

# The Merger of Electrochemistry and Molecular Electronics

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**ABSTRACT:** Molecular Electronics has the potential to greatly enhance existing silicon-based microelectronics to realize new functions, higher device density, lower power consumption, and lower cost. Although the investigation of electron transport through single molecules and molecular monolayers in “molecular junctions” is a recent development, many of the relevant concepts and phenomena are derived from electrochemistry, as practiced for the past several decades. The past 10+ years have seen an explosion of research activity directed toward how the structure of molecules affects electron transport in molecular junctions, with the ultimate objective of “rational design” of molecular components with new electronic functions, such as chemical sensing, interactions with light, and low-cost, low-power consumer electronics. In order to achieve these scientifically and commercially important objectives, the factors controlling charge transport in molecules “connected” to conducting contacts must be understood, and methods for massively parallel manufacturing of molecular circuits must be developed. This Personal Account describes the development of reproducible and robust molecular electronic devices, starting with modified electrodes used in electrochemistry and progressing to manufacturable molecular junctions. Although the field faced some early difficulties in reliability and characterization, the pieces are now in place for rapid advances in understanding charge transport at the molecular level. Inherent in the field of Molecular Electronics are many electrochemical concepts, including tunneling, redox exchange, activated electron transfer, and electron coupling between molecules and conducting contacts.  
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## Introduction

Electron transport (ET) is a pervasive topic in chemistry and physics, as well as being the underlying phenomenon for microelectronics in its many and widespread manifestations. The exchange of electrons between a conducting solid (or liquid)

and a molecule in solution is the basis of electrochemistry as well as a significant sector of the world economy. Most readers of a special issue commemorating the discovery of polarography are familiar with the scientific and technological importance

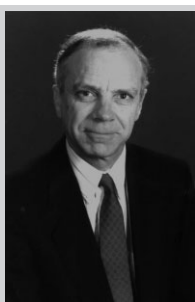
of heterogeneous electron transfer in chemical analysis, electrosynthesis, corrosion, and energy conversion. While the common forms of electrochemistry generally involve electrolyte solutions and solid electrodes, some of the same phenomena are involved in broader areas of solid-state electronics. A notable example is Organic Electronics,<sup>1,2</sup> in which electrons are transported through organic thin films or polymers, often by a series of redox reactions.<sup>3</sup> Organic light-emitting diodes (O-LEDs) and organic field effect transistors (O-FETs) provide a low-cost and possibly flexible alternative to silicon microelectronics, and are beginning to emerge in consumer electronics. As described below, Molecular Electronics (ME) is a subset of Organic Electronics which was proposed in 1974, when Aviram and Ratner described theoretically that a single molecule could act as a rectifier by favoring electron transport in one direction along the molecular axis.<sup>4</sup> The field grew rapidly starting in the late 1990s, when scanning probe microscopy and monolayer fabrication techniques permitted probing and constructing devices with much shorter length scales than those in conventional microelectronics.<sup>5–9</sup> This Personal Account describes the development of molecular electronics from the perspective of an electrochemist, with particular attention to the importance of electron transport to both fields.

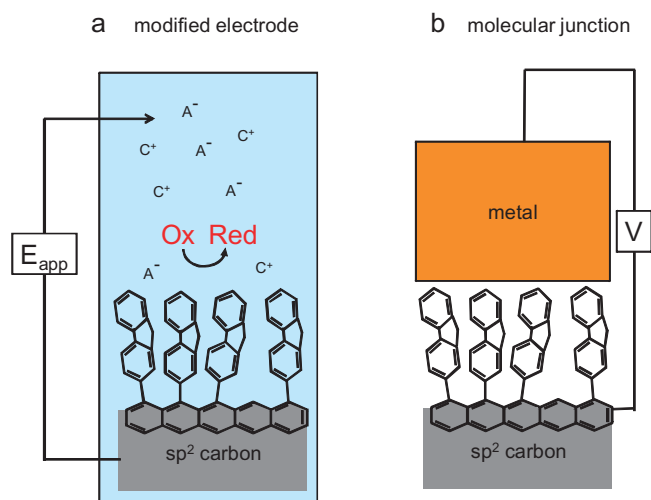
Given that Organic Electronics and Molecular Electronics share some of the same molecules and are governed by similar principles, one might ask “why all the fuss” over Molecular

Electronics? The initial excitement was over the small size potentially achievable for molecular devices, due to the inexorable decrease in feature size which has characterized the micro-electronic industry for ca. 40 years. If useful electronic functions such as rectification, memory, or amplification could be achieved in a single molecule, the increase in device density over the best silicon technology would be at least a factor of  $10^6$ . Furthermore, the great variety of molecular structures available should lead to a broad range of potential electronic functions, including chemical and biochemical recognition, which are difficult with silicon.<sup>9,10</sup> In the author's opinion, the more interesting distinction between “organic” and “molecular” electronic deals with length scale and associated physical phenomena. ET in OLEDs and related phenomena occur over distances of 10–1000+ nm, and involves many “hopping” events involving redox exchange and the formation of radical ions. Such transport is “activated”, meaning it has positive temperature dependence and a characteristic activation energy.<sup>1</sup> If the same organic film is decreased in thickness to 1–5 nm, however, “hopping” might not be necessary and electron tunneling becomes the dominant transport mechanism.<sup>8,11,12</sup> As will be discussed later, the temperature dependence vanishes, and transport is not “dissipative”, meaning the character and mechanism of ET have changed completely. The structural factors controlling ET in molecular electronic devices are still being investigated, but it is clear that provided at least one dimension of the device is short compared to the “hopping” length, the device behaves fundamentally differently from the relatively thick films common in “organic” electronics. Examples of these differences appear below.

The author considered the features of ME sufficiently profound and important to shift his entire research program to studying ET in solid-state electronic devices, and this Personal Account describes the scientific steps involved in that transition. A useful starting point is the familiar “modified electrode”, an example of which is shown in Figure 1a. A molecular layer is bonded to a solid electrode (or Hg) by one of several reactions, the most common being “self assembly” of alkanethiols on Au. In order for a redox process to occur in solution, an electron must traverse through the molecular layer, and the approach provides a good paradigm for studying “long range” electron transfer through molecules.<sup>13</sup> The redox system in this case is an “outer-sphere” system which does not require contact with the electrode itself, such as ferrocene or  $\text{Ru}(\text{NH}_3)_6^{+3/+2}$ . Extensive research in the 1990s and thereafter investigated the dependence of the electron transfer rate constant ( $k^0$ ) between the electrode and a redox system on the structure and thickness of the modification layer, and several examples from these studies are cited below. The author's laboratory reported extensively on carbon electrodes modified by diazonium chemistry starting in 1995,<sup>14</sup> including a report relating  $k^0$  to the molecular layer thickness.<sup>15</sup> As will be discussed later, the electro-

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**Fig. 1.** Comparison of modified electrode in solution (a) and a molecular junction (b), with the junction resulting from replacing the electrolyte solution with a conducting contact.  $A^-$  and  $C^+$  represent ions in solution, while Ox and Red are components of a redox reaction.  $E_{app}$  represents the applied potential relative to a reference electrode.

chemical investigation of ET at modified electrodes has significant mechanistic consequences in molecular electronics.

