University of Alberta

Microfabrication and Characterization of Carbon/Molecule/Metal Molecular Junctions

by

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Dedicated to my family

ABSTRACT

Carbon/molecule/Cu/Au molecular junctions were fabricated on 4-inch silicon wafers using microfabrication techniques common in commercial semiconductor manufacturing. Electron-beam deposited carbon films are introduced as substrates, and the junctions exhibited high yield and excellent reproducibility. Current density-voltage characteristics of the devices were area scaling, weakly dependent on temperature and exponentially on molecular film thickness, and quantitatively similar to those of devices made with other techniques reported previously in our group, which contained pyrolyzed photoresist films as substrates. Furthermore, the test of cycle life and thermal stability reveals that the devices can survive at least under several millions of potential cycles at room temperature in air, and elevated temperature up to 150 °C in vacuum for >40 hours. Parallel fabrication, thermal stability, and high yield are required for practical applications of molecular electronics, and the reported results provide important steps toward integration of molecular electronic devices with commercial processes and devices.

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LIST OF ABBREVIATION

ACN	acetonitrile
AFM	atomic force microscopy
BOE	buffered oxide etching
CCD	charge coupled device
cm	centimeter
CMOS	complementary metal-oxide semiconductor
CP-AFM	conducting probe atomic force microscopy
CV	cyclic voltammetry
EGaIn	eutectic Gallium-Indium
Fc	ferrocene
FL	fluorene
HMDS	hexamethyldisilazane
HOMO	highest occupied molecular orbital
LB	Langmuir-Blodgett
LOFO	lift-off-float-on
LUMO	lowest unoccupied molecular orbital

MCBJ	mechanically controllable break junction
µm	micrometer
NAB	4-nitroazobenezene
nm	nanometer
NDR	negative differential resistance
PECVD	plasma enhanced chemical vapor deposition
PEDOT:PSS	poly(3,4-ethylenedioxythiophene) stabilized with poly(4-styrenesulphonic acid)
PPF	pyrolyzed photoresist films
PR	photoresist
QCM	quartz crystal microbalance
RGA	residual gas analyzer
Rms	root mean square
Rsd	relative standard deviation
SAMs	self-assembled monolayers
SCE	saturated calomel electrode
SEM	scanning electron microscope
SPM	scanning probe microscopy

STM	scanning tunneling microscopy
$TBABF_4$	*n*-tetrabutylammonium tetrafluoroborate
TEM	transmission electron microscopy
THF	tetrahydrofuran
UHV	ultra high vacuum
via	vertical interconnect access
XPS	X-ray photoelectron spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Introduction of molecular electronics

The term “molecular electronics” is used to describe “electronic components based on a single molecule or an assembly of molecules”.[1] In 1974, Aviram and Ratner first proposed a method to make “molecular rectifier” by use of a single molecule,[2] which initiated the theoretical and experimental studies of molecular electronic devices. The potential advantages of these devices compared to current microelectronic devices based on semiconductor technology mainly include lower fabrication cost, higher density and most interestingly, more functions arising from various molecules. Major research efforts have been made and some interesting electronic characteristics of the molecular devices have been reported, such as conductance switching[3] and negative differential resistance (NDR)[4, 5]. In particular, due to the advance of experimental measurement and device fabrication techniques, this field has grown very fast in the past decade. Readers can find several recent reviews to learn more about the field of molecular electronics.[1, 6-9] Although it is uncertain when Moore’s Law will approach a limit with the current silicon-based semiconductor microelectronics, molecular electronics is considered as an alternative to extend Moore's Law. However, to date, no evidence shows that molecular electronics can compete with silicon-based microelectronics in terms of operation speed, power consumption, stability, etc.[1] The possible future for molecular electronics would be integration with current silicon-based technology instead of taking the place of silicon-based microelectronics.[8]

The purpose of this chapter is to provide a brief overview of past research in molecular electronics. Firstly, the components of a molecular junction including several substrate/molecule systems and a variety of molecular electronics testbeds are reviewed in section 1.2. Secondly, an example of integration of molecular junctions is illustrated in section 1.3. Finally, the research objective of this thesis is described.

