>
<td>NBP (4.5)</td>
<td>2</td>
<td>14/14</td>
<td>3.44 x 10⁴ (19.9%)</td>
<td>2.06</td>
<td>1.52</td>
<td>1.36</td>
</tr>
<tr>
<td>Molecule absent</td>
<td>1</td>
<td>7/7</td>
<td>1.50 x 10² (23.3%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Ti deposition pressure was 2.7 x 10⁻⁷ torr (“low pressure”)

b. Inverse slope of i/V (dV/di) for V = ± 50 mV.

c. Percent relative standard deviation in parentheses.

d. Number in parentheses refers to thickness of molecular layer in nm.

e. “Sample” refers to independently prepared pieces, with 14 junctions each.

f. Junctions were rejected if low voltage resistance was significantly lower than 200 Ω or if second i/V curve greatly differed from first.
That is, a decrease in thickness by a factor of 2.8 brings about a decrease in resistance by a factor of 209. Current densities were also dependent on film thickness. For instance, NBP (1.7) showed $J(+2V)$ of 4.75 A/cm$^2$ and $J(-2V)$ of 4.68 A/cm$^2$, while NBP (4.2) displayed 2.33 A/cm$^2$ at $+2V$ and 1.75 A/cm$^2$ at $-2V$. Finally, NBP (4.5) exhibited current densities of 2.01 A/cm$^2$ at $+2V$ and 1.47 A/cm$^2$ at $-2V$. The rectification ratio ranged from 1.02 for NBP (1.7), 1.32 for NBP (4.2) to 1.37 for NBP (4.5).

Figure 3.12: J-V traces for nitrobiphenyl, fluorene and biphenyl taken at RT, at a scan rate of 1000 V/s. Top contact and residual gas pressure indicated.

J –V curves for the NBP series of different thickness are shown in Figure 3.13. The average low voltage resistance values were $188 \pm 55 \Omega$ for NBP (1.7), $17200 \pm 6000 \Omega$ for NBP (4.2) and $39300 \pm 9200 \Omega$ for NBP (4.5). That is, a decrease in thickness by a factor of 2.8 brings about a decrease in resistance by a factor of 209. Current densities were also dependent on film thickness. For instance, NBP (1.7) showed $J(+2V)$ of 4.75 A/cm$^2$ and $J(-2V)$ of 4.68 A/cm$^2$, while NBP (4.2) displayed 2.33 A/cm$^2$ at $+2V$ and 1.75 A/cm$^2$ at $-2V$. Finally, NBP (4.5) exhibited current densities of 2.01 A/cm$^2$ at $+2V$ and 1.47 A/cm$^2$ at $-2V$. The rectification ratio ranged from 1.02 for NBP (1.7), 1.32 for NBP (4.2) to 1.37 for NBP (4.5).
The lowest deposition pressure of < 2.7 x 10^{-7} torr yielded a Ti oxyhydroxide deposit likely to be very disordered, thus preventing the evaluation of junctions containing only metallic Ti. To circumvent this problem, junctions were prepared with Cu as the top contact instead of Ti. J–V curves for “low pressure” PPF/BP(1.5)/Ti/Au and PPF/BP(1.5)/Cu/Au are compared in Figure 3.14A, while those for “low pressure” (2.7 x 10^{-7} torr) PPF/NBP(4.2)/Ti/Au and PPF/NBP(4.2)/Cu/Au are shown in Figure 3.14B. The Cu junctions had consistently lower resistance at low voltage, even though
the J–V curve shapes were similar. Table 3.4 includes junction yield, low bias resistance, current density and rectification ratio values for all Cu junctions, including standard deviations for multiple junctions on two separate samples. The reproducibility of the Cu junctions was significantly improved in comparison to Ti junctions, and very few Cu junctions exhibited anomalous behavior. In fact, of the 147 Cu junctions fabricated, none were rejected due to inconsistent low bias resistance or unstable J/V curves. A comparison of Tables 3.3 and 3.4 reveals that the Cu junctions consistently had lower resistance than the corresponding “low pressure” Ti junctions, often by as much as 50%.

Figure 3.14: Comparison J–V (1000 V/s) curves for (A) BP monolayer and (B) NBP multilayer junctions prepared with Ti and Cu top contacts deposited at 2.7 x 10⁻⁷ torr. Thickness of films is given in parentheses.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sample</th>
<th>Yield</th>
<th>Resistance (±0.2V), Ω</th>
<th>Mean J⁺ +2V A/cm²</th>
<th>Mean J⁻ -2V A/cm²</th>
<th>RR J⁺(2)/J⁻(2) Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP(1.5)</td>
<td>1</td>
<td>14/14</td>
<td>3.67 x 10² (16.8%)</td>
<td>4.546 (11.8%)</td>
<td>4.330 (14.3%)</td>
<td>1.058</td>
</tr>
<tr>
<td>BP(1.5)</td>
<td>2</td>
<td>7/7</td>
<td>2.30 x 10² (12.1%)</td>
<td>5.092 (0.4%)</td>
<td>4.965 (2.5%)</td>
<td>1.019</td>
</tr>
<tr>
<td>FL(1.3)</td>
<td>1</td>
<td>14/14</td>
<td>3.88 x 10² (9.9%)</td>
<td>5.098 (0.3%)</td>
<td>4.998 (2.3%)</td>
<td>1.017</td>
</tr>
<tr>
<td>FL(1.3)</td>
<td>2</td>
<td>14/14</td>
<td>2.29 x 10² (8.2%)</td>
<td>&gt;5 g</td>
<td>&gt;5 g</td>
<td>~1</td>
</tr>
<tr>
<td>NBP(1.7)</td>
<td>1</td>
<td>14/14</td>
<td>2.15 x 10² (12.1%)</td>
<td>4.156 (10.2%)</td>
<td>4.079 (10.5%)</td>
<td>1.020</td>
</tr>
<tr>
<td>NBP(1.7)</td>
<td>2</td>
<td>14/14</td>
<td>3.16 x 10² (12.1%)</td>
<td>3.536 (4.1%)</td>
<td>3.416 (4.7%)</td>
<td>1.036</td>
</tr>
<tr>
<td>NBP(4.2)</td>
<td>1</td>
<td>14/14</td>
<td>2.44 x 10³ (10.1%)</td>
<td>1.726 (10.0%)</td>
<td>1.537 (7.0%)</td>
<td>1.128</td>
</tr>
<tr>
<td>NBP(4.2)</td>
<td>2</td>
<td>14/14</td>
<td>1.72 x 10³ (10.0%)</td>
<td>3.340 (4.2%)</td>
<td>3.086 (4.0%)</td>
<td>1.082</td>
</tr>
<tr>
<td>NBP(4.5)</td>
<td>1</td>
<td>14/14</td>
<td>4.92 x 10³ (20.2%)</td>
<td>1.660 (17.6%)</td>
<td>1.420 (17.8%)</td>
<td>1.166</td>
</tr>
<tr>
<td>NBP(4.5)</td>
<td>2</td>
<td>14/14</td>
<td>5.05 x 10³ (16.0%)</td>
<td>2.238 (17.8%)</td>
<td>1.989 (17.8%)</td>
<td>1.135</td>
</tr>
<tr>
<td>Molecule absent</td>
<td>1</td>
<td>14/14</td>
<td>80.8 (7.0%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Cu deposition pressure was 2.7 x 10⁻⁷ torr.
b. Inverse slope of i/V (dV/di) for V = ± 50 mV.
c. Percent relative standard deviation in parentheses.
d. Number in parentheses refers to thickness of molecular layer in nm.
e. “Sample” refers to independently prepared junctions.
f. Junctions were rejected if low voltage resistance was significantly lower or if second i/V curve greatly differed from first.
g. Exceeded instrumental limit.

Table 3.4: PPF/molecule/Cu/Au Junction Statistics
Current density –voltage curves for PPF/monolayer/Cu/Au molecular junctions of NBP, FL and BP are shown in Figure 3.15. Average low bias resistance values for all junctions of NBP, FL and BP were 267 ± 58 Ω, 306 ± 87 Ω and 316 ± 82 Ω respectively. Each curve is the average of those from four independent junctions. At first glance the current density trend differs from previous observations of Ti junctions since NBP J(A/cm²) values are comparable or lower to those of FL. For NBP the mean J values were 3.85 A/cm² at +2V and 3.74 A/cm² at –2V. Similarly, FL displayed current densities of 5.10 A/cm² and 5.06 A/cm² at +2V and –2V respectively. BP J (+2V) value was 4.72 A/cm² and 4.54 A/cm² for J (-2V). The average rectification ratio for all NBP, FL and BP junctions was 1.0.

Since the resistance values for Cu and “low pressure” (2.7 x 10⁻⁷ torr) Ti junctions are quite small, a concern arises that Cu penetrated the molecular layer and the observed response is due to Cu filaments acting as metallic conductors. This possibility was investigated by making NBP junctions with varying thickness. J/V traces for junctions consisting of three thicknesses of NBP with Cu top contact are displayed in Figure 3.15. The observed resistance and current densities increases rapidly with thickness of the molecular layer. For example, the mean low bias resistance for NBP (1.7) was 267 Ω, increasing to 690 ± 72 Ω for NBP (2.5), 2072 ± 424 Ω for NBP (4.2) and 5068 ± 795 for NBP (4.5). In other words, an increase in film thickness by a factor of 2.8 resulted in a decrease in conductivity by a factor of 19. The current density values for the NBP series decreased with increased film thickness and the specific J values can be found in Table 3.4.
Figure 3.15: Current density –voltage curves for nitrobiphenyl, fluorene and biphenyl taken at room temperature, with a scan rate of 1000 V/s. The top contact was Cu deposited at $2.7 \times 10^{-7}$ torr.
Figure 3.16: J –V curves for a nitrobiphenyl series of different thicknesses obtained at room temperature and a scan rate of 1000 V/s. Top contact and residual gas pressure indicated

Inspection of Figures 3.11 –3.15 reveals that J/V curves approach a similar slope at high bias. The value of dV/di at both positive and negative voltages is in the range of 150 Ω to 300 Ω. At +2V the mean dV/di values for all junctions of BP, NBP (1.7), NBP (2.5), NBP (4.2) and NBP (4.5) were 176 ± 13 Ω, 191 ± 15 Ω, 186 ± 5 Ω, 252 ± 79 Ω and 301 ± 92 Ω respectively. These observations imply that the background resistance, which mainly results from the PPF substrate, limits currents at high bias. Due to the
variation of the $V_{\text{drive}}$ probe location (1-10 mm from the junction), the background resistance is expected to vary. Figure 3.17A shows PPF/monolayer/Cu/Au J–V curves corrected for background resistance by subtracting the iR product from the applied voltage: $E_{\text{corr}} = E_{\text{applied}} - iR$. The assumed background resistance was 120 $\Omega$ for NBP and 80 $\Omega$ for FL and BP. Figure 3.17B displays the J–V curves for the NBP series corrected to a constant series resistance of 120 $\Omega$.

In an effort to compensate for the ohmic losses in the PPF substrate a 3-wire geometry as described in Figure 3.4B was introduced. Figure 3.18A exhibits J–V plots for PPF/NBP monolayer/Cu/Au junctions probed with a 2-wire configuration with no background resistance compensation, 2-wire geometry with 120 $\Omega$ of iR compensation, and the 3-wire configuration. In the case of the NBP monolayer, the J–V curves for the 2-wire iR corrected approximation closely tracks the J–V curves obtained with the 3-wire setup. Similar behavior was observed for FL and BP as presented in Figures 3.18B and 3.18C. All J–V traces were the average of four independent junctions. Furthermore, the low voltage resistance observed with 3-wire is lower than that for 2-wires.
Figure 3.17: (A) J−V curves as shown in Figure 3.15, but with voltage corrected by $V_{\text{corr}} = V - iR$. The iR correction applied was 120 $\Omega$ for NBP and 80 $\Omega$ for FL and BP monolayers. (B) J−V traces as displayed in figure 3.16 with 120 $\Omega$ of iR correction.
Figure 3.18: A comparison between a 2-wire uncorrected geometry, 2-wire corrected geometry and 3-wire configuration for (A) NBP, (B) FL and (C) BP monolayers.
A plot of J/V curves for the monolayers tested with a 3-wire configuration is displayed in Figure 3.19. Once the background resistance has been partially subtracted, the molecular effects on conductivity are more clearly visible, since the J/V curves are no longer being distorted by the ohmic losses due to the PPF. The J/V curves for each molecule presented are the average of curves from four independent junctions. The applied voltage was reduced to \( \approx 0.5 \) volts in order to keep the currents below 10 mA. For NBP monolayer, the low bias resistance decreases from 267 \( \Omega \) (2-wire) to 45 \( \Omega \) (3-wire), for FL 306 \( \Omega \) (2-wire) to 54 \( \Omega \) (3-wire) and for BP 315 \( \Omega \) (2-wire) to 297 \( \Omega \) (3-wire).
Figure 3.19: Plots of J/V curves for nitrobiphenyl, fluorene and biphenyl monolayers taken at room temperature, with a scan rate of 1000 V/s and a 3-wire geometry. The top contact was Cu deposited at $2.7 \times 10^{-7}$ Torr.
3.3 Discussion

The high yield and moderate reproducibility of the junctions, as seen in Figure 3.9, is at least partly due to the strong C–C bond between the substrate and the molecular layer. The irreversible formation of a ~100 Kcal/mole by diazonium reduction apparently prevents penetration of vapor deposited Ti. Since the monolayer molecules are densely packed, lateral mobility of the molecules is significantly decreased to the extent of preventing metal incursion \textsuperscript{124,125}.