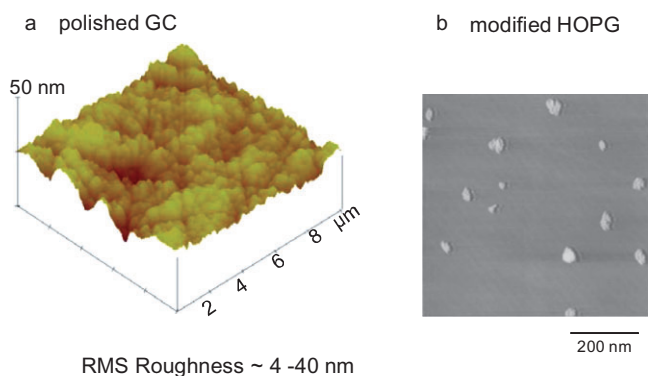
The transition from the modified electrode (Figure 1a) to the “molecular junction” of Figure 1b is conceptually simple: the electrolyte solution is replaced by a second conducting “contact”. The molecular junction is the basic “2-terminal” component of ME, and has been studied extensively.<sup>8–10,16</sup> Although an electrolyte solution is absent, ET in a molecular junction should still be dependent on molecular structure, layer thickness, reorganization, etc. While the concept may be simple, the fabrication and mechanistic understanding of the molecular junction proved to be quite difficult. Nobody knew in ca. 1997 how a structure like that shown in Figure 1b should behave electronically, so there was no “standard” to compare paradigms and results. Analytical techniques for characterizing monolayers or single molecules within conducting contacts are difficult,<sup>12,17</sup> resulting in several cases of inadequate structural verification of ME devices. In addition, establishing the “top contact” on a molecular layer a few nm thick without “short circuits” between the conducting substrate and the top contact proved very difficult. This account of our laboratory’s development of molecular junctions describes the transition from modified electrode to molecular junction in the three following sections: fabrication, electronic behavior, and electron transport mechanism.

## Fabrication

The many paradigms for studying molecular junctions can be broadly classified into two types: single molecule and

“ensemble” junctions.<sup>9,10,12,18</sup> The former often involve scanning tunneling microscopy (STM), in which a single molecule by itself or in a monolayer is probed by an STM tip. A variant of STM is the “break junction” in which a molecule is suspended between two metal tips, often Au.<sup>19,20</sup> Ensemble junctions contain  $>10^3$  oriented in parallel between two conductors, and can be as large as  $0.0025 \text{ cm}^2$  and contain ca.  $10^{12}$  molecules. The merits of the two approaches have been compared,<sup>9</sup> but we chose the “ensemble” approach for several practical and fundamental reasons. As already noted, we knew how to make modified electrodes and had characterized them with both electrochemistry and optical spectroscopy. Although single-molecule paradigms have provided some fascinating scientific insights, there is a significant problem with integration into useful electronic devices. Most commercial microelectronics involves billions of devices produced for a few dollars, and massively parallel manufacturing is essential. Incorporating ensemble molecular junctions into an existing semiconductor manufacturing line is at least technically feasible. While single-molecule paradigms hold the uncontested record for small device size, ensemble devices can be “nanoscale” in at least one dimension, with accompanying mechanistic consequences described below. Finally, ensemble junctions reflect the collective behavior of a large number of molecules, and are less subject to stochastic variations in bonding geometry, local contact morphology, and thermal fluctuations, which can significantly affect the electronic behavior of single molecules.

The choice of carbon substrates modified by diazonium chemistry to make the structure of Figure 1b was initially dictated by past experience with similar modified electrodes,<sup>14,15,21,22</sup> but there are some consequences of this choice in the context of ME.<sup>9</sup> Alternative approaches are based mainly on Au/thiol self assembled monolayers (SAMs)<sup>23–26</sup> and Langmuir-Blodgett (LB) films<sup>27–29</sup> on metals or metal oxides. These approaches lead to ordered monolayers which result from “assembly” of the molecules involved by surface diffusion into a low energy state. Both SAMs and LB films have been well characterized, but they are dynamic and capable of restructuring. It was recognized quite early that metal deposition on SAMs resulted in movement of SAM molecules followed by direct substrate-metal contacts.<sup>30–32</sup> An additional problem was the difficulty of making large metal surfaces which were flat on the scale of the molecular length. Obviously a ca. 1 nm thick molecular layer on a surface with  $>1 \text{ nm}$  roughness is prone to defects and “shorts”, and special methods are required to assure sufficiently low substrate roughness.<sup>33–35</sup> Our carbon/diazonium route has two advantages for making molecular junctions: a very flat substrate surface, and a stable, conjugated carbon-carbon bond between the substrate and molecular layer. An unavoidable disadvantage of the irreversible surface bond is less order than in SAMs and LB structures, since the



**Fig. 2.** a) Atomic force microscopy image of polished glassy carbon (GC). b) STM image of the basal plane of highly ordered pyrolytic graphite modified by reduction of 4-Diazo-*N,N*-diethylaniline ion.<sup>52</sup> Features observable on the modified surface are multilayers of disordered oligomeric diethylaminoaniline.

molecules are not mobile once bonded. These three aspects of the carbon/diazonium paradigm will be considered in turn.

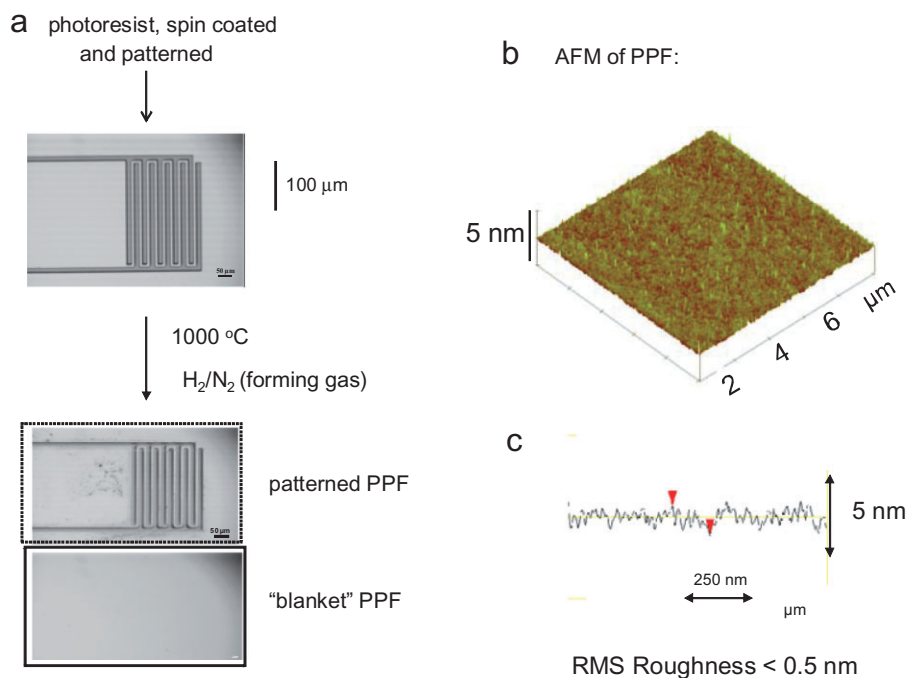
For about 15 years before embarking on molecular electronics, our group studied the properties of carbon electrode materials, notably glassy carbon.<sup>36–40</sup> Most electrochemists are quite familiar with carbon paste and glassy carbon electrodes, in which the conducting graphitic  $sp^2$  carbon replaces a metal as the working electrode. The main objective of our investigations was determination of the factors which control the electrochemical reactivity of carbon electrodes, and the results of those and related studies were recently reviewed.<sup>41</sup> In addition, the covalent attachment of molecular layers to electrode surfaces by reduction of aryl diazonium reagents was initially developed for carbon materials,<sup>42–44</sup> so a versatile, high-coverage modification route was available. Our experience with glassy carbon (GC)<sup>37,39,45,46</sup> and highly ordered pyrolytic graphite (HOPG)<sup>47–50</sup> made them natural choices for molecular junction substrates, but unfortunately there are problems with these materials. GC is made by heat-treating a polymer such as polyacrylonitrile, resulting in a bulk sample which must be shaped and polished before use as an electrode. As shown in Figure 2a, even a well-polished GC surface has an rms roughness of about 4 nm,<sup>51</sup> much greater than a typical molecular length (~1 nm). The basal plane of HOPG is atomically flat (observed rms ~ 0.24 nm)<sup>51</sup>, but difficult to modify with diazonium reduction. Diazonium-derived radicals preferentially bond to edge plane defects, resulting in nucleation and growth to yield the uneven coverage apparent in Figure 2b.<sup>52,53</sup> The edge plane of HOPG can readily be modified, but is very rough and difficult to prepare<sup>54</sup>.