1.2 Components of a molecular junction

As shown in Figure 1.1, a molecular junction contains two electrodes and a single molecule or an ensemble of molecules sandwiched between the two electrodes. The electrodes are usually either metals or semiconductors. The molecules are usually attached to the bottom electrode or substrate by chemical reactions, chemical adsorptions, e.g., self-assembled monolayers (SAMs) on Au, or electrostatic interaction, e.g., Langmuir-Blodgett (LB) films. The fabrication of a molecular junction generally employs a bottom-up approach, in which one electrode is used as the substrate, and then a monolayer or multilayer of organic molecules is deposited, then finally a second electrode or top contact is fabricated on top of the molecular layer to make a complete junction.

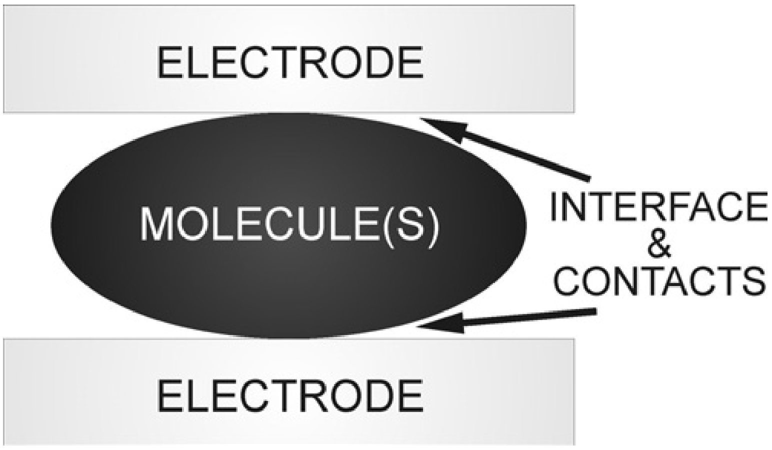


Figure 1.1 Schematic illustration of a molecular junction. Adapted from ref 1.[1]

1.2.1 Substrate/molecules

The substrates used for making molecular junctions include metals, e.g., Au, Cu, Hg etc., and semiconductors, e.g., Si and GaAs. Based on the methods used for attaching molecules to substrates, the molecular devices can be categorized into three types: Langmuir-Blodgett (LB) films[10, 11], self-assembled monolayers (SAMs)[12] and molecular layers irreversibly bonded on carbon or silicon substrates. Figure 1.2 shows several linker types for anchoring the molecules onto different substrates used in single-molecule or ensemble junctions. The nature of the interaction between the molecules and substrate determines the bonding strength, surface dipoles, orientation of molecules, molecular film stability, the degree of film order, etc., all of which can significantly affect the overall electronic properties of the junction.

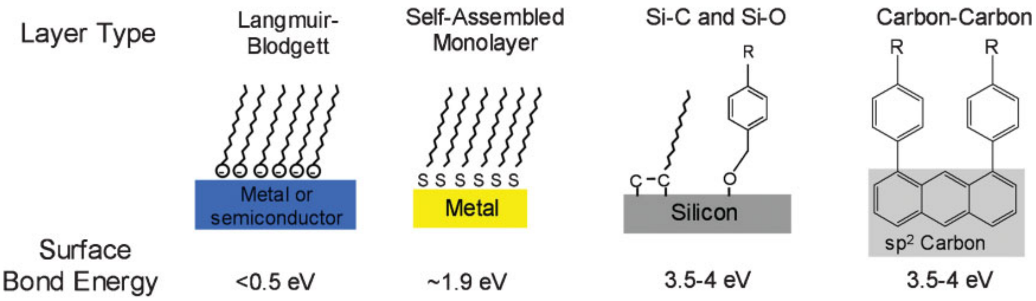


Figure 1.2 Schematic of different types of surface attachment. Adapted from ref 8.[8]

1.2.1.1 Langmuir-Blodgett films

The Langmuir-Blodgett (LB) technique is used to deposit well ordered and compact thin organic films on solid substrates. The molecules comprising the films are amphiphilic and one end of the molecule is hydrophilic and the other end is hydrophobic. The interaction between the molecular layer and substrate is physical adsorption, for instance, electrostatic force, which is very weak (<10 kcal/mol or 0.5 eV, see Figure 1.2). In LB technique (see Figure 1.3), the molecular film is spread at the air/water interface and then compressed to form a highly ordered monolayer known as a Langmuir film. By transferring the Langmuir film to a solid substrate, e.g., Au, a Langmuir-Blodgett (LB) film is created at the air/solid interface. If the transfer procedure is repeated, a multilayer may be produced. Several groups have fabricated molecular electronic devices based on LB monolayers or multilayers and the most interesting results are the observations of electrical rectification behavior through LB films of hexadecylquinolinium tricyanoquinodimethanide[13-16] and the fabrication of conductance switches based on LB films of rotaxanes and catenanes.[17-21]