The molecular junctions described in this chapter can be classified according to the level of oxide content present. The PPF/molecule/Cu/Au junctions have limited oxide present and are essentially carbon/molecule/metal junctions with relatively high conductivity. The Ti junctions appear to be carbon/molecule/semiconductor/metal devices with quite different behavior from Cu junctions. The important distinctions between “high”, “medium” and “low pressure” Ti junctions presumably correlate with the composition of Ti intermediate oxidation states: Ti\textsuperscript{0}, Ti\textsuperscript{II}, Ti\textsuperscript{III} and Ti\textsuperscript{IV}.

The dramatic effect of residual gases on PPF/molecule/Ti/Au junctions apparent in Figures 3.5 and 3.6 indicates the importance of Ti oxides to junction behavior. A comparison of Cu junctions, listed in Table 3.4, and “low pressure” Ti junctions listed in Table 3.3 is appropriate considering they represent the conceptually simplest case. Figure 3.6 shows that substantial Ti oxide is present for the lowest base pressure studied, and the continuing decrease in resistance with decreasing deposition pressure implies that the resistance for a junction of purely metallic Ti is lower than that observed for Ti deposition at $2.1 \times 10^{-7}$ torr. The redox potential of Cu ($E^\circ = 0.34$ vs NHE) is nearly 2V positive of Ti (-1.6V), and the sticking coefficient of oxygen on Cu is at least four orders
of magnitude lower than that on Ti\(^{144}\). Therefore, Cu should be less prone to react with residual water or molecular oxygen during electron-beam vapor deposition. As exhibited in Figure 3.6, Cu is much less sensitive to oxidation and the Cu junctions have a resistance near that of the “low pressure” Ti junctions, as shown in Figure 3.14. It appears then that Cu is yielding junctions with characteristics similar to those fabricated with Ti, but with much lower likelihood of containing insulating oxides. It is worth noting that Ti(II) and Ti(III) oxides are conducting, while Ti(IV) is an insulator.

Electron transfer between molecules sandwiched between two metals may or may not be accompanied by molecular rearrangement. Slow kinetics of the overall reaction is manifested through scan rate dependence and hysteresis. A distinction is made here between junctions displaying molecular rearrangement termed \textit{molecular redox} junctions and junctions exhibiting electron transfer with limited nuclear motion, or \textit{molecular electronic} junctions. The various Ti junctions fabricated above 4 \times 10^{-7} \text{ torr} displayed both scan rate dependence and hysteresis as seen in Figure 3.5, presumably due to a molecular rearrangement of the monolayer. On the other hand, Ti junctions deposited at < 2.7 \times 10^{-7} \text{ torr}, and Cu junctions, independently of the deposition pressure, exhibited electron transfer behavior lacking any apparent molecular rearrangement.

The symmetry of the “low pressure” (2.7 \times 10^{-7} \text{ torr}) Ti and Cu junctions implies that the work function difference between carbon and the metal is unable to induce significant rectification and hysteresis. The strong rectification and hysteresis observed for “high pressure” Ti junctions\(^{125}\) requires Ti oxide to be present and is completely absent for the Cu junctions. The observation that Cu and “low pressure” Ti junctions all exhibit high conductivity for high voltages could be due to several ET mechanisms,
including coherent tunneling though HOMO-LUMO gap, resonant tunneling, Fowler–Nordheim tunneling or Schottky emission.

The XPS results in Figure 3.6 indicate a mixture of Ti$^0$, Ti$^{II}$, Ti$^{III}$ and Ti$^{IV}$, all in a presumably disordered oxide deposit. The absence of hysteresis for the “low pressure” Ti junctions implies a change in mechanism associated with the presence and composition of the Ti oxide layer. The small difference in the XPS results for “high” and “low pressure” junctions is surprising, given the large change in electronic properties. A possible explanation is based on the observation that the TiO$_2$ content increases with time, presumably by permeation of O$_2$ or H$_2$O through the protective Au film covering the Ti layer. TiO and Ti$_2$O$_3$ are only slightly less conductive than Ti metal $^{145}$, but TiO$_2$ has a conductivity approximately 10 orders of magnitude lower. That is, small amounts of TiO$_2$, possibly formed as a layer at the Au/Ti interface, could have large effects on conductivity. This possibility is supported by the observation that 1-year old junctions with significantly higher TiO$_2$ content (Figure 3.6c) have very low conductivity and exhibit pronounced hysteresis.

Electron transfer in carbon/molecule/Ti “high pressure” junctions is under active investigation, but at least two mechanisms may be responsible for the increase in current and hysteresis under positive and negative voltages. It has been previously shown using Raman spectroscopy that NAB on PPF is partially reduced upon Ti deposition to a mixture of NAB and NAB anion radical$^{124}$ and that structural changes in “high pressure” PPF/NAB/Ti/Au junctions were observed in-situ with Raman spectroscopy through a partially transparent metal top contact$^{146}$. The spectra showed unequivocally that structural changes occurred in the NAB layer under negative bias (PPF relative to Ti),
and that these changes were similar to those observed during electrochemical reduction of NAB chemisorbed to glassy carbon\textsuperscript{97}. It was also apparent during the spectroscopic experiment that both NAB and TiO\textsubscript{x} must be present for rectification to be observed\textsuperscript{146}. Therefore, the conductance changes and hysteresis observed in “high pressure” (6 x 10\textsuperscript{-6} torr) PPF/NAB/Ti junctions as well as PPF/BP/Ti/Au (Figure 3.5) are associated with a redox process in which electrons are transferred between the NAB/NAB\textsuperscript{-} and Ti/TiO\textsubscript{x} layers. An applied voltage in the range of 2-3 V should be energetically sufficient to cause redox reactions, given that the difference in redox potentials between BP and NBP in acetonitrile (-1.34 V and -1.08 V vs. NHE respectively) and Ti/Ti\textsuperscript{2+} (-1.6 V) varies from 0.26 V for BP to 0.52 V in the case of NBP. Solution redox potentials are only a guide to solid-state behavior, but it is clear that a negative bias on a PPF/NBP/Ti/Au junction will promote formation of NBP anion at the negative electrode, while a positive bias should oxidize NBP anion and inject electrons into the Ti/TiO\textsubscript{x} layer. One explanation for the hysteresis in “high pressure” junctions is a change in Ti/TiO\textsubscript{x} or NBP/NBP\textsuperscript{-} conductivity accompanying such electron injection. This injection may provide charge carriers in the semi-conducting Ti oxide, or may produce Ti metal, which provides metallic conductivity between the bulk Ti metal and the molecular layer. It is also possible that the insulating TiO\textsubscript{2} present in “high pressure” Ti junctions is reduced to the more conductive Ti\textsuperscript{II} or Ti\textsuperscript{III} oxides. In any case, electron injection into the initial, low conductivity Ti oxide generates a more conductive phase under positive bias in the case of NBP. In the limit of complete conversion of Ti oxide to a metallic phase, we expect the junction conductivity to approach that of the “low pressure” case. This electron injection process has several properties of a redox reaction, including
dependence on time and applied voltage. The hysteresis results from the relatively slow kinetics of the overall reaction. The stoichiometry of the redox process will depend on the products of the reactions of trace gases with deposited titanium, and it is difficult to narrow down the possible reactions without more information about Ti oxide composition. Furthermore, observed conductivity is a function of the electronic properties of both the TiO\textsubscript{x} and films, both of which are modified by a redox process. Nevertheless, the key point is the association between electron transfer between the layers and TiO\textsubscript{x} phases and changes in junction conductivity.

The spot junction design with the 2-wire geometry exhibits significant distortion from background resistance, mostly in the PPF. Current/voltage response is especially distorted for those molecular junctions such as NBP and FL (Figure 3.15), which have relatively high currents and iR error. It is evident that careful attention needs to be given to the testing configuration. The 3-probe configuration as illustrated in Figure 3.4B partially compensates for the ohmic losses in the PPF in the spot configuration, to the extent that variations in junction behavior with molecular structure are more apparent as observed in Figure 3.19.

Given past reports of metal penetration into Au/thiol self assembled monolayers\textsuperscript{136,147-150}, a question arises about whether the properties of the i/V curves observed for Cu junctions are affected by metallic filaments. Although the observed resistances for NBP, FL and BP monolayers with Cu contacts (267, 306 and 315 Ω, respectively for spot junctions characterized with a 2-wire configuration, and 45, 54, and 297 Ω respectively for spot junctions tested with a 3-wire geometry) are indeed close to each other, there are several strong arguments against the involvement of metallic Cu
“short circuits.” First, metallic conduction through Cu should be linear with voltage, rather than the nonlinear behavior apparent in Figures 3.5 and 3.8–3.17. The possibility that the nonlinear i/V response results from dynamic formation of Ti filaments at high bias is very unlikely, given the repeatability and scan rate independence (from 0.1 to 1000 V/sec) of the i/V curves. Second, NBP, FL and BP junctions having similar monolayer thicknesses displayed different low bias resistance values and current densities. For instance, NBP was 7 times a better conductor at low bias than BP. Furthermore, fluorine whose only structural variation to BP is the bridging methyl group, rendering the molecule 2-dimensional, was 6 times a better conductor. These are strong molecular effects for which filamentary conduction is unlikely responsible. Third, metallic conduction should show a weak dependence on layer thickness (∼ d⁻¹), yet NBP shows a much stronger dependence, with resistance increasing by factors of 20 for a factor of 2.8 in the thickness of the molecular layer. Fourth, the good reproducibility of the resistance of Cu junctions is unlikely if the conductivity is controlled by metallic defects, unless the defects are numerous and uniform. Furthermore, the “control” junctions without molecules exhibit linear i/V curves, with a slope reproducibly higher than that observed for molecular junctions. Finally, if recently reported resistances for similar molecules (e.g., 4,4’ bipyridine, 1.3 MΩ) are scaled up to junctions with ~10¹¹ molecules in parallel, the observed junction resistances should be less than 1 Ω without invoking metal filaments. This observation does not prove that filaments are absent, but it does indicate that low observed resistances for the current monolayer junctions are consistent with reported single molecule results. While pinholes or other defects cannot be totally ruled out for the Cu junctions, the strong dependence of junction behavior on
the structure (Figure 3.19) and thickness (Figure 3.16) of the molecular layers indicates
that such defects cannot be the main determinants of junction conductivity. It is quite
likely that the ability to make functioning reproducible molecular junctions by metal
deposition onto the monolayers studied here is due to the strength of the substrate-
molecule bond (~ 100 kcal/mole) compared to a much weaker Au/thiol (~ 40 kcal/mole)
bonds in SAMs, and electrostatic bonds in L-B structures.

3.4 Conclusion

In summary, the behavior of carbon/molecule/metal molecular junctions is a
strong function of preparation conditions, particularly those resulting in a semi-
conducting metal oxide layer. Reduction of residual gas pressure during metal deposition
causes the junction current/voltage behavior to change from those exhibiting rectification
and hysteresis to symmetric, frequency independent responses with much higher current
densities. The extreme sensitivity of titanium to trace gases is a likely source of the
greater variability in Ti junction resistance and behavior compared to Cu. If the residual
gases were controlled more accurately than possible with the apparatus used here, this
variability should be reduced. Cu junctions are quite distinct from Ti junctions, and more
closely resemble a true carbon/molecule/metal structure. For Ti or other metals, control
of oxide level may permit useful exploitation of the hysteresis and rectification associated
with the oxide, e.g., in memory devices based on the conductivity of various redox states.
It is somewhat speculative at this point, but it is also possible that trace water or oxygen
is actually beneficial during Ti deposition, in that it allows Ti oxide formation in lieu of
“destruction” of the monolayer by titanium atoms reported for SAMs\textsuperscript{134,151}. For
fundamental investigations of electron transport in molecules, however, copper appears to be superior to titanium, with its much lower sensitivity to residual gases. The current PPF/molecule/metal platform offers several important features that allow observation of the effects of molecular structure and thickness on conductivity. The next step in using a Cu top contact is to significantly reduce the junction area in order to minimize the effects of local heating, construct a crossed bar design by lithography to relieve the pressure on the junction during electrical testing, and to probe the electrical properties with a 3-wire geometry in an effort to completely compensate for ohmic losses due to the PPF substrate. Several of these improvements are described in the next chapter.
CHAPTER 4

STRONG EFFECTS OF MOLECULAR STRUCTURE ON ELECTRON TRANSPORT IN CARBON/MOLECULE/COPPER ELECTRONIC JUNCTIONS

A major goal of research in molecular electronics is the correlation of molecular structure with electron transport behavior, since such a correlation provides strong evidence that observed electronic effects are molecular, and not some artifact of the device or measurement. In donor-bridge-acceptor molecules, electron transfers through monolayers in electrochemical cells and in scanning probe microscopy experiments, electron transport has been shown to depend strongly on the length, conjugation, conformation and substituents of the molecule(s) through which electron transfer occurs. Such correlations have proven difficult in metal/molecule/metal junctions, however, partly due to poor junction yield and a variety of electronic effects observed for junctions of nominally identical design. Junction fabrication is difficult for a variety of reasons, including penetration of the metal top contact through the molecular layer, degradation of the molecule during metal deposition, and the presence of metal
oxides within the junction $^{20, 134, 147-150, 168}$. Of pivotal importance is also the geometry of the junction and the testing configuration being employed. As shown in the previous chapter, the substrate employed in the current paradigm has a significant resistivity, which can greatly affect junction electrical measurements. The results indicate that the 3-wire testing configuration is superior to that of 2-wires, mainly because it minimizes PPF background and contact resistance. However, it is apparent that the “spot” geometry utilized so far does not permit for complete subtraction of background resistance.