The solution to the problem of finding a flat substrate which is reactive toward diazonium-derived aryl radicals arose in the form of “pyrolyzed photoresist film” (PPF).<sup>55–58</sup> The fabrication process was used initially for making carbon inter-

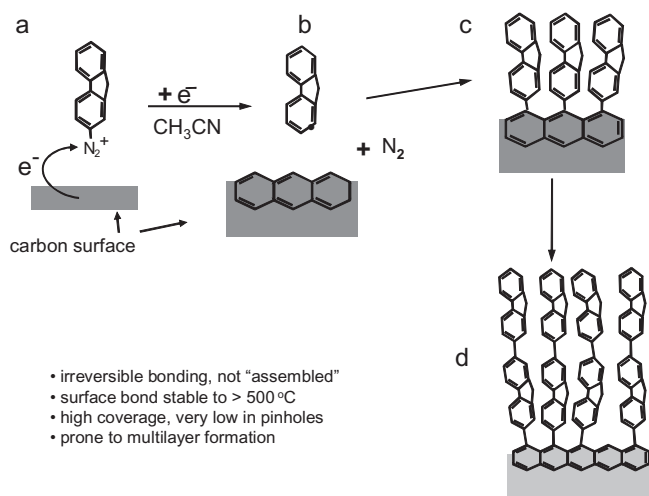
digitated electrodes by pyrolysis of lithographic structures made from commercial photoresist used in the microelectronics industry. As shown in Figure 3a, patterns of photoresist are easily made with photolithography on glass or silicon surfaces, with feature sizes in the submicron range with “benchtop” techniques. The photoresist is a phenolic resin (e.g., “novolac”), which is pyrolyzed to mainly  $sp^2$  hybridized carbon in a reducing atmosphere (usually 5%  $H_2$  in  $N_2$ ) at ca. 1000 °C. As is the case with the formation of glassy carbon, the heteroatoms are vaporized during pyrolysis, and the result is a disordered, nearly pure graphitic carbon. The shape of the original lithographic pattern is retained, permitting fabrication of complex lithographic patterns (described later). The spectroscopic and electrochemical properties of PPF are very similar to GC, but the surface is very flat, as shown in the AFM image (3b) and line scan (3c). The rms roughness of <0.5 nm is retained over large areas of the PPF surface, and there are no visible defects or features observable with either AFM or SEM. There are presumably variations in the exposure of the edges and planes of benzene rings at the PPF surface, but modification by diazonium reduction leads to very even and high surface coverage.<sup>59</sup> The coverage of surface oxides on PPF is significantly lower than that of GC, but the electrochemical behavior is otherwise quite similar for the two materials.<sup>58</sup>

As noted above, the reduction of aryl diazonium reagents leads to irreversible bonding of aromatic molecules to carbon surfaces, by the scheme depicted in Figure 4. Unlike SAM and LB formation, diazonium reduction is not self-limiting, and can result in either monolayers or multilayers, depending on deposition conditions.<sup>59</sup> The reaction is quite versatile, having been applied to metals<sup>60</sup> and semiconductors<sup>61–63</sup> as well as carbon, and the diazonium ion may be generated in-situ from an aromatic amine<sup>64</sup> or reduced chemically rather than electrochemically.<sup>65</sup> Several reviews are available on diazonium modification of carbon and metal surfaces,<sup>41,60,66</sup> but several features of value to ME include a strong C–C surface bond (3.5–4 eV), high surface coverage, ability to form both mono- and multilayers, and conjugation between the graphitic  $\pi$  system and the aromatic surface molecule. The fact that the reactive phenyl radical is generated at the electrode surface causes the modification reaction to “patch” pinholes in the growing film, since those pinholes are the most likely sites for radical formation. Furthermore, the thinner regions of a growing multilayer are more electrochemically reactive, generating more radicals locally and preserving the flatness of the substrate at the monolayer surface. The surface coverage observed for diazonium derived molecular layers determined from XPS and other methods is somewhat lower than that expected for a close packed monolayer,<sup>14</sup> but there is no evidence for bare spots or pinholes in AFM scans of large (>1  $\mu m$ ) areas of the modified surface. The fact that copper<sup>67,68</sup> and other materials<sup>69</sup> may be deposited on such layers without resulting in direct metal-





**Fig. 3.** Process for making pyrolyzed photoresist film (PPF): a) Conventional positive photoresist is patterned with photolithography, then heated to 1000 °C in flowing  $\text{H}_2/\text{N}_2$  gas. b) AFM image of PPF after pyrolysis. c) AFM line scan across PPF surface, showing an rms roughness of  $< 0.5\text{ nm}$ .



**Fig. 4.** Surface modification by reduction of a diazonium reagent (a), formation of an aryl radical (b), surface bonding to form a covalent, conjugated monolayer (c), and further reduction to form a multilayer (d). Also listed are some features important in fabricating molecular electronic devices.

carbon "short circuits" (described below) is additional evidence for the absence of pinholes. Although multilayer formation from diazonium reduction can be considered an advantage, it is imperative that the final film thickness is verified by ellipsometry, AFM, or both.<sup>59,70–72</sup>

As noted earlier, the irreversible bonding of diazonium-derived aryl radicals to carbon surfaces prevents "assembly" into an ordered structure similar to a SAM or LB film. Nevertheless, diazonium-derived layers are partially ordered, with an average tilt angle relative to the PPF surface normal of  $31\text{--}44^\circ$ .<sup>73</sup> When multilayers are formed, the bonding between layers is covalent, and usually conjugated,<sup>60,74</sup> thus extending conjugation all the way from the interior of the PPF  $\pi$  system to the top surface of a multilayer film. Perhaps most importantly for practical applications, the strong bonding responsible for the disorder is also the basis of the high temperature tolerance described below for finished molecular junctions. Our group made the conscious decision that stability during metal deposition and of finished devices was sufficiently valuable to forego the order of the more fragile SAM and LB approaches. An alternative perspective of this issue is to consider the diazonium-derived adlayer to be an oligomer bonded to a very flat surface, and similar to a variation of organic electronics with very short transport distance. We will see below that when the "thickness" of an organic electronic device decreases to a few nanometers, new phenomena occur which are not observed in bulk materials. The bonding and conjugation of our 1–5 nm thick molecular junctions are responsible for their unusual behavior, and disorder is tolerable as long as junction performance is reproducible.