There are several advantages of LB film based molecular devices. The film has a highly ordered structure which can be transferred to almost any kind of solid substrate, and the thickness of the LB multilayer can be controlled precisely since it is formed in a layer by layer technique. However, LB film based molecular devices have their own limitations: (i) due to the weak bonding strength between LB film and the substrate, the structure of the film might change over time;[22] (ii) the transfer ratio of the LB film (defined as the ratio of monolayer area removed from the water subphase and the substrate area coated[23]) is low, which hinders its application as manufacturing technique.[24] For instance, a transfer ratio of 17% was observed by the Metzger group;[25] (iii) the applications of LB based devices are limited to amphiphilic molecules.[24]

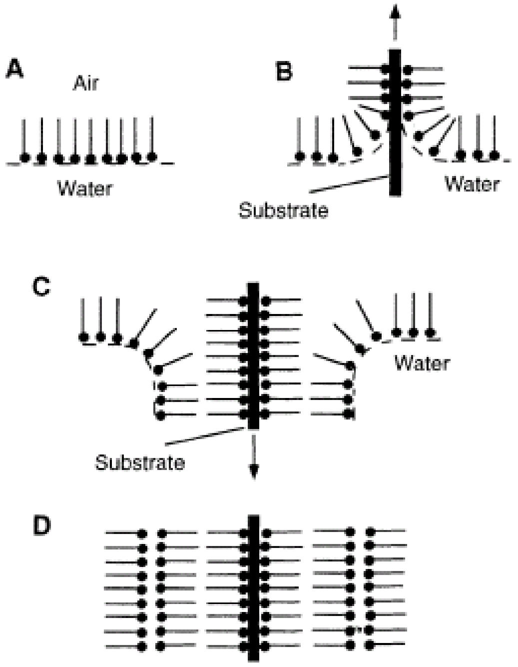


Figure 1.3 Conventional schematic of the LB technique using a hydrophilic substrate. In the first step **(A)**, a suitable amphiphilic molecule is dissolved in a volatile solvent that is then spread at the air water interface to form a Langmuir monolayer. With a barrier, the area of the trough can be altered to change the local density of the molecules, and usually the local organization and order as well. To form the LB film **(B)**, a substrate is passed through the interface a given number of times, with each pass adding another monolayer to the LB film with alternating molecular orientations **(C)** and **(D)**. Adapted from ref 26.[26]

1.2.1.2 Self-assembled monolayers (SAMs)

Self-assembled monolayers, or SAMs, unlike LB films, are ordered monolayers of organic molecules formed by spontaneous chemisorption on solid substrates (see Figure 1.4). The head groups of the molecules in the SAMs are chemically adsorbed to the substrate while the tail groups of the molecules form the exposed surface of the SAMs. The field of self-assembled monolayers has grown very fast since 1980s when Nuzzo and Allara reported that SAMs were prepared on Au surface by adsorption of disulfides from dilute solutions.[27] Many systems of SAMs have been investigated, for instance, fatty acids on metal oxides,[28-30] organosilion derivatives on hydroxylated surfaces,[12, 31, 32] and thiols on metal or semiconductor surfaces, e.g., Au[33, 34], Hg[35], GaAs[36], etc. To date, the most extensively studied system has been the SAMs of alkanethiolates on Au surface. The reasons are probably (i) Au does not form a stable oxide surface in air,[22] and therefore it is easy to clean the surface; (ii) compared to SAMs made by organosilanes which are very moisture-sensitive, SAMs of thiols on Au with high quality are much easier to prepare.[22] As a result, molecular electronic devices based on thiols/Au especially alkanethiols on Au have been recognized as one of the most commonly used systems in molecular electronics. An immense literature about molecular junctions based on SAMs/Au including device fabrication and electron transport mechanism study is available. Compared to LB films, SAMs of thiols on Au show a stronger Au-S bond (~40 kcal/mol or 1.7 eV) and thus greater stability. However, the Au-S bond is still susceptible to bond rearrangement and external disruption. Consequently, molecular electronic devices based on thiols/Au structure have suffered low yield problems when device area is larger than the domain size of the SAMs.[37] Electrical short circuits often occur in SAM based devices during the vapor deposition of metal top electrode due to the disruption of SAMs by evaporated metals and metal penetration into SAMs.[38-40]