Another point of concern with the “spot” geometry is the pressure that the junctions experience during testing, for in order to make a proper circuit, it is necessary to gently place a wire lead onto the top Au metal contact. As described in the preceding chapter, the metal of choice can significantly influence the electrical behavior of the junction. However, it was observed that Cu is superior to Ti mainly for its chemical stability in ambient conditions. Finally, it was evident that upon subtraction of the background and contact resistance in the “spot” junctions, the observed conductivity increased to close to the instrumental limit. The issue of junction size also needs to be properly addressed, for by reducing junction area the current densities can be diminished well within the instrumental limit. In addition, reduced junction area also minimizes local heating due to high current densities. Therefore, a different junction design was required to deal with the aforementioned concerns of background resistance, pressure on junctions, top metal contact and high current densities. The junction geometry used here is similar to “crossbar” or “crossed wire” junctions $^{26, 33, 121, 169, 170}$, with a molecular layer bridging the gap between two conventional conductors. The junction structure described in this
chapter has a graphitic carbon substrate and a Cu/Au top contact in a “crossed wire” configuration in all cases.

The primary motivation for the current work was to establish a reproducible, robust junction design, which would allow investigation of the effects of molecular structure on electronic behavior. If junction electronic properties consistently and strongly depend on monolayer molecular structure, it is certain that the molecule is playing a role in electron transport. Within the confines of a single junction design, molecules were chosen which would reveal the effect of small changes in structure (biphenyl vs. fluorene), top contact bonding (biphenyl vs. nitro-biphenyl), and molecular layer thickness (nitro-biphenyl, 1.6 to 4.5 nm in thickness) on the electronic behavior of the molecular junctions. In other words, for monolayers of comparable thickness, we were interested in determining how conductivity is affected by changes in molecular structure only. Furthermore, although the dependence of conductivity on film thickness was investigated for multilayers of NBP in the previous chapter, such a study is reassessed here with multilayers of BP and NBP in part to confirm previous findings, but also to “validate” the “crossed” junction design proposed in this chapter.

4.1 Experimental

Molecular junctions were fabricated with a procedure adapted from that reported previously \(^{64,70}\) and also described in more detail in chapter 3, but with “crossed junction” rather than “spot” configuration. Polished silicon wafers with ~1500 Å thick silicon nitride coatings were cut into 15 x 30 mm pieces, which acted as insulating, flat substrates for the pyrolyzed photoresist films (PPF) which formed the bottom “contact”
of the molecular junction. Cut pieces were sonicated in nanopure water (18 MΩ-cm) for 5 minutes, followed by a 30 second rinse with nanopure water then stored in nanopure water in a clean glass vial with a protective plastic cap for no more than 30 minutes. The samples were then dried in a stream of argon gas, placed in a glass Petri dish, and dried in an oven at 90 °C for 5 minutes. After cooling, PPF films were prepared as described previously 39,71, except for an added lithography step before pyrolysis. Two or three applications of positive photoresist (AZ-P4330-RS, AZ Electronic Materials (formerly Clariant Corp), Somerville, NJ) were applied by spin coating at 6000 rpm. Individual samples were then placed under a lithographic contact mask (Photo Sciences, Inc., Torrance, CA) with a pattern of four stripes 0.5 mm in width (Figure 4.1). A 500-Watt Hg arc lamp (model 68810, Oriel Corp., Stratford Connecticut) was used to expose the uncured photoresist to soft UV radiation for 120 seconds at a power setting of 350 Watts. Immediately after UV exposure, the samples were transferred to a 1:4(v/v) solution of photoresist developer (AZ 400K, Clariant Corp. Somerville, NJ) in Nanopure water for 20 to 30 seconds, then rinsed with nanopure water, Ar-dried, and soft baked at 90 °C for 20 minutes. Pyrolysis was carried out as described previously, to 1100 °C in a reducing 5% H2 in N2 atmosphere. A profilometer (Detak3 ST, Sloan) was used to determine final PPF dimensions, yielding a final thickness of 1 µm and width of 0.45 mm. The resistivity of PPF film was similar to that of glassy carbon, approximately 5 x 10⁻³ Ω-cm² 39,71. Prior to surface modification, the pyrolyzed samples were sonicated in acetonitrile (Sigma-Aldrich, 99.5+ %) for 1 minute and dried with an argon stream. Electrochemical derivatization was performed with a BAS 100-W Potentiostat (Bioanalytical Systems, West Lafayette, IN), as described previously 60,64 and depicted in more detail in chapter
2. An Ag+/Ag (0.01M) (Bioanalytical Systems) reference electrode calibrated with ferrocene to be +0.22 V vs. aqueous SCE was used for derivatization. Modification of PPF surfaces was carried out by the reduction of a 1 mM solution of the corresponding diazonium salt in 0.1M n-tetrabutylammonium tetrafluoroborate (TBABF₄, Sigma-Aldrich 99.5+ %) in acetonitrile. It was important that the diazonium salt solutions were freshly prepared and degassed thoroughly with Ar for 20 minutes. Monolayers of FL, BP, and NBP, as well as multilayers of NBP were deposited as indicated in Table 4.1. Film thicknesses were verified with AFM “scratching” as described elsewhere⁶⁰ and in chapter 2, with the results listed in Table 4.1. The number in parentheses following each junction type, for instance BP(1.54), indicated the AFM-determined molecular layer thickness in nanometers. The AFM technique was shown to yield thickness consistently higher than that expected from the geometric size of a perpendicularly oriented molecule by 0.3 to 0.4 nm, presumably due to a layer of adsorbed water as well as other potential factors described elsewhere⁶⁰ and also addressed in chapter 2. AFM thicknesses between 1.5 and 1.7 nm in Table 4.1 indicate monolayers of BP, NBP and FL (which have geometric lengths of 1.1, 1.1 and 1.2 nm). Several authors have pointed out that diazonium reduction can result in multilayer formation, due to attack of additional electrogendated radicals on the first modification layer to yield molecular layers with thicknesses of 6 nm or more⁵⁵, ⁵⁷, ⁶⁰, ⁷⁸, ⁷⁹.
Table 4.1: Observed Thickness of Molecular Films Formed by Diazonium Reduction

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sample</th>
<th>Line</th>
<th>AFM mean Thickness, nm&lt;sup&gt;a&lt;/sup&gt;</th>
<th>AFM, std dev, nm&lt;sup&gt;b&lt;/sup&gt;</th>
<th>RMS roughness, nm</th>
<th>yield&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP-2d (-1.0 V)</td>
<td>1</td>
<td>1&lt;sup&gt;f&lt;/sup&gt;</td>
<td>1.540</td>
<td>0.253</td>
<td>0.901</td>
<td>4/4</td>
</tr>
<tr>
<td>BP-2 (-1.0 V)</td>
<td>1</td>
<td>2</td>
<td>1.856</td>
<td>0.330</td>
<td>0.426</td>
<td>4/4</td>
</tr>
<tr>
<td>BP-2 (-1.0 V)</td>
<td>2</td>
<td>1</td>
<td>1.815</td>
<td>0.320</td>
<td>0.629</td>
<td>4/4</td>
</tr>
<tr>
<td>BP-2 (-1.0 V)</td>
<td>2</td>
<td>2</td>
<td>2.872</td>
<td>0.294</td>
<td>0.307</td>
<td>4/4</td>
</tr>
<tr>
<td>BP-2 (-1.0 V)</td>
<td>3</td>
<td>1</td>
<td>1.603</td>
<td>0.183</td>
<td>0.365</td>
<td>4/4</td>
</tr>
<tr>
<td>BP-2 (-1.0 V)</td>
<td>3</td>
<td>2</td>
<td>1.847</td>
<td>0.167</td>
<td>0.410</td>
<td>4/4</td>
</tr>
<tr>
<td>FL-1 (-0.8 V)</td>
<td>4</td>
<td>1</td>
<td>2.170</td>
<td>0.283</td>
<td>0.416</td>
<td>4/4</td>
</tr>
<tr>
<td>FL-1 (-0.8 V)</td>
<td>4</td>
<td>2</td>
<td>1.713</td>
<td>0.272</td>
<td>0.436</td>
<td>4/4</td>
</tr>
<tr>
<td>FL-1 (-0.8 V)</td>
<td>5</td>
<td>1</td>
<td>1.797</td>
<td>0.215</td>
<td>0.486</td>
<td>4/4</td>
</tr>
<tr>
<td>FL-1 (-0.8 V)</td>
<td>5</td>
<td>2</td>
<td>1.743</td>
<td>0.171</td>
<td>0.451</td>
<td>4/4</td>
</tr>
<tr>
<td>NBP-1 (-0.6 V)</td>
<td>6</td>
<td>1</td>
<td>2.068</td>
<td>0.259</td>
<td>0.465</td>
<td>2/4</td>
</tr>
<tr>
<td>NBP-1 (-0.6 V)</td>
<td>6</td>
<td>2</td>
<td>1.665</td>
<td>0.089</td>
<td>0.290</td>
<td>3/4</td>
</tr>
<tr>
<td>NBP-1 (-0.6 V)</td>
<td>7</td>
<td>1</td>
<td>1.780</td>
<td>0.188</td>
<td>0.637</td>
<td>4/4</td>
</tr>
<tr>
<td>NBP-1 (-0.6 V)</td>
<td>7</td>
<td>2</td>
<td>1.659</td>
<td>0.137</td>
<td>0.455</td>
<td>4/4</td>
</tr>
<tr>
<td>NBP-4 (-0.9 V)</td>
<td>8</td>
<td>1</td>
<td>2.805</td>
<td>0.309</td>
<td>0.422</td>
<td>4/4</td>
</tr>
<tr>
<td>NBP-10 (-0.9 V)</td>
<td>9</td>
<td>1</td>
<td>3.774</td>
<td>0.172</td>
<td>0.445</td>
<td>4/4</td>
</tr>
<tr>
<td>NBP-20 (-0.9 V)</td>
<td>10</td>
<td>1</td>
<td>4.511</td>
<td>0.437</td>
<td>0.518</td>
<td>4/4</td>
</tr>
<tr>
<td>NBP-20 (-0.9 V)</td>
<td>11</td>
<td>1</td>
<td>4.331</td>
<td>0.175</td>
<td></td>
<td>4/4</td>
</tr>
</tbody>
</table>

a. “Sample” refers to independently prepared substrate/PPF/molecule samples
b. Based on 1 scratch, 2 rectangles, and 10 total AFM profiles through the scratch (see chapter 2). Scratch was positioned immediately adjacent to a junction, on the PPF.
c. Junctions were rejected if the second i/V scan differed significantly from the first.
d. Number of derivatization scans, all at 0.2 V/sec, starting at +0.4 V vs. Ag/Ag<sup>+</sup>, then to the negative potential indicated and back to +0.4 V.
e. Negative potential limit for derivatization scan, stated vs. Ag<sup>+</sup>(0.01M)/Ag.
f. “Line” refers to the upper or lower position within the PPF stripe surfaces where junctions were fabricated (see Figure 4.1).
FTIR\textsuperscript{79} and SIMS\textsuperscript{171} results indicate formation of phenyl-phenyl bonds during coupling of additional layers beyond a monolayer, and the resulting multilayer is unlikely to be as ordered as the initial monolayer. Of all the molecules studied, NBP forms multilayers quite readily, with the thickness depending on deposition time and potential. Table 4.1 includes the AFM thicknesses for several multilayers made from NBP and BP.