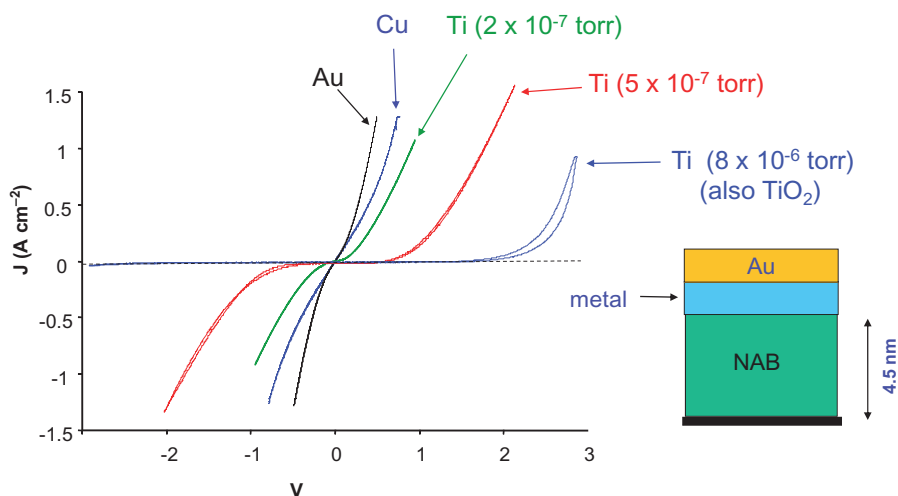
As noted in the Introduction, the application of the "top contact" to make a complete molecular junction has been a

difficult and often controversial process.<sup>9,16,31</sup> An early approach by our lab and several others was a Hg drop lowered onto a substrate/monolayer combination such as Hg/thiol,<sup>75,76</sup> Au/thiol<sup>77–79</sup> or PPF/aryl.<sup>80–82</sup> While the approach provided interesting results, reproducibility was a problem due in part to variable device area, and there was uncertainty about the presence of impurities on the Hg surface. A more recent variation is the indium-gallium eutectic,<sup>83–85</sup> which is liquid at room temperature, but the standard deviation of junction current is still quite large. The use of a conducting polymer as a top contact in SAM junctions has proven successful and can be applied in a massively parallel fashion with high yield,<sup>86–88</sup> but the resulting devices degrade above 50 °C.<sup>89</sup>

Our group is very interested in molecular devices which are amenable to massively parallel fabrication, but also have sufficient temperature stability to survive real-world applications. Vapor deposition of metals is widely used in the semiconductor industry, and was investigated early in ME experiments. However, there are some serious problems with vapor deposition which caused much confusion in the early literature, including the possibility of metal penetration of molecular layers, oxidation of the deposited metal, and reactions between “hot” metal atoms and the molecular layer, possibly with structural changes. These issues have been discussed extensively,<sup>9,16,67,83,90</sup> but the case of titanium provides an informative example. Early experiments in ME used Ti as an “adhesion” layer between the molecules and a conductor such as Au, in part because of the common use of Ti in promoting adhesion of metals to glass and silicon oxide surfaces.<sup>91,92</sup> Direct deposition of Au onto molecules usually resulted in

substrate-Au “shorts”, so it was reasoned that a Ti layer would prevent Au penetration. We followed the lead of these early papers in 2002, and started depositing Ti/Au contacts on diazonium-derived molecular layers on PPF.<sup>93,94</sup> Contemporary reports stated that Ti caused significant disruption to SAMs due to the high reactivity of Ti and its tendency to form Ti carbide during deposition on organic molecules.<sup>31</sup> We used Raman spectroscopy and XPS to show that our molecular layers were tolerant of Ti deposition,<sup>93</sup> but others reported serious damage,<sup>31,95,96</sup> so what is the truth?

As is often the case with microfabrication, the answer depends on the conditions. Ti atoms are indeed reactive, particularly with O<sub>2</sub> and H<sub>2</sub>O to form TiO<sub>x</sub> (usually mixed valent), and organics to form carbides. The residual gases in vacuum systems (mostly H<sub>2</sub>O) can react with Ti atoms vapor during deposition, to significantly alter the Ti species which interacts with the molecular layer on the sample. At very low backpressure (<10<sup>-7</sup> torr), the Ti metal is likely to form carbides and alter the structure of the sample, while at higher pressures the deposit is mostly Ti oxide. The effect of backpressure is shown rather dramatically in Figure 5, for the case of deposition onto a 4.5 nm thick layer of nitroazobenzene on PPF. The current-voltage behavior changes character completely between a backpressure of 8 × 10<sup>-6</sup> and 2 × 10<sup>-7</sup> torr, and the higher pressure produces a response similar to that obtained by depositing TiO<sub>2</sub> instead of Ti. We were unaware of this issue initially,<sup>97</sup> but ironically it may have been a benefit, since the rapid formation of TiO<sub>x</sub> might have reduced damage to the molecules by reactive Ti atoms. After correcting the problem,<sup>98</sup> we then pursued TiO<sub>2</sub> as an active component



**Fig. 5.** Effect of vacuum system pressure on the deposition of metals onto 4.5 nm thick layers of nitroazobenzene bonded to PPF. All cases were finished with a 15 nm thick Au layer to provide contact. Deposition of Ti at 8 × 10<sup>-6</sup> torr yielded very similar electronic response to that of direct deposition of TiO<sub>2</sub> from rutile. Current-voltage curves were obtained at 1000 V s<sup>-1</sup>, and  $V$  is stated as PPF relative to Au.