For instance, a yield of ~1% of SAM/Au working devices made by direct metal vapor deposition was reported by Lee group.[41, 42] Moreover, the stability of SAM based electronic devices is another issue. It was reported that the electronic devices based on SAMs of conjugated thiolate molecules showed a lifetime of less than 2 weeks.[43] The disadvantages of low yield and poor stability of SAM based devices have limited their commercial applications.

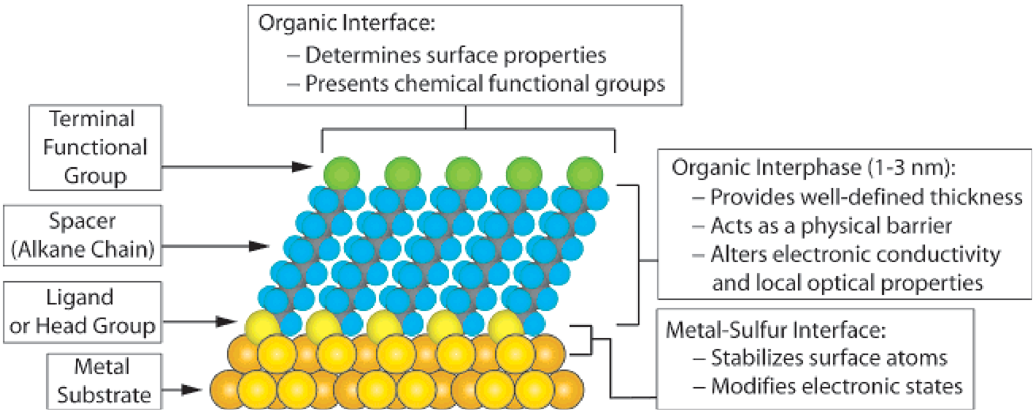


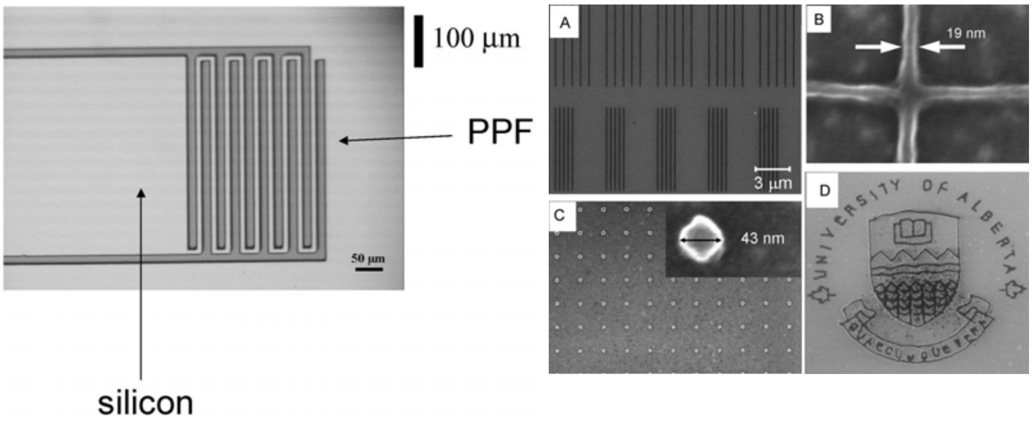
Figure 1.4 Schematic diagram of an ideal, single-crystalline SAM of alkanethiolates on gold (111) surface. Adapted from ref 44.[44]

1.2.1.3 Irreversibly bonded molecules

The irreversibly bonded molecular films on solid substrates are quite different from the LB films and SAMs in the nature of bonding between the molecules and substrates. The bond is strong and irreversibly formed, but the molecular film is less ordered than LB films and SAMs. One might expect that those features will play an important role in the properties of electronic devices based on irreversibly bonded molecular films. The commonly used solid substrates for these electronic devices involve semiconductors such as silicon and non-metal conductors like carbon.