Following surface modification all samples were immediately transferred to a clean acetonitrile solution (Sigma-Aldrich, 99.5+ %) for 60 seconds to remove residual diazonium salt, then rinsed in acetonitrile for 20 seconds and dried with an argon stream. Finally, samples were rinsed with isopropyl alcohol for another 20 seconds (Sigma-Aldrich), dried with Ar gas stream, rinsed again with acetonitrile and finally dried with the argon stream.

Following surface derivatization and cleaning, the modified samples were loaded into a vacuum chamber for metal deposition through a shadow mask consisting of two 100 µm wide parallel lines (see Figure 4.1). The mask and samples were positioned on a rotating holder ~50 cm from the crucible of an electron-beam source (Telemark, Freemont, CA). After cryopumping to $< 2.7 \times 10^{-7}$ torr, Cu was deposited at just above the threshold current to yield a rate of initially 0.03 nm/s gradually increasing to 0.08 nm/s until a Cu thickness of 10 nm was achieved. An additional 20 nm of Cu was deposited at a rate of 0.35 – 0.55 nm/s, and then Au was deposited through the same mask without breaking vacuum at 1.0 nm/s for a thickness of 10 nm. The gold layer both protected the Cu and yielded good electrical contact. The dimensions of the junctions were confirmed with an optical microscope with a video measuring accessory (Olympus BX60) to be 100 x 450 µm, for a junction area of $4.5 \times 10^{-4}$ cm$^2$. The sample temperature
was not controlled during deposition, but the chamber temperature increased from 15 °C to 25 °C during metal deposition.

Each sample was comprised of either 4 (1 crossed metal line) or 8 (2 crossed metal lines) crossed-junctions as shown in Figure 4.1. Each junction was contacted individually using 3 Au-plated Pt wires (MM Micromanipulator, Carson City, NV) positioned with three 3-axis micropositioners. Contact with the PPF was made with 100 µm diameter metal tips 1 to 4 millimeters away from the junction and with a 50 µm diameter tip wire on the more delicate Au top contact strip, about <1 mm from the junction. To compensate for ohmic losses in the PPF, the voltage was applied at $V_{\text{drive}}$ (shown in Figure 4.1), but the junction voltage was monitored at point $V_{\text{sense}}$. Under the assumption that the Cu/Au strip remains at virtual ground, $V_{\text{sense}}$ represents the iR corrected junction voltage. The resistance of the Cu/Au strip between the junction and the probe was measured to be < 20 Ω, including contact resistance, resulting in a maximum uncompensated ohmic loss of 20 mV at 1 mA. This “3-wire” configuration is analogous to the three electrodes typically used by potentiostats in electrochemical experiments. The Au wire electrode was connected to a current amplifier (Keithley, model 428), and both $V_{\text{corr}}$ and the current amplifier outputs were monitored simultaneously by two channels of a National Instruments model 6120 data acquisition board controlled by Labview (National Instruments). A complete block diagram of the board is sketched in Figure 4.2 below.
The molecular layer thickness for a particular set of modified PPF strips in a given samples decreases down the modified PPF line as determined by the AFM “scratching” technique, presumably due to ohmic losses from the PPF resistance during diazonium electro-reduction. The thicknesses of the BP layer adjacent to each line of 4 junctions are shown in Figure 4.4 and Table 4.1. Figure 4.4 shows overlays of four i/V curves obtained for the junctions within each “line”. Although the line comprised of four monolayer junctions (1.54 nm) shows a high relative standard deviation for the low voltage resistance (32 %), the i/V curves at higher bias are very reproducible. Given the variation in layer thickness along each PPF strip, AFM was used to determine the molecular layer thickness adjacent to all of the “lines” examined, as listed in Table 4.1 60.

Electronic testing was carried out with a Labview-based system using a National Instruments 6120 data acquisition board. As noted earlier, a 3-wire configuration was used, with two A/D channels monitoring the current signal from a Keithley model 428 current amplifier and the iR-corrected applied voltage (V_{sense}, Figure 4.1). Except where noted, all measurements were carried out at room temperature within 1 day after fabrication. Samples rested on a Cu stage containing a thermocouple.
Figure 4.1: Schematic of PPF/molecule/Cu/Au molecular junction sample. Numbers adjacent to each junction are the observed low voltage (±50 mV) resistance values in KΩ for BP multilayer (1.9 nm, line 1) and BP monolayer (1.5 nm), line 2. Inset in lower right shows contacts to the junction in a 3-wire configuration, with the iR corrected junction voltage equal to $V_{\text{sense}}$ relative to the metal strip at virtual ground.
The Cu was in thermal contact with a liquid nitrogen reservoir that was periodically filled with liquid nitrogen in order to reach temperatures below 20 °C. For temperatures above room temperature, the Cu stage was heated by a Digi-Sense temperature controller, model 68900-01 (Eutech Instruments Pte Ltd). Low temperatures were reproducibly maintained by heating the Cu stage with the temperature controller while simultaneously keeping thermal contact between the liquid nitrogen reservoir and the Cu stage. A second thermocouple positioned in close contact with the sample was used to confirm the sample temperature, and this value is reported in the plots and tables.

Junction capacitance was measured with a Stanford Research SR720 LCR meter, using a 4-wire geometry and frequencies of 0.1, 1, 10, and 100 kHz, with a drive voltage of 0.1 V and in parallel configuration. The “+ drive” and “+sense” leads were contacted to opposite sides on the junction, on the PPF, and the “- drive” and “-sense” leads were on opposite sides of the junction on the metal stripe.
Figure 4.2: Block diagram of the National Instruments Data Acquisition Board.
Figure 4.3: Typical BP monolayer low voltage i/V curve. Resistance values reported were calculated from linear region (± 50mV) as shown.
Figure 4.4: Overlays of i/V curves for each of the four junctions along Line 1 and Line 2 of the biphenyl sample shown in Figure 4.1. Junction area was $4.5 \times 10^{-4} \text{ cm}^2$ in all cases, and the scan rate was 1000 V/s.
4.2 Results

Current density vs. voltage curves for monolayer junctions of nitrobiphenyl (NBP), fluorene (FL) and biphenyl (BP) are shown in Figure 4.5. The inset shows a linear region at low voltage (± 0.1 V), and nonlinearity at higher bias. Each of the J-V curves presented in Figure 4.5 is the average of four independent junctions. In order to avoid junction breakdown due to local heating, the scan rate was generally 1000 V/s, and the current limited to < 8 mA. Several PPF/molecule/Cu/Au junctions for each molecule were examined for the effect of voltage scan rate, and exhibited i/V curves that were independent of scan rate between 0.1 V/s to 1000 V/s. A biphenyl junction cycled for 7.2 million cycles at 320 V/s exhibited no observable change in the i/V response. The potential range for the NBP J-V trace was ± 0.35 V, with a rectification ratio (J+/J−) of 1.5 at 0.35 V. For example, the i/V curve shown in Figure 4.5 had a current density of 11.3 A/cm² at + 0.31 V and -7.4 A/cm² at -0.31 V. The fluorene monolayer is less conductive than the NBP monolayer but more conductive than BP. For fluorene, at +0.31 V the current density was 1.5 A/cm², while at -0.31 V it was 1.1 A/cm², yielding a rectification ratio of 1.4. The J-V characteristics of BP indicate that the monolayer is a poor conductor compared to NBP and fluorene monolayers, with a current density of 0.16 A/cm² at + 0.31 V and -0.13 A/cm² at – 0.31 V. For low applied voltage (± 50 mV) NBP monolayer (1.7) exhibited a resistance of 286 Ω, FL monolayer (1.7) was 886 Ω and BP monolayer (1.6) was 9893 Ω. Thus, for both the low voltage region and the higher-voltage nonlinear regions of the i/V curves, the monolayer junctions exhibited a large range of conductivity, with variations of factors of 20-35 for a variation in thickness of only 9%. The magnitude of the observed current densities and observed low voltage
junction resistances clearly indicate a strong dependence on the monolayer molecular structure.

Figure 4.5: J-V curves for nitrobiphenyl, biphenyl and fluorene taken at room temperature with a scan rate of 1000 V/s. Monolayer thickness as verified by AFM was 1.7, 1.7 and 1.6 nm respectively. Inset shows expanded scale near the origin. “Molecule absent” curve in the main figure is from a control junction prepared identically but without the diazonium reduction step. Each curve is an average of four junctions along a given “line”.
Current density-voltage curves of a NBP series of different thicknesses are shown in Figure 4.6. The measured NBP film thicknesses were 1.659 nm, 2.805 nm and 4.511 nm, as indicated. Figure 4.6 shows clearly that the J-V curves and junction conductivity are strongly dependent on film thickness. For example, at +0.31V, the current density ranged from 11.3 A/cm² for NBP monolayer (1.7) to 0.067 A/cm² for NBP multilayer (2.8), and 0.0083 A/cm² for NBP multilayer (4.5). Therefore, a change in thickness by a factor of 2.8 caused a decrease in current density by a factor of >1360.

Figure 4.6: J-V traces for a nitrobiphenyl series of different thicknesses obtained at room temperature and a scan rate of 1000 V/s. Each curve is an average of four junctions, and the NBP layer thickness as determined by AFM is indicated.
Table 4.2 lists all of the junctions and samples studied, in order to demonstrate the yield of working junctions. A junction was rejected only if subsequent scans after the first showed a large increase in current density. This increase appeared to result from dielectric breakdown of the molecular layer, and occurred in four of the 72 crossed junctions studied. A complete listing of low voltage resistances, current densities and rectification ratios is shown in Table 4.2, which classifies junctions according to molecular structure and film thickness. The low voltage resistance values across a given line of junctions exhibited relative standard deviations of 5 to 15% in most cases, with only three of eighteen “lines” having relative standard deviations above 20%.

Figure 4.7A is a plot of differential conductance (di/dV) vs. applied voltage for NBP, FL and BP monolayers along with a similar plot for the series of NBP multilayers (Figure 4.7B). The high conductivity at high biases indicates rapid electron transport through the molecular layer, especially for NBP and FL. In no case was a plateau in the conductance vs. V plots observed, and the voltage range considered was limited by the current limit of the current amplifier. In order to visualize a wider range of currents near V = 0, Figure 4.8A shows an overlay of ln (current) vs. applied bias for NBP, FL and BP monolayers. Each curve is an average of i/V responses for four junctions of the same molecule and thickness. Figure 4.8B shows a similar plot for NBP multilayer junctions having a range of thicknesses. Electron transport mechanisms such as thermionic emission and the Poole-Frenkel effect exhibit a linear dependence of ln (i) vs. V^{1/2}, and such plots for the various junctions studied here are shown in Figure 4.9. For BP, NBP, and FL monolayers (Figure 4.9A) and different thicknesses of NBP multilayers (Figure
4.9B), the ln (i) vs. V^{1/2} are more linear than ln (i) vs. V, particularly when the bias is greater than ~ 0.1V.

| Junction Type | AFM b thickness nm | Resistance (V= ±0.2V) KΩ | \(^a\)Mean J \(^a\) A/cm\(^a\) \(^a\) (±0.5V) A/cm\(^a\) \(^a\) (±0.5V) A/cm\(^a\) \(^a\) \(^a\) Mean RR | \(^a\)Mean J \(^a\) A/cm\(^a\) \(^a\) (-0.5V) A/cm\(^a\) \(^a\) (-0.5V) A/cm\(^a\) \(^a\) \(^a\) Mean J(J(+)J(−)) |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| BP            | 1.540           | 3.6 ± 1.2       | 0.38 ± 0.07     | 0.364 ± 0.075   | 1.053 ± 0.022   | (32.9%)\(^b\)   | (19.1%)\(^b\)   |
|               |                 | (26.6%)         | (27.7%)         | (20.7%)         | (2.1%)          |
| BP            | 1.603           | 9.90 ± 2.6      | 0.53 ± 0.15     | 0.303 ± 0.093   | 1.71 ± 0.088    | (1.2%)          | (11.8%)         |
|               |                 | (27.7%)         | (30.7%)         | (4.9)           | (5.8%)          |
| BP            | 1.815           | 42.1 ± 0.5      | 0.106 ± 0.012   | 0.067 ± 0.004   | 1.57 ± 0.091    | (1.2%)          | (11.8%)         |
|               |                 | (1.2%)          | (6.5%)          | (5.8%)          | (2.3%)          |
| BP            | 1.847           | 8.74 ± 0.16     | 0.570 ± 0.016   | 0.330 ± 0.005   | 1.726 ± 0.039   | (1.8%)          | (2.8%)          |
|               |                 | (1.8%)          | (1.5%)          | (2.3%)          | (5.1%)          |
| BP            | 1.856           | 54.9 ± 0.8      | 0.120 ± 0.006   | 0.092 ± 0.003   | 1.312 ± 0.020   | (1.5%)          | (3.4%)          |
|               |                 | (1.5%)          | (3.4%)          | (1.5%)          | (2.3%)          |
| BP            | 2.872           | 115. ± 21(17.9%)| 0.059 ± 0.009   | 0.034 ± 0.007   | 1.75 ± 0.09     | (8.5%)          | (11.4%)         |
|               |                 | (15.1%)         | (19.4%)         | (5.1%)          | (4.2%)          |
| FL            | 1.713           | 0.886 ± 0.075   | 6.70 ± 0.77     | 3.26 ± 0.32     | 2.05 ± 0.09     | (8.5%)          | (11.4%)         |
|               |                 | (8.5%)          | (9.8%)          | (4.2%)          | (2.3%)          |
| FL            | 1.743           | 0.514 ± 0.045   | 9.3 ± 1.9       | 4.98 ± 0.85     | 1.87 ± 0.07     | (8.7%)          | (20.6%)         |
|               |                 | (14.8%)         | (20.0%)         | (3.7%)          | (7.0%)          |
| FL            | 1.797           | 0.682 ± 0.101   | 9.8 ± 1.97      | 4.4 ± 1.0       | 2.21 ± 0.15     | (14.8%)         | (20.0%)         |
|               |                 | (20.0%)         | (23.3%)         | (7.0%)          | (2.3%)          |
| FL\(^d\)     | 2.170           | 1.30 ± 0.16     | 4.59 ± 0.53     | 2.20 ± 0.22     | 2.09 ± 0.036    | (12.5%)         | (11.5%)         |
|               |                 | (12.5%)         | (9.8%)          | (1.7%)          |

a. Resistance, current density, and rectification ratio entries are based on 4 different junctions per sample unless stated otherwise.
b. AFM statistics are shown in table 4.1.
c. Percent relative standard deviation stated in parentheses.
d. Statistics obtained from 3 junctions.
e. Statistics obtained from 2 junctions.