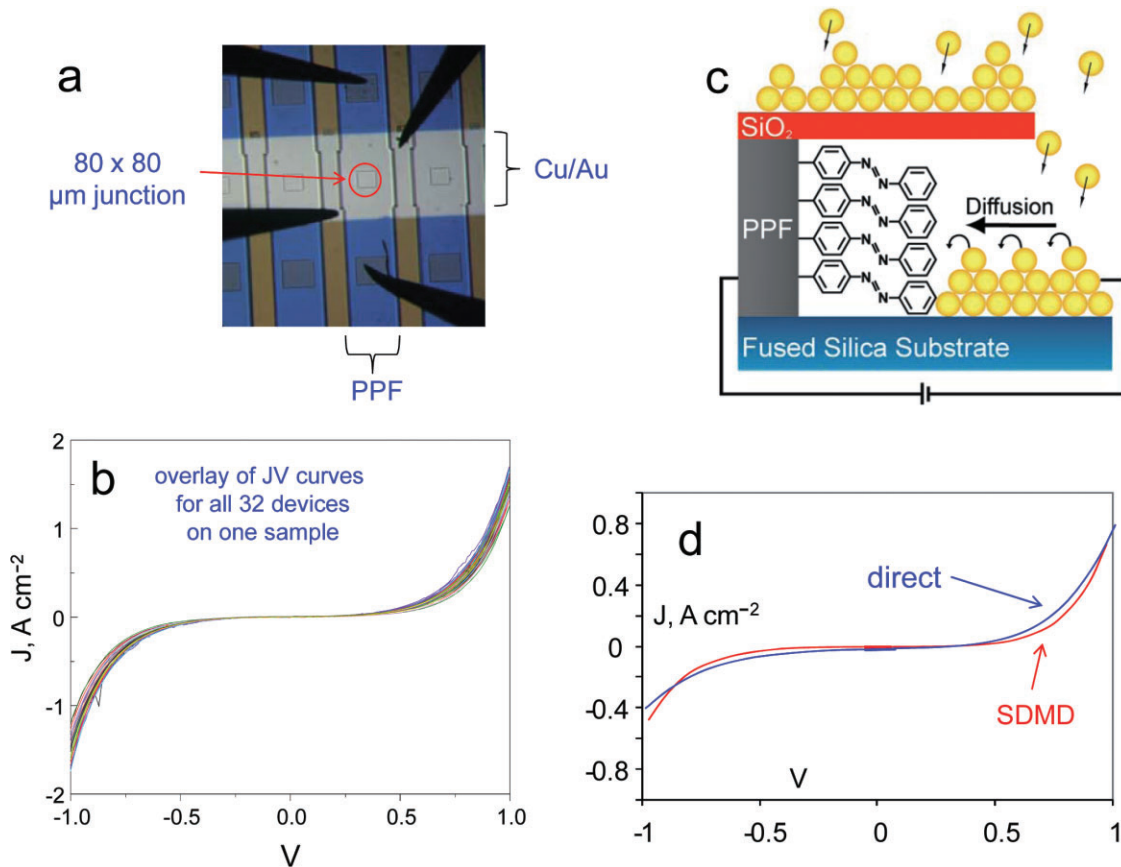
in “molecular heterojunctions” for investigating nonvolatile memory.<sup>94,99–103</sup> It is quite possible that some of the early “molecular memory” devices were actually based on TiO<sub>2</sub> redox chemistry,<sup>91,104–106</sup> and more recent papers propose a “memristor” device based on similar phenomena.<sup>107–110</sup> Similar devices have been reported which use redox reactions in metal oxides for memory,<sup>111</sup> many of which do not include a “molecular” component at all. The dramatic effect of backpressure on fabrication of molecular devices containing titanium is only one example of the many factors causing variability in results and difficulties in reaching firm scientific conclusions.

### Electronic Behavior

In order to avoid Ti and Au, we used electron-beam evaporated Cu as a top contact, with excellent results.<sup>68,112–114</sup> The current density-voltage ( $J/V$ ) behavior of microfabricated carbon/NAB/

Cu/Au molecular junctions is shown in Figure 6, along with a photo of the finished devices. There is no evidence of direct substrate-to-Cu “shorts”, which would appear as a vertical line through the origin in Figure 6b. The  $J/V$  behavior is independent of scan rate, and can be cycled for  $>10^9$  cycles to current densities  $>0.5$  A/cm<sup>2</sup>. As noted below, the devices are stable over a 5–450 K temperature range, and can tolerate 150 °C for  $>40$  hr<sup>113</sup> or 400 °C for five minutes.<sup>112</sup> Concerns about partial Cu penetration into the NAB layer prompted development of a “soft” deposition technique shown schematically in Figure 6c, in which Cu atoms are deposited remotely from the molecules and lose their thermal and kinetic energy before diffusing onto the molecules as “cold” atoms.<sup>67</sup>

Not only is very little energy imparted to the molecules, but Cu atoms must overcome the Cu-Cu binding energy (2–3 eV) in order to detach from the diffusing Cu “front” and enter the molecular layer. As shown in Figure 6d, the diffusion method yields very similar  $J/V$  curves to those obtained with the



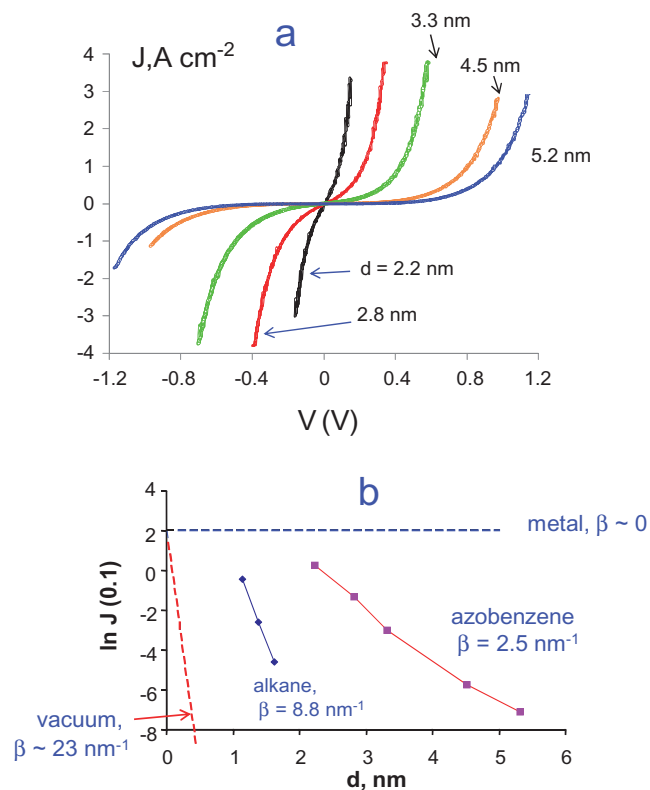
**Fig. 6.** a) Image of microfabricated PPF/NAB/Cu/Au molecular junction, showing the probes used to make contact. b) Overlay of  $J/V$  curves obtained from all 32 junctions on one “chip” of the type shown in panel a, recorded at  $1000 \text{ V s}^{-1}$ . c) Schematic of surface diffusion mediated deposition (SDMD) of Au onto NAB molecules bonded to PPF. d) Comparison of  $J/V$  curves for “direct” deposition with those from SDMD, stated as current density to compensate for quite different devices areas.

“direct” deposition used to obtain the curves of Figure 6b. Furthermore, the magnitudes of the current density for the same molecule and thickness are consistent over a wide range of device area, different fabrication methods, several investigators, and a three-year time span.<sup>113</sup> The success of “direct” Cu deposition is likely due to several factors, including the high stability of the C-C surface bond between PPF and a diazonium-derived radical, the higher surface energy of Cu compared to Au, and chemical interactions between Cu and the molecular layer.<sup>9,112,113</sup> Whatever the cause of successful deposition of Cu onto molecular layers, it may have practical importance to the eventual commercial applications of molecular electronics, since “direct” metal vapor deposition is commonly used in the semiconductor industry.