Silicon is the most widely used semiconductor in microelectronics, which partially explains why it has received much attention in molecular electronics. Furthermore, there are a number of surface modification reactions available for silicon substrates, which usually involve anchoring the molecules via Si-C or Si-O bonds.[45, 46] Thirdly, the molecular layers covalently bonded to the silicon surface are highly robust and stable due to the high bond strength of Si-C and Si-O-C (80-100 kcal/mol or 3.5-4 eV). It has been shown that silicon surface modified with hydrocarbons can survive under the treatment of acids, bases, organic and aqueous solvents, as well as high temperature.[47-50] Fourthly, by changing the dopant type and concentration, the interaction between the silicon and molecules can be tuned, leading to novel electrical behavior, e.g., negative differential resistance (NDR).[51, 52]

Carbon materials such as graphite, glassy carbon, diamond, etc. have been widely used in electrochemistry as electrodes for a long time. The advantages of carbon electrodes include low cost, wide potential window, relatively inert electrochemistry and a variety of available surface modification reactions.[53] Recently, pyrolyzed photoresist films (PPF) have been used as substrates to fabricate molecular junctions due to their unique features.[6, 54, 55] First, the C-C bond between the substrate and organic molecules is formed irreversibly and thus very strong (~100 kcal/mol or 4 eV) compared to Au-S (40 kcal/mol or 1.7 eV) in SAMs and electrostatic force in LB films (<10 kcal/mol or 0.5 eV). Secondly, the PPF surface is very flat with a root-mean-square (rms) roughness of <0.5 nm as measured by atomic force microscope (AFM),[56] which is crucial for making molecular devices since the length scale of the molecules is several nanometers. PPF is structurally and electronically similar to glassy carbon. Transmission electron microscopy (TEM) and Raman spectroscopy indicate that PPF is made of disordered graphitic carbon.[55] The resistivity is ~0.006 Ω·cm, compared to 0.0055 Ω·cm for glassy carbon heat treated at 2000 ˚C. Electronically, PPF behaves like a metal with no apparent band gap. Thirdly, it is easy to prepare PPF and it can be patterned with photolithography. After spin coating and patterning the photoresist film on a substrate, e.g., Si or quartz, with conventional photolithography, the film is pyrolyzed at 1000 ˚C under a reducing atmosphere of 5% H_2 and 95% N_2.[55] A micrograph of patterned PPF on silicon is shown in Figure 1.5 (a).[53] Even smaller features can be fabricated with e-beam lithography as shown in Figure 1.5 (b).[57] Moreover, PPF surface can be modified easily by electrochemical reduction of aromatic diazonium reagents or electrochemical oxidation of amines. Since both reactions are radical based, they are not self-limiting and multilayers can be formed.[58] However, by controlling the reaction parameters during the electrochemical deposition of molecular films, monolayers or multilayers with desired thicknesses can be obtained. The resulting molecular layers are compact with low density of pinholes, but randomly orientated due to the strong bond of C-C.



(a) (b)

Figure 1.5 **(a)** Photomicrograph of pyrolyzed photoresist film pattern on silicon substrate. Adapted from ref 53.[53] **(b)** SEM images of various carbon nanostructures. A) Arrays of 50-nm-wide lines. B) Cross pattern with a 19-nm linewidth. C) Array of 40-nm-diameter disks. Note that the disks appear to be rings due to the scattering of the SEM e-beam off the edges of the structures during imaging. D) University of Alberta seal with 50-nm linewidths. Adapted from ref 57.[57]

More recently, Blackstock et al. reported a method to prepare thin-film carbon electrode by electron beam evaporation on silicon substrate.[59] Raman spectra indicate that the e-beam carbon film has an amorphous structure. The electrochemical properties of the electrodes resemble glassy carbon, with the measured electron transfer rate to redox systems in solution comparable to that of glassy carbon. The e-beam carbon thin film on silicon exhibits an extremely flat surface with an rms roughness of ~1 Å, which will potentially find applications requiring very flat surfaces such as molecular electronics. Moreover, the carbon film can be deposited through a shadow mask or a patterned photoresist mask so that features as small as ~1 μm can be obtained.

1.2.2 Top contacts and molecular electronics testbeds

Depending on how the top contacts are made on the molecules, a variety of experimental paradigms have been developed. In the following sections, several commonly used approaches will be reviewed. Every approach has its advantages and limitations. Therefore, none of these has become a dominant method for junction investigations. Based on the number of molecules involved in making a molecular junction, the testbeds can be categorized into two classes: single-molecule and ensemble (~10^3-10^{12} molecules) molecular junctions.[8, 60] In general, scanning probe microscopy (SPM) and break junctions are used to test single-molecule junctions, and other methods described in the following sections including cross wire, liquid metal, physical vapor deposited metal and conducting polymer are for ensemble junctions.