Table 4.2: Resistances and Current Densities for PPF/molecule/Cu Junctions.
Table 4.2 continued

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Absent</th>
<th>NBP 1.659</th>
<th>0.286 ± 0.060</th>
<th>10.8 ± 1.3</th>
<th>6.78 ± 0.90</th>
<th>1.59 ± 0.042</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>1.665</td>
<td>0.799 ± 0.058</td>
<td>7.2 ± 3.9</td>
<td>4.4 ± 2.5</td>
<td>1.63 ± 0.018</td>
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<tr>
<td></td>
<td></td>
<td>1.780</td>
<td>0.258 ± 0.035</td>
<td>12.0 ± 4.7</td>
<td>9.3 ± 2.6</td>
<td>1.26 ± 0.19</td>
</tr>
<tr>
<td>NBP e</td>
<td></td>
<td>2.068</td>
<td>1.254 ± 0.078</td>
<td>7.1 ± 2.9</td>
<td>4.1 ± 1.8</td>
<td>1.73 ± 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.805</td>
<td>25.5 ± 0.35</td>
<td>0.363 ± 0.008</td>
<td>0.243 ± 0.008</td>
<td>1.50 ± 0.044</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.774</td>
<td>43.4 ± 1.5</td>
<td>0.118 ± 0.004</td>
<td>0.083 ± 0.002</td>
<td>1.42 ± 0.028</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.331</td>
<td>346. ± 5.2</td>
<td>0.048 ± 0.001</td>
<td>0.025 ± 0.001</td>
<td>1.89 ± 0.020</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.511</td>
<td>362. ± 24</td>
<td>0.041 ± 0.002</td>
<td>0.020 ± 0.001</td>
<td>2.03 ± 0.017</td>
</tr>
<tr>
<td>Molecule</td>
<td>Absent</td>
<td>0.009</td>
<td>(0.014%)</td>
<td>(0.014%)</td>
<td>(0.014%)</td>
<td>(0.014%)</td>
</tr>
</tbody>
</table>
Figure 4.7: (A) Differential conductance (dI/dV) for nitrobiphenyl, fluorene and biphenyl monolayers at room temperature and a scan rate of 1000 V/s. (B) Similar plot for a nitrobiphenyl series of various thicknesses. Differential conductance was determined as the slope of the i/V curve for ~ 20 mV segments of the i/V curves.
Figure 4.8: (A) Ln (i) vs. V for nitrobiphenyl, fluorene, and biphenyl monolayers obtained at room temperature and a scan rate of 1000 V/s. (B) Ln (i) vs. V for a series of nitrobiphenyl thicknesses acquired under the same conditions. Layer thickness is indicated.
Figure 4.9: Plots of ln (i) vs. $V^{1/2}$ for (A) nitrobiphenyl, fluorene, and biphenyl monolayers, and (B) a nitrobiphenyl series with the indicated thicknesses, obtained at room temperature and a scan rate of 1000 V/s.
The well known exponential dependence of electron tunneling on molecular layer thickness was tested by plotting \( \ln (i) \) vs. thickness for low voltage (+ 0.1 V), shown in Figure 4.10A. The observed slopes were -0.21 Å\(^{-1}\) for BP and -0.22 Å\(^{-1}\) for NBP. Each point shown in Figure 4.10 is the average of four junctions, with the error bars indicating the standard deviations. Similar plots were constructed for various bias voltages, and the slopes are shown in Figure 4.10B. For BP junctions of various thicknesses, the slope decreases slightly with applied voltage, while that for NBP is comparatively constant with bias. The results for FL were not analyzed in this fashion because too few film thicknesses were available.

Finally, the temperature dependence of the \( i/V \) curves was examined over a range of approximately 214 to 325 K, with the results shown in Figure 4.11. Although such temperature effects were quite reproducible, the curves in Figure 4.11 were determined from one junction of each type. In all cases, the current decreased with decreasing temperature, at a rate that was similar for BP, FL and NBP monolayers and NBP multilayers. The changes with temperature were completely reversible upon returning the junction to room temperature, at least for the temperature and voltage ranges studied. The capacitance of all junctions decreased with increasing frequency. For example, a typical NBP multilayer 4.5 nm thick junction had an observed capacitance of 7.74, 6.69, 4.35, and 2.1 \( \mu F/cm^2 \) for 0.1, 1, 10 and 100 kHz, respectively. At 100 kHz, all junctions studied had capacitances in the range of 2.1 to 3.3 \( \mu F/cm^2 \), and the capacitance decreased as molecular layer thickness increased for the NBP multilayer series. The frequency dependence of observed capacitance may be due to the relatively low junction resistance, which makes accurate measurement of the capacitive current difficult.
Figure 4.10: (A) Plots of the natural log of the current at $V = +0.1\text{V}$ vs. molecular layer thickness for BP and NBP. (B) Absolute value of slope ($\beta$) of $\ln (i)$ vs. thickness plots at several bias voltages for both biphenyl and nitrobiphenyl. Each point is an average of four junctions.
Figure 4.11: i/V curves obtained at 1000 V/s at the indicated temperatures for junctions made with biphenyl, fluorene and nitrobiphenyl monolayers, and for a 3.8 nm thick nitrobiphenyl multilayer.
Figure 4.11 continued

[Graph showing current density (J) vs. voltage (V) for NBP monolayer and multilayer at different temperatures: 308 K, 265 K, 214 K, 313 K, and 221 K.]

- For NBP monolayer:
  - 308 K: Red line
  - 265 K: Black line
  - 214 K: Blue line

- For NBP multilayer:
  - 313 K: Red line
  - 221 K: Blue line
4.3 Discussion

The high yield and reproducibility of the crossed junction design shown in Figures 4.1 and 4.4 is at least partly the result of the strong C–C bond between the substrate and molecular layer. Irreversible formation of a ~ 100 Kcal/mole bond by diazonium reduction apparently prevents penetration of vapor deposited Cu, as has been reported for the Au/Thiol and Langmuir-Blodgett monolayers. Since the monolayer molecules are immobile and densely packed, they are unable to move laterally to permit metal incursion\textsuperscript{61,62}. The crossed junction design also avoids direct physical contact between the probes and the junction, and a 3-wire configuration corrects for possible variation in wire/PPF contact resistance. The higher current densities observed with the current junctions compared to those reported previously are largely a consequence of the correction of ohmic losses in the PPF.

Figures 4.5 and 4.6 provide strong evidence that metallic “short circuits” or pinholes in the molecular layer do not contribute significantly to junction electronic characteristics. Biphenyl, fluorene, and nitrobiphenyl monolayer junctions with similar thicknesses (1.6, 1.7, 1.7 nm, respectively) have very different low voltage resistances, varying from 9893 $\Omega$ for BP to 286 $\Omega$ for NBP. Comparing FL to BP, the only structural change is a bridging CH$_2$ group which forces the phenyl rings of FL to be coplanar. FL and BP junctions have the same bonding to PPF, the same contact with Cu, the same thickness, and nearly identical compositions. However, the FL junction is eleven times more conductive than the BP junction at low voltage, and 12.5 times more conductive at +0.5V. If metallic “shorts” were present, they might be expected to be more prevalent for the BP case, since its ~ 36° dihedral angle should lead to less dense packing in the
monolayers. However, any packing differences between BP, NBP and FL were not apparent by AFM, and in any case would be much smaller than the observed differences in conductivity. The fact that conductivity is sensitive to the planarity of the phenyl rings is very difficult to explain with metallic shorts or coverage differences. Furthermore, the much higher conductivity of NBP compared to BP junctions (a factor of 28 higher at +0.5 V) is consistent with reports that a covalent bond at both ends of the molecule enhances conductivity \(^{23, 167, 172}\), but is not consistent with metal incursion into the monolayer. A reactive end group has been shown to prevent incursion by reacting with the vapor deposited metal \(^{147-150}\), and the nitro group of NBP is likely to form a covalent bond with Cu, as has been observed for Ti deposited on nitroazobenzene \(^{61, 62}\).

Figure 4.6 shows the strong thickness dependence for NBP with a factor of >1300 decrease in conductivity for an increase in thickness from 1.7 (monolayer) to 4.5 nm (multilayer). Such behavior is not expected for metallic filaments, unless the filament density decreases rapidly with molecular layer thickness. Furthermore, metallic filaments should behave as ohmic conductors, with linear \(i/V\) curves and an inverse proportionality with thickness. The highly nonlinear \(i/V\) curves observed with molecules present in the junctions, and their exponential thickness dependence are inconsistent with metal shorts or filaments. Finally, the decrease in conductance with temperature (Figure 4.11) for all junctions studied is opposite to the dependence expected for metals. While it is difficult to totally rule out the existence of metallic “shorts” in PPF/molecule/Cu crossed junctions, the observed structure, thickness, and temperature dependencies indicate strongly that shorts or pinholes cannot be a major factor controlling conductivity.
The observed junction capacitances of 2.1 to 3.3 µF at 100 kHz should be interpreted with caution, since they exhibited frequency dependence. A wider frequency range will be necessary in order to determine if the frequency dependence is due to a property of the molecules or to a measurement error. However, it is still useful to consider if the observed values are within reasonable expectations for 1.5 to 4.5 nm thick junctions. Using a simple parallel plate capacitor model, the observed capacitances correspond to an upper limit of dielectric constants for the molecular layer in the range of 3.8 to 9.0, with the larger values observed for nitrobiphenyl. While these values are higher than most hydrocarbons, they occur for conjugated molecules oriented along their long axis, for which the molecular polarizability is a maximum.

Given the variation in organic film thickness resulting from diazonium modification, a cautionary note about film structure is advisable. Although it is clear that diazonium reduction results in densely packed films with both monolayer and multilayer thicknesses, they are not as ordered as the more widely studied Au/thiol SAMs. The irreversible chemisorption of radicals generated by diazonium reduction prevents annealing over time, thus preventing formation of an ordered two-dimensional crystalline film. Furthermore, the PPF surface resembles a disordered glass with predominantly sp² hybridization. However, it is still informative to compare the conductance of junctions with organic layers of different structure provided the disorder of the PPF or molecular layer is kept constant. For example, biphenyl and fluorene junctions are identical except for the bridging CH₂ group and ring coplanarity, and small differences in packing density could not account for the factor of ~7 difference in conductivity at low voltage and a factor of 11 at +0.25V. Since PPF is a glass, it may not be possible to...
precisely determine the structure of the molecule/substrate interface, but it is both
possible and valuable to investigate the effects of molecular structural changes on
electronic behavior.