### Electron Transport Mechanism

Now that we have reproducible carbon/molecule/Cu devices in hand, we turn to the main scientific question: How are electrons transported through molecules? Important probes of transport mechanism are provided by the variation of  $JV$  response with molecular layer thickness and with temperature. Figure 7a shows  $JV$  curves for a series of azobenzene junctions which demonstrate the strong dependence of current on molecular layer thickness. A plot of  $\ln J(0.1 \text{ V})$  versus thickness (Figure 7b) has a slope of  $2.5 \text{ nm}^{-1}$ , indicating a decrease of  $e^{-2.5}$  or a factor of 12 for every additional nm of molecular layer thickness. Also shown in Figure 7b is similar data for a series of alkyl amines of different lengths bonded to PPF by electrochemical oxidation. The slope in this case is  $8.8 \text{ nm}^{-1}$ , indicating a much steeper decrease in current with molecular length. The temperature dependence for azobenzene junctions is shown in the Arrhenius plot of Figure 8a, along with an example of a  $JV$  curve at 5 K. The  $JV$  response changes very little between 5 and 200 K, with an apparent activation energy of  $<0.05 \text{ meV}$ . The slope at higher  $T$  is  $37 \text{ meV}$ , and is likely due to Fermi function broadening within the contacts.<sup>68</sup> Arrhenius plots for other molecules and thicknesses are similar, and there is no obvious variation with bias voltage. Finally, Figure 8b compares the room temperature  $JV$  response for three different molecules, illustrating the strong effect of molecular structure. Note that fluorene and  $\text{C}_{12}\text{H}_{25}\text{N}$  layers with comparable thicknesses exhibit a large difference in  $JV$  behavior, with the current densities ca. 200 times greater for fluorene than for the alkane.

Many electrochemists would look at the  $JV$  curves of Figure 6a and immediately think “activated electron transfer, a la Butler-Volmer, Marcus-Levich”, since it shows an exponential dependence on voltage. There is no (known) mass transport in a molecular junction, so the linear plot of  $\ln J$  versus  $V$  is analogous to the Tafel plot used to probe electron transfer

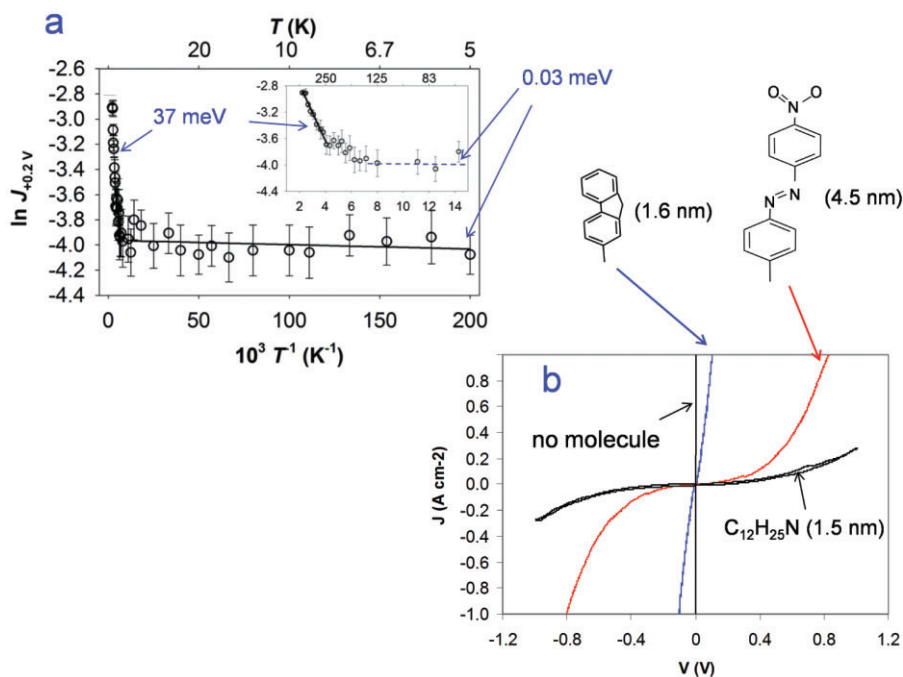


**Fig. 7.** a.  $JV$  response for PPF/azobenzene/Cu/Au molecular junction with varying molecular layer thicknesses, as indicated. b. Plots of  $\ln(J)$  at  $V = 0.1 \text{ V}$  for alkanes<sup>67</sup> and azobenzene<sup>68</sup> vs. the molecular layer thickness. For a vacuum, the slope depends on the contact work function, and is  $23 \text{ nm}^{-1}$  for a work function of  $5.0 \text{ eV}$ .

kinetics. However, the near-zero Arrhenius slope and the significant current density observed at 5 K (Figure 8a) are not consistent with any activated process, including the reorganization energy inherent in Marcus-Levich theory. The thickness dependence of Figure 7b shows an exponential decrease in current density with molecular layer thickness, but with quite different slopes for aliphatic compared to aromatic molecules. Furthermore, the symmetry of the  $JV$  curves would be expected only for equal concentrations of oxidized and reduced species as well as a transfer coefficient of 0.5 in a system abiding by Marcus-Levich theory. Whatever electron transport mechanism is proposed to account for the  $JV$  behavior of molecular junctions, it must be consistent with exponential dependencies on thickness and voltage, near-zero Arrhenius slopes, and the symmetric  $JV$  curves, which are independent of scan rate and may be repeated for billions of voltage cycles.

Electron tunneling in “metal/insulator/metal” structures has been studied for several decades, but electrochemical experiments on tunneling through molecular layers in the 1990s are particularly relevant to the present discussion. The





**Fig. 8.** a) Arrhenius plot of  $\ln J(0.2 \text{ V})$  vs  $1/T$  for an azobenzene molecular junction, with the inset showing a narrower temperature range.<sup>68</sup> Apparent slope in the range of 5–200 K is  $<0.05 \text{ meV}$ . b) Overlaid  $JV$  curves for decylamine, fluorene, and NAB junctions with the thicknesses indicated. Response of a PPF/Cu device with no molecular layer is shown for comparison.

apparent heterogeneous electron transfer rate constant,  $k^0$ , for a redox reaction in electrolyte solution was determined for modified electrodes, usually SAMs on Au. Prominent among these experiments was the case of ferrocene (Fc) bonded to the end of an alkyl monolayer, in which the length of the alkyl chain was varied from  $\sim\text{C}_8$  to  $\text{C}_{20}$ .<sup>13,115–118</sup> The redox reaction  $\text{Fc}/\text{Fc}^+$  was conventional, but the electron involved was transported through the alkane chain. The mechanism was determined to be quantum mechanical tunneling, in which an electron in the Fc unit had a finite probability of appearing in the Au, thus enabling Fc oxidation by tunneling through the alkane layer. The dependence of the  $k^0$  for Fc oxidation was exponential, with a slope of  $\ln(k^0)$  versus alkane length of ca.  $8 \text{ nm}^{-1}$ . A series of careful experimental studies and theoretical predictions concluded that the attenuation coefficient ( $\beta$ ) for the alkanes was smaller than that predicted for a vacuum ( $\sim 23 \text{ nm}^{-1}$ ) due to interactions between the molecular orbitals and the tunneling electron, a process referred to as “superexchange”.<sup>119–121</sup> In a molecular junction, the Fc and electrolyte are replaced by a second conductor, but the electron can still tunnel through the molecular layer. Comparisons of  $\beta$  for different paradigms and molecules can be quite informative, since  $\beta$  is not dependent on the magnitude of the current; just its thickness dependence. Table 1 is a list of observed  $\beta$  values from electrochemistry, molecular junctions, and single-molecule experiments. Note

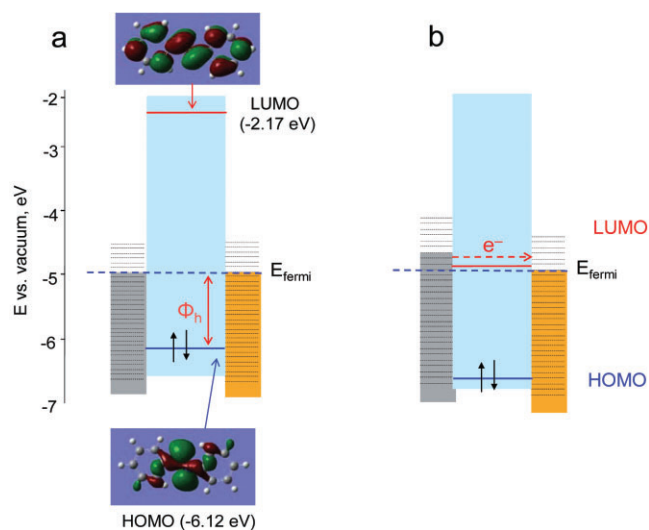
that there is good consistency between  $\beta$  values for quite disparate paradigms for molecules with similar chemical structures. For example, a single molecule of the polyolefin carotene suspended between an STM tip and an Au surface has a  $\beta$  value of  $2.2 \text{ nm}^{-1}$ , while electrochemistry through a layer of conjugated aromatic molecules has a  $\beta$  value of  $2.1 \text{ nm}^{-1}$ . Older experiments with donor-bridge-acceptor molecules with a polyolefin bridge reported  $1.4 \text{ nm}^{-1}$ , while PPF/azobenzene/Cu molecular junctions yielded  $2.5 \text{ nm}^{-1}$ . Consistency across experiments involving quite different structures, with either 1, 2, or no conducting “contacts” is good evidence that similar phenomena control ET through molecules.<sup>34,86</sup> Note also that the  $\beta$  values fall into three distinct regions: alkanes with  $\beta = 7\text{--}10 \text{ nm}^{-1}$ , conjugated and aromatic molecules with  $\beta = 2\text{--}6 \text{ nm}^{-1}$ , and very low values ( $<1 \text{ nm}^{-1}$ ) for porphyrins and oligothiophenes.

A great deal has been written about the factors controlling tunneling in molecular junctions, based on the Simmons model, the Landauer-Buttiker approach, and the non-equilibrium Green’s function formalism. Only some of the consequences of these discussions to the PPF/molecule/metal devices will be noted here, as the theoretical details are extensive. The Simmons model<sup>122–124</sup> is based on tunneling in metal/insulator/metal junctions and in simplified form states that:

**Table 1.** Experimental attenuation coefficients ( $\beta$ ).<sup>[a]</sup>

Molecule type	Method	System	$\beta$ nm <sup>-1</sup>	Ref.
alkane	electrochemistry <sup>[b]</sup>	Au/alkanethiolate	8.0	[136]
alkane	single-molecule junction	Au/alkanedithiol/Au	8.4	[137]
alkane	ensemble junction	Au/alkanedithiol/PEDOT:PSS	5.7–6.6	[87]
alkane	ensemble junction	Ag/alkanethiolate/eGaIn	4.3	[85]
alkane	ensemble junction	PPF/alkane diamine/Au	8.8	[67]
aromatic	electrochemistry <sup>[b]</sup>	carbon/phenylene	2.2	[15]
phenylene ethynylene	electrochemistry <sup>[b]</sup>	Au/thiolate	3.3	[138]
oligothiophene (OTP)	STM break junction	Au/OTP/Au	1.0	[139]
azobenzene, nitroazobenzene	ensemble junction	PPF/AB/Cu/Au	2.5	[68]
carotenoid polyenes	STM break junction	Au/CP/Au	2.2	[140]
phenylene ethynylene	cp-AFM <sup>[c]</sup>	Au/PE/Au	2.1	[141]
oligophenyleneimines	cp-AFM	Au/OPI/Au	3.0	[126]
porphyrins	STM break junction	Au/porphyrin dithiol/Au	0.4	[127], [142]

[a] Adapted and updated from reference [9]. [b] Redox couple in solution, tunneling through a molecular layer on a modified electrode. [c] Conducting-probe atomic force microscopy of self-assembled monolayers.



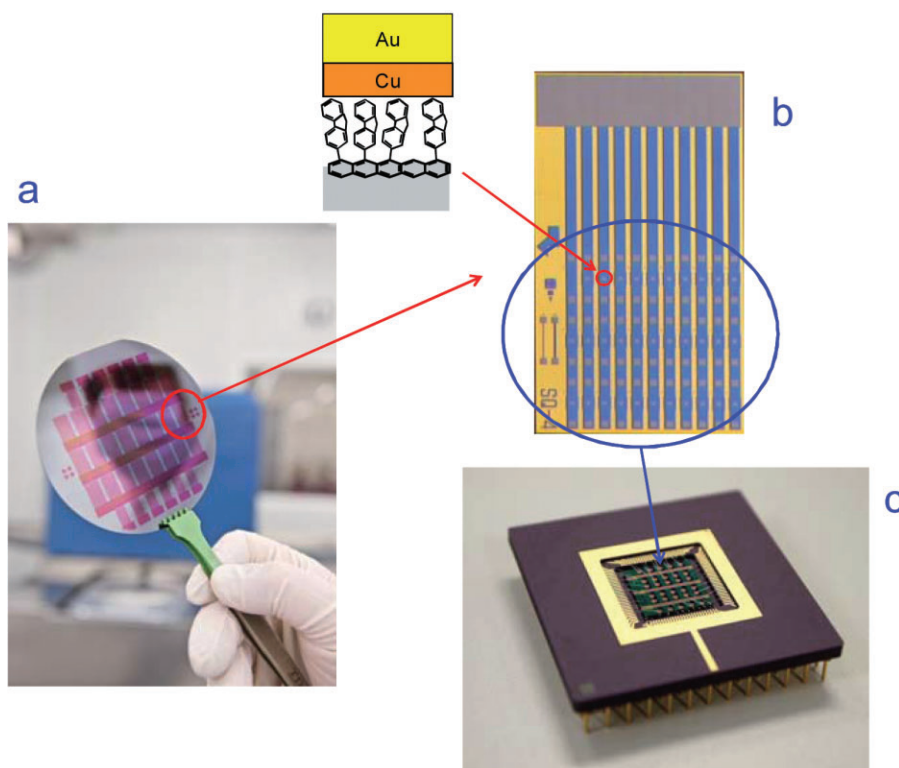
**Fig. 9.** a) Schematic energy levels for a PPF/azobenzene/Cu molecular junction. Orbital energies for the free azobenzene molecule are shown, and the shaded areas represent filled orbitals in the two contacts.  $\phi_h$  is the tunneling barrier for hole transport mediated by the molecular HOMO. b) Resonant transport of electrons through the molecular LUMO, which is possible when the LUMO energy is close to the contact Fermi level.