Before considering possible electron transfer mechanisms through the molecular
layer, several observations must be accounted for by any conduction model. First,
conduction in monolayers is strongly dependent on structure, both the ring planarity
noted above, and the presence of a NO2 group. The higher conductivity of NBP over BP
is presumably due to a more covalent Cu-NO2 interaction compared to Cu-phenyl,
analogous to that observed when titanium is deposited on nitroazobenzene61,62. Second,
although the conductance depends exponentially on the thickness of an NBP layer, the
attenuation coefficient of 0.22 Å⁻¹ is small compared to that reported for phenylethynyl
oligomers (0.3 to 0.6 Å⁻¹)157-160 or alkanes (1.0 Å⁻¹). The observed attenuation factor is
weakly dependent for NBP, decreasing to 0.20 Å⁻¹ at +0.5 V and 0.21 Å⁻¹ at -0.5 V. A
similar attenuation factor was observed for electrochemical ET through a series of
aromatic molecules on carbon electrodes for both Ru(NH3)₆⁺³/⁺² (0.21 Å⁻¹) and
chlorpromazine (0.20 Å⁻¹) redox systems in aqueous solution100,173. In addition, an STM
study of conductance through single polyolefin molecules174 of varying length reported
an attenuation factor of (0.22 ± 0.04) Å⁻¹. Third, the conductance decreases with
decreasing temperature but with a small apparent activation barrier. Preliminary
estimates of activation barriers determined from plots of ln (conductance, ± 50 mV) vs.
l/T over the 214 to 325 ºK temperature range are 0.064 eV for BP, 0.075 eV for FL and
0.083 eV for NBP monolayers, and 0.152 eV for NBP (3.8) multilayer. There is no
obvious effect of structure on temperature dependence, with biphenyl, fluorene and NBP monolayers having approximately equal barriers despite the differences in the Cu/molecule contact and in ring planarity. Fourth, plots of ln (i) vs. V are nonlinear for all molecules and temperatures studied, while ln (i) vs. V^{1/2} plots show linearity for voltages greater than approximately 0.1V. Finally, if we assume that the ~ 10^{10} molecules in a typical junction are acting as parallel resistors, the per-molecule resistance for the lowest resistance observed (258 Ω for NBP monolayer) would be 2.6x10^{12} Ω. This value is significantly higher than that reported for a single bipyridyl molecule (~10^7 Ω)^{175, 176} or a C_{12} alkane thiol (~10^{10} Ω)^{18, 167}. Given that the conductance plots show no sign of reaching a plateau in the voltage range examined (Figure 4.7), it is possible that the per-molecule conductance may be much higher than implied by the observed resistances, and that the rapid rise in conductivity with voltage is due to “recruitment” of an exponentially increasing number of molecules acting in parallel.

The observed rectification ratio presented in Table 4.2 for forward and reverse current densities for all junction types fell in the range of 1.1 to 2.2. This asymmetry is small compared to that reported for rectifying molecular junctions \cite{27, 65, 2, 116, 177-180} and implies that the current junctions are close to being electronically symmetric. The work functions of Cu (4.7 eV) and sp^{2} hybridized carbon (4.8-5 eV) are similar\cite{181}, with the slightly lower work function of Cu favoring electron injection from Cu rather than from PPF. Therefore the slight rectification observed to varying degrees for all junctions is consistent with the small work function difference between Cu and PPF. However, differences in the Cu/molecule contact and dipoles present in some of the molecules studied may also contribute to the observed rectification.
We have previously reported on PPF/biphenyl/Hg junctions which have very similar construction to the current junctions, with the exception of top contact material and larger area (0.00785 cm²)65. PPF/biphenyl/Hg junctions had an area-normalized low voltage resistance of 108.33 Ω-cm² and a current density of 0.003 A/cm² at +0.25 V. Similarly, recently reported 63 PPF/biphenyl/Cu/Au junctions consisting of a ~ 0.5 mm diameter spot (and 2-wire configuration) rather than crossed wire geometry had a low voltage resistance of 1.09 Ω-cm² and a J(+0.25 V) of 0.29 A/cm². When the PPF background resistance was partially compensated with a 3-wire geometry, the low voltage resistance obtained was 0.84 Ω-cm² and the J(0.25V) value 0.28 A/cm². The area-normalized resistance of 1.61 Ω-cm² for the current crossed wire junctions determined for the BP (1.5 nm) junctions listed in Tables 4.2 and 4.3 is significantly lower (by a factor of 67) than that observed for the analogous Hg junction, and close to that of the Cu “spot” junctions. Similarly, the J (+0.25 V) for the crossed BP monolayer junctions (0.17 A/cm²) is a factor of 57 higher than that of the Hg case, and within a factor of 1.6 of the Cu “spot”. Given the possibility of uneven electrical contact of Hg across the BP monolayer, plus likely contamination of the Hg drop before making contact, it is not surprising that the Cu junctions exhibit higher conductivity at both low voltage and at +0.25 V. The reasons for the higher conductivity of the Cu “spot” (by a factor of 2) compared to the “crossed junction” geometry are not clear, but at least two measurement differences are present, and could account for the disparity. The crossed junction geometry does not require a probe to make contact directly over the junction molecules, thus avoiding pressure or possible damage. The “spot” geometry does not lend itself for complete PPF resistance correction with a “3-wire” system. Furthermore,
leakage through the doped silicon substrate (1 \, \Omega\text{-cm}^2) underneath the PPF may have contributed to the slightly higher conductivity. Finally, the smaller area of the crossed junctions (by a factor of 4.4 in this case) may result in fewer low-resistance defects compared to the “spot”.

Table 4.3: Low voltage resistance and current densities for BP, FL and NBP for several junction geometries and testing configurations.

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Junction Geometry</th>
<th>Testing Configuration</th>
<th>Resistance (\Omega\text{-cm}^2)</th>
<th>(J (+0.25V)) A/cm(^2)</th>
<th>(J (-0.25V)) A/cm(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>Hg (^a)</td>
<td>2-wires</td>
<td>108</td>
<td>0.003 (^b)</td>
<td>0.004 (^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(44.9%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP</td>
<td>Spot</td>
<td>2-wires</td>
<td>1.09</td>
<td>0.29</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(16.3%)</td>
<td>(31.0%)</td>
<td>(28.8%)</td>
</tr>
<tr>
<td>BP</td>
<td>Spot</td>
<td>3-wires</td>
<td>0.84</td>
<td>0.28</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(30.0%)</td>
<td>(20.0%)</td>
<td>(19.2%)</td>
</tr>
<tr>
<td>BP</td>
<td>Crossed</td>
<td>3-wires</td>
<td>1.61</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(32.9%)</td>
<td>(20.8%)</td>
<td>(22.0%)</td>
</tr>
<tr>
<td>FL</td>
<td>Spot</td>
<td>2-wire</td>
<td>1.07</td>
<td>0.33</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(5.9%)</td>
<td>(9.8%)</td>
<td>(10.4%)</td>
</tr>
<tr>
<td>FL</td>
<td>Spot</td>
<td>3-wire</td>
<td>0.15</td>
<td>2.11</td>
<td>1.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(26.7%)</td>
<td>(27.2%)</td>
<td>(25.0%)</td>
</tr>
<tr>
<td>FL</td>
<td>Crossed</td>
<td>3-wire</td>
<td>0.23</td>
<td>1.86</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.7%)</td>
<td>(7.1%)</td>
<td>(3.8%)</td>
</tr>
<tr>
<td>NBP</td>
<td>Spot</td>
<td>2-wires</td>
<td>0.64</td>
<td>0.39</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(16.1%)</td>
<td>(16.1%)</td>
<td>(16.2%)</td>
</tr>
<tr>
<td>NBP</td>
<td>Spot</td>
<td>3-wires</td>
<td>0.13</td>
<td>2.44</td>
<td>2.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(22.3%)</td>
<td>(20.5%)</td>
<td>(20.4%)</td>
</tr>
<tr>
<td>NBP</td>
<td>Crossed</td>
<td>3-wires</td>
<td>0.13</td>
<td>6.63</td>
<td>4.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(21.0%)</td>
<td>(23.4%)</td>
<td>(22.5%)</td>
</tr>
</tbody>
</table>

- a. Top contact of junctions was accomplished by lowering a Hg drop (A \sim 0.00785 \, cm\(^2\)) onto the monolayer
- b. Relative standard deviation not available
Table 4.4: Observable quantitative molecular differences between BP, FL and NBP according to junction geometry and testing configuration.

Due to the various junction geometries (“spot” vs. “crossed”), testing configurations (2-wire vs. 3-wire), and top metal contacts (Hg vs. Cu) employed on previous and current molecular junctions, a comparison of observed molecular effects between the monolayers seems appropriate. Since “spot” junctions tested with a 2-wire configuration suffer from significant background resistance contribution, they will be omitted for comparison purposes. For molecular electronic junctions where Hg was used
as the top contact, it has been previously determined that fluorene has a factor of 10 better conductivity than biphenyl, presumably due to greater electronic coupling between the aromatic rings in fluorene\textsuperscript{126}. In a similar trend, differences in conductivity between fluorene and biphenyl are evident in both “spot” and “crossed” junctions. For instance, in the “spot” case, fluorene is a better conductor at low voltage by a factor of 6 and by a factor of 8 at +0.25V. In the “crossed” junction design, this difference becomes more prominent. For example, at low voltage resistance fluorene is a better conductor by a factor of 7 while at +0.25V FL has a higher conductivity than biphenyl by a factor of 11, as can be observed in Table 4.4. It is remarkably that there is agreement in the superior fluorene conductivity over biphenyl in all cases, considering differences in junction geometry, testing arrangement, and top metal. Differences in conductivity between NBP and BP are shown in detail in Table 4.4. As it can be observed, both “spot” and “crossed” junctions indicated better conductivity through NBP than BP. In the case of “crossed” junctions, at low voltage BP is a poorer conductor by a factor of 12 and by a factor of 40 at 0.25V, presumably due to the covalent linkage between the nitro group and Cu.

As has been discussed in many reports, there are several electron transport mechanisms which may be invoked to explain the i/V characteristics of molecular junctions \textsuperscript{13, 65, 182-189}. Although the current results do not yet permit identification of a specific mechanism operative in carbon/molecule/copper junctions, the results do provide some useful insights. As noted above, the strong dependence of conductivity on molecular structure clearly indicates that the major and possibly dominant factor controlling conductivity is molecular in origin, rather than some property of the carbon or
metal layers. The weak temperature dependence implies that tunneling is important, particularly for junctions with molecular layers thinner than ~2 nm. As an indication that coherent tunneling is at least possible for the monolayer junctions, the rectangular Simmons tunneling model yields barrier heights of 1.99, 1.36, and 1.22 eV for BP(1.6), FL(1.7) and NBP(1.7) monolayer junctions, respectively. However, the weak thickness dependence observed for either BP or NBP is not compatible with coherent tunneling, nor is the observation of electron transport through >4 nm of the NBP multilayer. Incoherent (or “diffusive”) tunneling by a series of steps between potential wells does allow for transport across such large distances, with the potential wells possibly related to nitro groups in NBP or phenyl rings in BP. The linear behavior of ln (i) vs. \( V^{1/2} \) is characteristic of both thermionic (e.g., “Schottky”) emission at an interface and Poole-Frenkel transport between coulombic “traps”. If either of these mechanisms is important, the associated barriers must be shallow, in order to account for the small observed activation energies. A mechanism that is compatible with all of the current experimental observations, involves electron transport by either tunneling or Poole-Frenkel transport between potential wells within the molecular layer. In the limit of very low temperature, only tunneling should be operative, and ln(i) vs. \( V^{1/2} \) should be nonlinear. As the temperature is increased, Poole-Frenkel transport contributes, and is possibly dominant for the thicker NBP multilayers. While such a mechanism is possible, it does not uniquely account for all of the observations, and other phenomena may be involved. It is likely that a detailed analysis of the effect of temperature over a wide range currently underway will allow more specific conclusions about electron transport mechanisms.
4.4 Conclusion

The carbon/molecule/Cu/Au “crossed wire” junctions reported here offer (1) high yield, (2) reproducible and (3) robust platforms (4) for the investigation of the effects of molecular structure on the electronic behavior of molecular junctions. As it was compared in the discussion section above, three different junction types have been fabricated and tested (e.g., Hg, “spot,” and “crossed”). Based on the results of low voltage resistance and current densities displayed on Tables 4.3 and 4.4 (especially for the BP monolayer), the “crossed” junction design is superior to the other geometries, mainly because of its high yield and good reproducibility. Yield and reproducibility are closely related to the “crossed” junction geometry, as it permits noninvasive (no downward pressure onto the monolayer) testing of the electrical properties of the junction and allows for ohmic compensation in the substrate due to background and contact resistance. The choice of Cu as the top metal reduces possible contamination during the formation of the top contact, such as oxide formation in Ti vapor deposition, and adventitious contamination in the case of Hg. Furthermore, The high yield and good reproducibility of the carbon based molecular junctions are also likely to be direct consequences of the strong C–C bond between the carbon substrate and the molecular layer, which reduces the incursion of vapor deposited metals to a negligible level. Finally, the molecular electronic differences between the various structures were observed with remarkable clarity in the “crossed” junction design.

The major effects of molecular structure and molecular layer thickness on junction conductance strongly support the contention that molecular structure is the primary determinant of the electronic properties of the junctions. This is true for all
junction geometries –Hg, Cu “spot,” and Cu “crossed. The conductance difference between FL and BP is constant throughout all junction configurations. For instance, FL is more conductive than BP at low voltage resistance by a factor of 10 in Hg junctions, a factor of 6 for the “spot” junction case, and a factor of 7 in the “crossed” junctions. It is difficult to attribute such differences to properties of the bottom and top electrodes or some other artifact. In addition, conductivity was affected by molecular length, as shown in the phenyl series of phenyl, biphenyl and terphenyl in the Hg junction case, and NBP series of different thickness in both “spot” and “crossed” junctions. Thus, since conductivity is both affected by structure and molecular length, it can be concluded with certainty that the electron transport of the studied junctions is molecular in nature.