$$J = A \exp(-Bd\phi^{1/2}) \quad (1)$$

where  $A$  and  $B$  are constants,  $d$  is the molecular layer thickness, and  $\phi$  is the tunneling barrier. Equation (1) predicts the exponential dependence of thickness, and that beta is related to the tunneling barrier height. The probable energy level diagram which determines the barrier is shown in Figure 9a, for the case of PPF/azobenzene/Cu. The orbital with an energy closest to the Fermi level of the contacts is the molecular HOMO, resulting in

a tunneling barrier for hole transport of  $\phi_h$ . While this simple model correctly predicts the dependence of current density on the HOMO energy, the details are far from simple. The HOMO energy increases with the molecular length of an azobenzene oligomer, and this significantly decreases the apparent  $\beta$ .<sup>68</sup> Furthermore, the dielectric constant and the effective electron mass also depend on molecular length, and can have significant effects on a more detailed Simmons analysis. The reader might question the value of a theory which requires several adjustable parameters to fit the experimental results, and this concern applies to transport theories beyond Simmons.

It is worthwhile at this point to distinguish between “through-space” tunneling, which can occur across a vacuum gap, and “through-bond” tunneling, which relies on the presence of a molecule to increase the tunneling rate. As already noted, there is a strong dependence of the tunneling current on molecular structure and length (Figures 7 and 8b), although the specific factors underlying these effects are complex. While “through-bond tunneling” is a reasonable description of such enhanced currents, one should avoid the term “injection” which is often used to describe electron transport between a metallic contact and an organic semiconductor. Such “injection” involves residence of the electron (or hole) in orbitals of the organic semiconductor, with possible reorganization of the molecular structure and attendant activation barrier. In contrast, through-bond tunneling is not activated, and occurs with static nuclear positions, possibly at temperatures close to absolute zero. The control of tunneling current by molecular structure is one of the basic phenomena at the heart of Molecular Electronics. At the current juncture, it is clear that electron transport in molecular junctions is a complex process, and likely will require sophisticated treatments to “rationally design” electronic behavior by changes in molecular structure.



**Fig. 10.** Image of a 100 mm microfabricated PPF substrate for 36 samples with 32 junctions each (a), and a magnified image of one sample “chip” (b). Image (c) is a completed sample of 32 junctions which is wire bonded and mounted in a commercial integrated circuit package. The long axis of the “chip” in panel b is 3 cm, and the active junction area ranges from  $2.5 \times 2.5$  to  $300 \times 300$   $\mu\text{m}$ .

Nevertheless, there are interesting qualitative observations and questions related to the possible applications of charge transport through molecules, many of which involve concepts from electrochemistry. First, with an exponential dependence of transport on thickness, will there be severe limits on the “size” of molecular electronic circuits? If  $\beta = 10 \text{ nm}^{-1}$ , the current density should decrease by more than four orders of magnitude for every 1 nm of “circuit”, which is indeed a serious limitation. However, as  $\beta$  decreases transport can be extended significantly, and  $\beta$ 's approaching zero have been reported (Table 1). As will become apparent, the exponential,  $T$ -independent transport is characteristic of tunneling, but there are other transport modes which are much longer range. Second, a  $\beta$  value of  $<1 \text{ nm}^{-1}$  is likely due to a mechanism other than tunneling, notably “hopping”, also known as “redox exchange”. A quite clear transition from  $T$ -independent tunneling with  $\beta = 3 \text{ nm}^{-1}$  to  $T$ -dependent transport with  $\beta = 0.9 \text{ nm}^{-1}$  has been described for aromatic monolayers, with the transition occurring at a thickness of 4 nm.<sup>125,126</sup> However, a recent report indicates that very low  $\beta$  value may be observed for coherent, non-hopping transport.<sup>127</sup> Redox exchange is effective over long distances

( $>1 \mu\text{m}$ ), and has been described in detail for both redox polymers<sup>128–130</sup> and organic semiconductors.<sup>1,131</sup> Third, what happens when the tunneling “barrier” approaches zero, often called “resonant transport”, or sometimes the oxymoron “resonant tunneling”? Such transport should work over long distances, and may be more strongly dependent on orbital energies and shapes than tunneling. One could describe the behavior of the alkanes and aromatic molecules shown in Figure 7b as “barrier electronics”, in that the electron is tunneling through a barrier over quite short distances. With resonant transport, the electron is “injected” into an orbital, and may be transported long distances without losses. Fourth, if resonant transport is realized, under what conditions will the molecule reorganize, as expected for a molecule in solution? One treatment compares the “tunneling time” to the vibrational period, and proposes that reorganization to a radical anion or cation will occur once the tunneling time exceeds the time required for molecular reorganization.<sup>132,133</sup> We have reported several examples of redox reactions which occur in molecular junctions, in particular when an oxide tunneling barrier is present.<sup>94,98,99,101,103,134,135</sup> Readers will likely recognize that many of the concepts underlying the various transport

mechanisms are shared by both electrochemistry and molecular electronics: tunneling, alignment of energy levels, activated electron transfer, redox exchange, and reorganization during redox reactions.

## Summary and Outlook

The main outcome of an approach to molecular electronics based on flat carbon substrates, diazonium surface modification and direct metal deposition is the reproducible electronic behavior shown in Figure 6a. The strong dependence of electronic response on molecular structure (Figure 8b) and the insights into transport mechanism provided by thickness and temperature dependencies provide excellent evidence that the observed electronics is indeed “molecular” and not some artifact of defects or the device structure. Furthermore, the carbon/molecule/Cu junction design is amenable to fabrication of many devices in parallel, using methods common to the semiconductor industry. An example is shown in Figure 10, from a process involving PPF fabrication across a 100 mm wafer, formation of molecular layers via diazonium chemistry, and “direct” deposition of copper.<sup>113</sup> It is technically feasible to make massively parallel molecular junctions by straightforward adaptation of existing fabrication methods, and integration of molecular devices with existing microelectronics should not require fundamentally different approaches to manufacturing.

People often ask about when molecular electronic devices are likely to appear in consumer electronics or other end-uses. My response is quite pragmatic: as soon as molecular devices can outperform silicon, in terms of electronic performance, cost, power consumption, etc. I am sure that interesting science will continue to emerge in the area of molecular electronics, but commercial realization will depend on the ability to improve on silicon. Most people in the area envision an era of “hybrid” devices, in which highly advanced and existing silicon technology is used for addressing and support electronics, while molecular devices add some new function not readily achieved with silicon alone. Examples include chemical sensing, nonvolatile memory, and “flexible electronics” amenable to incorporation in clothing, packaging, windows, etc. Heat management and power consumption are currently serious problems with silicon devices due to their high device density, and molecular components may have much lower power demands in certain applications. As stated previously,<sup>9</sup> the current juncture may represent the “end of the beginning” for molecular electronics, in that various phenomena and paradigms have been investigated and understood, and the time has come to exploit the huge variety of molecular structures and electronic properties for both fundamental science and practical applications.

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