The observed electron conduction through biphenyl, fluorene, and nitrobiphenyl monolayers and nitrobiphenyl multilayers is weakly temperature dependent, and can occur across layers as thick as 4.5 nm. It is very likely that in order to discern possible mechanisms responsible for the observed conductivity, more extensive temperature studies need to be carried out. However, a possible mechanism for electron transport in the carbon-based junctions is a combination of coherent or diffusive tunneling at low temperatures and a thermally activated process with a small activation barrier at higher temperatures.

In addition to temperature studies, it is important to understand more about film deposition and monolayer formation. Although there is strong indirect evidence implying that the molecules arrange themselves perpendicular during film deposition, there is still a need to establish it with more certainty. A Raman polarization study and more thorough AFM experiments should shed light on this topic. Equally important is to
correlate electrical properties, such as low voltage resistance and current densities with junction area.
ASSESSING THE QUALITY OF DIAZONIUM FILMS ON MODIFIED CARBON ELECTRODES BY CYCLIC VOLTAMMETRY

Significant progress has been made toward understanding the reactivity of carbon surfaces, but their complex chemistry and microstructure remain to be completely elucidated. Surface impurities and a complex surface structural chemistry have rendered carbon electrode reactivity difficult to discern. Surface oxides, especially carbonyl and hydroxides, can enhance the carbon surfaces adsorption properties. In an effort to explain the readiness by which carbon surfaces adsorb adventitious material, a series of mechanisms has been proposed. They include the creation of local dipoles, electrostatic attraction, and covalent attachment between the surface and adsorbed species. For instance, polar adsorbates interact strongly with carbon, with adsorption strength increasing in the presence of oxides on the surfaces. However, nonpolar species can also adsorb to carbon surfaces by means of induced dipoles and Van der Waals interactions. As a result, the task of characterizing carbon surfaces has become a challenging one, mainly because carbon surfaces vary significantly with origin, history, and pre-treatment.
It is argued that carbon microstructure plays a pivotal role in electron transfer kinetics on carbon electrodes. A good example is the difference in kinetics of redox systems on highly ordered pyrolytic graphite (HOPG) and glassy carbon (GC). The microstructure reactivity affects the amount of surface impurities and the nature of the surface functionalities. For that reason, redox systems have been classified based on their electrokinetic response to surface preparation and composition. Outer-sphere systems such as Ru(NH$_3$)$_6^{2+/3+}$, IrCl$_6^{2-/3-}$, Co(Phe)$_3^{2+/3+}$, Co(en)$_3^{2+/3+}$ are insensitive to surface functional groups and/or impurities, but in turn are strongly affected by carbon microstructure. In contrast, oxide-catalyzed inner-sphere systems including Fe$_{aq}^{3+/2+}$, Eu$_{aq}^{2+/3+}$, V$_{aq}^{2+/3+}$ are sensitive to surface carbonyl density. Apparently, carbonyl derivatives provide an alternative catalytic pathway to an inherently slow outer-sphere rate. Finally, inner-sphere, not oxide-catalyzed systems such as ascorbic acid (AA), Fe(CN)$_6^{3-/4-}$ and dopamine (DA) are insensitive to surface oxide coverage, but responsive to monolayer adsorption.

Three very aggressive approaches for the preparation of glassy carbon surface electrodes have been reported:

1. Treatment by hot oxidizing acidic solutions such as sulfuric acid (H$_2$SO$_4$) and nitric acid (HNO$_3$). This treatment also results in an increase of the specific carbon surface area.

2. Oxidation by air or oxygen at high temperatures (500 – 800 °C) or by RF O$_2$ plasmas. This procedure may cause roughening of carbon surface and possible degradation.
3. Anodization or electrochemical oxidation using the carbon fiber as the anode in an aqueous solution at the O₂ evolution potential. In addition, there are other gentler procedures such as ultraclean polishing and AC/IPA cleaning.

A general approach to improving carbon surface uniformity is to prepare homogeneous surfaces through well-defined pretreatment and surface modification procedures. A well-known electrode preparation procedure for metals involves the spontaneous adsorption of thiols on gold electrode surfaces to form self-assembled monolayers (SAMs). The adsorption of thiols results in the formation of Au-S bonds that are in thermodynamic equilibrium, and the bonding is characterized by a partial covalent character. However, recent studies have shown that thiol monolayers contain undesirable features such as instability in hydrothermal environment of high pH and elevated temperatures, and propensity to be oxidatively and reductively desorbed.

A more recent promising technique involves the electrochemical reduction of phenyl diazonium derivatives. It offers distinct features such as a simpler, flexible and promising scheme for covalently binding moieties directly to the carbon surface. The surface modification entails the formation of an aryl diazonium radical followed by the covalent attachment of the diazonium to the carbon microstructure. A mechanism is shown in Figure A.1 below.
Presumably the heterogeneous reaction (R1) is fast compared with diffusion, suggesting that the heterogeneous reaction (R2) is the rate-determining step. The success of the modification of the carbon surface by electro-reduction depends on the observation that aryl radicals produced by R1 are not reduced at the potential at which these radicals are generated. Therefore, the aryl radicals react vigorously and irreversibly with the carbon surface (R2). It has been reported that molecular films formed by diazonium reduction are resilient and difficult to remove from carbon electrode surfaces. Glassy carbon modified electrodes have been ultrasonically rinsed in different organic polar and nonpolar solvents for 15 minutes without affecting its cyclic voltammetry. Saveant et al. has also reported that diazonium films have a durability of 6 months upon exposure to atmospheric air.
Aryl diazonium reagents containing a variety of functional groups have been employed in applications ranging from electroanalysis to electrocatalysis. Examples include: controlling protein adsorption, analysis of electron transfer kinetics of redox systems, demonstrating Raman spectroscopy methodology and assembling of composite biosensors. In addition, it has been reported the fabrication of a composite film of GC/4-nitrophenyl/SiW12O40^4+ device that provides a favorable environment for electron and proton transfer between SiW12O40^4+ and the GC electrode surface. Such an arrangement provides properties suitable for various applications in sensor and microelectronic devices.

The current work was designed to characterize the quality of the molecular films formed on carbon by diazonium reduction. Ru(NH3)6^{3+/2+} electrokinetic behavior was employed to provide a method for distinguishing between a true monolayer and a multilayer while monolayer-packing properties were investigated by examining the films’ ability to block dopamine activity.

A.1 Experimental

Synthesis of Diazonium Salts

Diazonium salts were prepared according to previously established procedures in the laboratory. When a primary aromatic amine is treated with nitrous acid in an ice-bath, the resulting product is a relatively unstable compound. The formation of a diazonium compound by the interaction of sodium nitrite, an inorganic acid (HBF₄), and the precursor primary amine, is known as diazotization. The amine precursors; 0.10 mole of 4-nitroaniline, 0.040 moles of trifluoromethylaniline, 0.020 moles of P-toluidine were
dissolved in 40 mL, 16 mL and 22 mL of fluoboric acid respectively, and the mixture was
cooled to below 0 °C in an ice-bath with the help of NaCl(s). 0.13, 0.05, and 0.03 moles
of sodium nitrite were dissolved in 10, 5, and 5 mL of nanopure water respectively.

Figure A.2: Structural representation of precursor amino compounds. (A) nitroaniline,
(B) trifluoromethylaniline and (C) p-Toluidine.

The solution of sodium nitrite was added dropwise to the precursor amine mixture while
monitoring temperature and keeping it below 4 °C. After sodium nitrite addition was
completed, the mixture was stirred for 30 min. The product was collected by vacuum
filtration and washed several times with cold ether, then recrystallized by dissolving in
acetonitrile and adding ether in a dropwise manner. Mass spectrometry (ESI-MS),
nuclear magnetic resonance (NMR) and UV-Vis analyses characterized final products.
Reagents

Sodium nitrite (Sigma) was used as received. Tetrabutyl ammonium tetrafluoroborate (n-Bu₄BF₄), 50% (v/v) fluoboric acid (Aldrich), p-Toluidine (Aldrich), p-nitroaniline (Aldrich), p-trifluoromethylaniline (Aldrich) were used as received. 1 M KOH was prepared using nanopure water and low carbonate KOH pellets. Phosphate buffer solution (1.0M KCl, 0.1M total phosphate, pH 7) was prepared by combining K₂HPO₄ . 3H₂O (J. T. Baker), KH₂PO₄ (J. T. Baker), KCl (J. T. Baker) and by adding KOH pellets to reach the desired pH. Other solutions include 0.1 M H₂SO₄, 1 mM dopamine and 1 mM Ru(NH₃)₆³⁺/²⁺. Oxygen gas (Linde Gas, ultrahigh purity) and Argon gas (Linde Gas, prepurified) were used as received. HPLC-grade acetonitrile (Aldrich) and isopropyl alcohol (Aldrich) were also used as received.

Equipment

Cyclic voltammetry was performed with a conventional 3-electrode cell potentiostat (BAS-100W, Bioanalytical Systems). An Ag/AgCl (3M KCl) and a Pt wire were used as the reference and auxiliary electrodes, respectively, while the working electrode was a glassy carbon electrode (Bioanalytical Systems). The saturated concentration of O₂ was estimated to be 1 x 10⁻³ M, and its diffusion coefficient was assumed to be 1.65 x 10⁻⁵ cm²/s. X-ray photoelectron spectra were acquired with VG Scientific Escalab MKII Spectrometer with a Mg anode. All spectra were obtained at a pressure of < 2 x 10⁻⁹ torr. The O/C and C/F ratios were calculated by integrating the area under the peaks ⁷⁴, ²⁰². Glassy carbon plates (Tokai-20, Bioanalytical Systems) Area = 1 cm² were employed for the XPS analysis. For the electrochemical measurements, GC
Electrodes (GC-20) with Area = 0.071 cm² were utilized. The lengths of the molecules were calculated by Spartan SYBYL Force field software. The rate constants were calculated using Digism 3.03 software (Bioanalytical Systems).

Electrode Preparation

Electrodes were polished successively in 1, 0.3, and 0.05 µm alumina powder (Buehler) with nanopure water slurries (Barnstead, 18 MΩ) on polishing cloth (Buehler). Electrodes were rinsed thoroughly with nanopure water while changing alumina grades. Commercial alumina slurries containing organic deagglomerating agents were avoided. After polishing, the electrodes were sonicated in nanopure water for 10 min, followed by sonication in a suspension of activated carbon (Norit) in isopropyl alcohol (IPA) in a 1:3 (v/v) ratio. The AC/IPA mixture was allowed to stand from 10-30 min before use. After sonication in AC/IPA, electrodes were sonicated for 2 sets of 5 min each in nanopure water. Electrodes were readied for modification after drying with an Ar stream ⁷⁷, ²⁰³.

Surface Modification

Chemisorption was accomplished by reducing the respective diazonium salt in a 1mM solution in Acetonitrile containing a 0.1M n-Bu₄BF₄ (TBATFB) solution. Reduction was achieved by cycling from +0.4 V to −0.8 V (vs Ag/Ag⁺) and back to +0.4V at 0.2 V/s for nitrobiphenyl and methylphenyl. For trifluoromethylphenyl the cycle started at +0.2 V to −0.8 V and back to +0.2 V (v = 0.2V/s). Prior to surface modification, 1mM diazonium solutions were de-aerated with Ar gas for 20 min. An Ar
stream was maintained over the diazonium solution without disturbing it during the modification process\textsuperscript{203 77}.

Figure A.3: Sketch of A) nitrophenyl (NP), B) trifluoromethylphenyl (TFMP) and C) methylphenyl (MP) monolayers tethered to a carbon surface

Electrochemical Measurements

Electrochemical Ru(NH$_3$)$_6^{3+/2+}$ responses were carried out in a phosphate buffer solution pH 7. After each measurement, copious rinsing and sonication in water cleaned the electrode. Afterwards, dopamine (pH 1) electrochemical behavior was measured on the same electrode. Since outer-sphere redox systems, such as Ru(NH$_3$)$_6^{3+/2+}$ display tunneling behavior, several cyclic voltammograms were run without observing a decrease in kinetics, which implied that the redox system did not absorbed to the carbon surface. In contrast, only a single cyclic voltammograms measurement was possible for
dopamine, as the redox system adsorbs to the carbon surface, reducing the kinetics of subsequent measurements.

A.2 Results

Carbon surfaces modified by diazonium reduction have been previously characterized by several techniques, including X-ray photoelectron spectroscopy, Raman spectroscopy and electrochemistry. Figure A.4 shows XPS spectra taken under the same conditions, comparing an unmodified carbon surface (control) to that of a TFMP-modified. The O$_{1s}$ peak indicates the presence of oxides on both surfaces, with almost twice the percentage on the bare carbon surface. The F$_{1s}$ peak is only observable in the TFMP-modified surface, presumably due to the fluorinated methyl groups. The calculated ratio by integrating the area under the peak was $F_{1s} / C_{1s} = 0.348$.

The Ru(NH$_3$)$_6^{3+/2+}$ electrochemical response on a freshly prepared TFMP-modified GC electrode is shown in Figure A.5. The modified electrode had undergone rinsing with acetonitrile and sonication in AC/IPA for 1 minute before acquiring the cyclic voltammograms. The voltammograms are not background subtracted. The post-modification cleaning treatment in AC/IPA apparently increases the observed Ru(NH$_3$)$_6^{3+/2+}$ kinetics. However, inspection to Figure A.6 reveals that AC/IPA treatment on the same electrode also increases dopamine (DA) response. Since dopamine requires contact between the DA and the GC surface, the decrease in its $\Delta E_p$ upon IPA sonication treatment can be attributed to the formation of pinholes through the monolayer by which dopamine can reach the carbon surface. In other words, pinholes are created presumably
due to the collisions of activated carbon particles with the grafted monolayer during sonication. As a result, AC/IPA treatment as a procedure to remove physisorbed material from the monolayer surface upon modification was avoided. Instead a different post-derativatization procedure had to be devised.

Figure A.4: X-ray photoelectron spectroscopy (XPS) of a polished GC electrode and a trifluoromethylphenyl modified GC electrode.

\[
\frac{F_{1s}}{C_{1s}} = 0.348
\]

Figure A.4: X-ray photoelectron spectroscopy (XPS) of a polished GC electrode and a trifluoromethylphenyl modified GC electrode.
Figure A.5: Ru(NH$_3$)$_6^{3+/2+}$ kinetics on a trifluoromethylphenyl modified GC electrode after rinsing with acetonitrile and sonicking with a 1:3 (v/v) solution of activated carbon and isopropyl alcohol for 1 minute. Voltammograms were not background subtracted. $v$ = 20 V/s
Figure A.6: Dopamine kinetics on a TFMP modified electrode after rinsing with acetonitrile and after sonicating with a 1:3 (v/v) solution of activated carbon and isopropyl alcohol for 1 minute. Cyclic voltammograms were not background subtracted. \( v = 0.2 \text{ V/s} \)

Figure A.7 shows background subtracted Ru(NH\(_3\))\(_6^{3+/2+}\) cyclic voltammograms (\( v = 20 \text{ V/s} \)) for a polished GC surface and two TFMP-modified electrodes, which differ in the post-modification cleaning procedure. The modified electrode rinsed with nanopure water and isopropyl alcohol (IPA) immediately after derivatization shows the faster Ru(NH\(_3\))\(_6^{3+/2+}\) kinetics. All electrodes discussed below underwent this procedure.
Figure A.7: Shows different Ru(NH₃)₆³⁺/²⁺ electrochemical response to various cleaning procedures. Cyclic voltammograms were background subtracted and taken at room temperature. \( v = 20 \text{ V/s} \). “Poorly rinsed monolayer” refers to a TFMP monolayer that has been rinsed with acetonitrile and nanopure water. “Clean monolayer” refers to a TFMP monolayer that has been rinsed with acetonitrile, isopropyl alcohol and nanopure water.

Figure A.8 contrasts Ru(NH₃)₆³⁺/²⁺ electrochemical behavior on polished GC to that of a TFMP-GC monolayer. For two polished GC electrodes, \( \Delta E_p \) did not significantly vary, exhibiting the following values: 74, 83, 83, 86 mV for an average and standard deviation of 82 ± 5 mV. In contrast, Ru(NH₃)₆³⁺/²⁺ response was slower by a factor of 1.7 (\( \Delta E_p = 143 ± 7 \text{ mV} \)) when the electrode had been modified with a TFMP
Cyclic voltammograms were background subtracted and taken at room temperature. \( \nu = 0.13 \) cm/s for polished GC electrodes and 0.027 cm/s for TFMP-GC monolayers.

Figure A.8: Ru(NH\(_3\))\(_6\)\(^{3+/2+}\) kinetics at a polished GC electrode and a TFMP monolayer. Cyclic voltammograms were background subtracted and taken at room temperature. \( \nu = 20 \) V/s.

Figure A.9 exhibits the effect of Ru(NH\(_3\))\(_6\)\(^{3+/2+}\) kinetics on a TFMP multilayer. The multilayer was achieved by carrying out 11 cycles (\( \nu = 0.2 \) V/s) between +0.2V and –0.8V and back to +0.2V. The electron transfer rate of the redox system is significantly
decreased. On the other hand, $\Delta E_p$ for two polished GC electrodes were 98, 100, 100, 104 mV, providing an average and standard deviation of 101 ± 3 mV. The TFMP monolayer, obtained by carrying out 1 cycle between +0.2V to –0.8V and back to +0.2V vs. Ag/AgCl, is capable of blocking any dopamine activity as demonstrated by its $\Delta E_p$ >1000 mV, as shown in Figure A.10 below.

Figure A.9: Ru(NH$_3$)$_6$$^{3+/2+}$ kinetics at a polished GC electrode and a TFMP multilayer. Cyclic voltammograms were background subtracted and acquired at room temperature. $v = 20$ V/s.
Figure A.10: Blocking effect of a TFMP monolayer on dopamine kinetics. Cyclic voltammograms were background subtracted and taken at room temperature at a scan rate of 0.2 V/s.

Figure A.11 exhibits Ru(NH$_3$)$_6^{3+/2+}$ kinetics for a methylphenyl (MP-GC) monolayer. The monolayer increased $\Delta E_p$ to 148 ± 2 mV, yielding an observed rate constant of 0.034 cm/s. However, dopamine activity was blocked by the same MP monolayer, as shown in Figure A.12.
Figure A.11: Ru(NH$_3$)$_6^{3+/2+}$ kinetics at a polished GC electrode and a MP monolayer. Cyclic voltammograms were background subtracted and acquired at room temperature. $\nu=20$ V/s.
Figure A.12: Blocking effect of a MP monolayer on dopamine electrochemical response. Cyclic voltammograms were background subtracted and taken at room temperature.

v = 0.2 V/s.

Figure A.13 shows the effect of nitrophenyl (NP-GC) monolayer on the Ru(NH$_3$)$_6^{3+/2+}$ response. $\Delta E_p$ decreases to 157 ± 1 mV, providing a $K_{obs}$ of 0.045 cm/s. As it can be observed in Figure A.14, dopamine activity is suppressed by the nitrophenyl monolayer.
Figure A.13: Ru(NH$_3$)$_6^{3+/2+}$ kinetics at a polished GC electrode and a NP monolayer. Cyclic voltammograms were background subtracted and acquired at room temperature. $v =$ 20 V/s.
Figure A.14: Blocking effect of a MP monolayer on dopamine. Voltammograms were background subtracted and taken at room temperature. $v = 0.2 \text{ V/s}$.

### A.3 Discussion

In the case of the TFMP film for which data was collected the coverage calculated was to be $\Gamma = 847 \text{ picomoles/cm}^2$. Current surface coverage is 1.4 times higher than a previous reported value of 614 pmol/cm$^2$. However, it can be concluded that the
fluorine XPS signal in TFMP and the nitrogen XPS signal in NP provide a convenient marker for estimating film surface coverage.

A closer look at Figure A.11 reveals that Ru(NH₃)₆³⁺/²⁺ reductive and oxidative currents have been significantly diminished by the blocking effect of the TFMP multilayer film, but ΔEₚ remains comparable to that of a monolayer. This observation implies that the multilayer has unevenly grown, however, still possesses areas with monolayer thickness. The effect is analogous to having an array of monolayer-thick areas or “channels” in the film to which the redox system diffuses in order to undergo redox reactions. In this proposed scheme, the number of available “channels” controls observed current response.

Observed k° values for Ru(NH₃)₆³⁺/²⁺ on metals and carbon surfaces vary from 0.1 – 1.0 cm/s.²⁰³ The current value of 0.13 cm/s falls within reported range and is comparable to a previous reported rate of 0.24 cm/s.⁷³,¹⁹⁶. In another study, ΔEₚ was observed to be 78 ± 7 mV for a polished electrode (no AC/IPA treatment) and 85 ± 5 mV for an AC/IPA treated surface²⁰³, at scan rates of 20 V/s. Previously reported dopamine ΔEₚ values ranged from 61 ± 8 mV to 36 ± 6 mV for polished glassy carbon electrodes, and 41 ± 2 mV for AC/IPA treated surfaces²⁰³ ⁷⁴. The current ΔEₚ value is higher by a factor of ~3. The discrepancy can be the result of differences in carbon surface origin and history. Furthermore, differences in AC/IPA suspension formulation and use, as well as variation in experimental design can additionally account for the slower dopamine kinetics.

Electrochemical response studies for carbon surfaces modified with monolayers of aryl diazonium salts have shown a variety of results ranging from blocking effects of
inner-sphere systems\textsuperscript{198} to kinetics decreasing by a factor of 8\textsuperscript{75}. Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+/2+} kinetics observed here decreased by factors of 4.8, 3.8 and 2.9 for monolayers of TFMP, MP and NP respectively. On the other hand, the blocking effects of the monolayers on dopamine response confirmed previous findings\textsuperscript{74}. A correlation between electron transfer kinetics and monolayer thickness can be established, subject to some assumptions. For outer-sphere systems such as Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+/2+}, electron transfer occurs through a tunneling mechanism. Tunneling is governed by the following equation:

\[ k_{\text{obs}} = k^\circ e^{-\beta d} \quad \text{(Equation A1)} \]

where \( k^\circ \) is the rate constant on a bare electrode, \( \beta \) is the tunneling attenuation factor, and \( d \) refers to the thickness of the modifier. \( \Delta E_p \), \( k_{\text{obs}} \) and experimental length for various monolayers studied are summarized in Table A.1. An attenuation factor of 0.21 Å\textsuperscript{-1} was used in equation 1 to calculate the experimental tunneling length. A similar tunneling coefficient has been observed for electrochemical electron transfer through a series of conjugated molecules on carbon surfaces for both Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+/2+} (0.21 Å\textsuperscript{-1}) and chlorpromazine (0.20Å\textsuperscript{-1})\textsuperscript{100,207}. Furthermore, a recent study of electron transport through biphenyl and nitrobiphenyl films molecular electronic junctions resulted in an attenuation coefficient of 0.21 Å\textsuperscript{-1} and 0.22Å\textsuperscript{-1} respectively\textsuperscript{208}. 

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</table>

Table A.1: Summary of Ru(NH₃)₆³⁺/²⁺ kinetics on bare and modified carbon surfaces

The difference in calculated molecular length and experimental monolayer thickness varies from 1.3% for TFMP to 35.3% for NP. See Table A.1. The relative standard deviation varies in the following order: –CF₃ < -CH₃ < -NO₂. The observed sequential decrease in the electrochemical response for the positive charged Ru(NH₃)₆³⁺/²⁺ species can be related to the interaction between the redox system and the nature of the partial charge on the end of the monolayer. For example, -CF₃ is electron withdrawing, creating a partially negative charged monolayer to which the Ru(NH₃)₆³⁺/²⁺ will be attracted. By contrast, -NO₂ has a negative partially charge on the oxygen atoms, followed by a positive partially charge on the nitrogen atom. The different end groups differ somewhat in their effects on Ru(NH₃)₆³⁺/²⁺ kinetics, possibly due to electronic differences related to F and NO₂.

A.4 Conclusion

A post-modification cleaning treatment to remove physisorbed material from grafted monolayers was devised. This procedure was employed during the fabrication of molecular junctions addressed in chapters 2 - 4. The cleaning procedure consists of:
(1) Rinsing the tethered films with acetonitrile (ACN) followed by drying with an argon stream.

(2) Rinsing with isopropyl alcohol (IPA) and Ar-drying.

(3) And rinsing with acetonitrile again and thoroughly drying the films with Ar.

Monolayer formation of diazonium ions can be achieved by controlling deposition time and applied voltage: that is, scan rate, potential range and number of derivatization cycles. In a broad sense, an electrochemical test –herein termed the *Anariba test* –for assessing the quality of grafted diazonium monolayers was developed. Its main criteria are outlined below.

1. Ru(NH$_3$)$_6^{3+/2+}$ electrochemical response was used to distinguish the formation of monolayers versus multilayers (> 2 layers) at $v = 20$ V/s. Depending on molecular length, a $\Delta E_p$ values of < 200 mV is considered a monolayer.

2. Dopamine kinetic response was utilized to assess the extent of pinhole density in the modified surfaces at a scan rate of 0.2 V/s. An $\Delta E_p > 800$ mV suggests a negligible pinhole density.

3. Applicable to monolayers of < 20 Å, for which tunneling is most effective.

4. Electrochemical results should be used as a complementary technique.
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