1.2.2.1 Scanning probe microscopy (SPM)

Scanning probe microscopy (SPM) methods including scanning tunneling microscopy (STM) and conducting probe atomic force microscopy (CP-AFM) are used to study the conductance of single molecules or a small collection of a few molecules. For the junction measurement, an STM tip or CP-AFM tip acts as the top electrode, and a bias is applied between the tip and substrate while the current is monitored. During the measurement, the molecules involved in the junction do not need to be isolated from the neighboring molecules.

In STM (see Figure 1.6[1]), the tips are ideally atomically sharp and the substrate is required to be conducting in order to observe a tunneling current. The measurement can be performed in constant current mode, constant height mode or the combination of both. In current constant mode, the tunneling current is kept constant while the tip height is varied to record a topographic image. In a height constant mode, the position of the tip is kept constant, and the current change across the surface is measured. One remarkable advantage of STM is that it allows one to record the current and image of individual molecules adsorbed on the substrate at atomic level simultaneously. To date, many interesting electronic properties of molecular junctions have been shown using this technique. Examples include conductance switching,[3] negative differential resistance (NDR),[5, 61] and a molecular rectifier.[62] Another advantage of the STM method is that the tip can be moved up and down to repeatedly make molecular junctions, permitting thousands of measurements and statistical analysis. The inherent drawback of the STM experiment is the fact that the electrical contact has an air gap between the molecule surface and the STM tip (or vacuum gap in UHV-STM), which can result in difficulty determining the true conductance of the molecules.

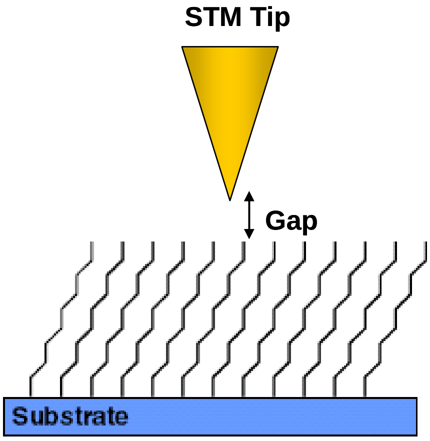


Figure 1.6 Schematic representation of an STM. The tunneling current between the STM tip and bottom electrode is recorded to measure the conducting properties. Adapted from ref 1.[1]

A CP-AFM is schematically illustrated in Figure 1.7 (a).[1] There are several differences between CP-AFM and STM in terms of the working mechanisms and applications in molecular electronics. CP-AFM can make a direct contact between the tip and molecules by controlling the force, which can avoid the current reduction caused by the air or vacuum gap in STM. However, it was found that the conductance of the molecules is dependent on the force exerted on the molecules by AFM tips.[63, 64] Furthermore, since CP-AFM tips are usually larger than STM tips,[64] the exact number of molecules contacted by CP-AFM tips is unknown. In order to solve these problems, Lindsay et al. proposed a method using gold nanoparticles to measure the conductance of dithiolated molecules on gold (Figure 1.7 (b)).[65, 66] Alkanedithiols were inserted into a monolayer of monothiols on Au substrate, and the gold nanoparticles were attached to the end groups of dithiols via an Au-S linkage. A direct electrical contact was obtained by pushing the gold coated CP-AFM tip onto the gold nanoparticle. The results indicate that there are almost no effects of the applied force of CP-AFM tips on the current-voltage characteristics of the junction in this case. Moreover, since the size of the nanoparticle is well defined, the actual number of the molecules in contact is known. However, side effects such as the contact resistance between the CP-AFM tip and the nanoparticle, and the charging of the nanoparticles need to be separated from the conductance of molecules. Another advantage of the CP-AFM approach is that the tips can be coated with different metals, e.g., Au, Ag, Pt, etc., providing a convenient way of studying the effect of electrode work function on the electron transport through junctions. Although both STM and CP-AFM offer good tools for exploring electron transport of molecular junctions, one common drawback is that they are not amenable to industrial manufacturing due to the nature of the instrument.

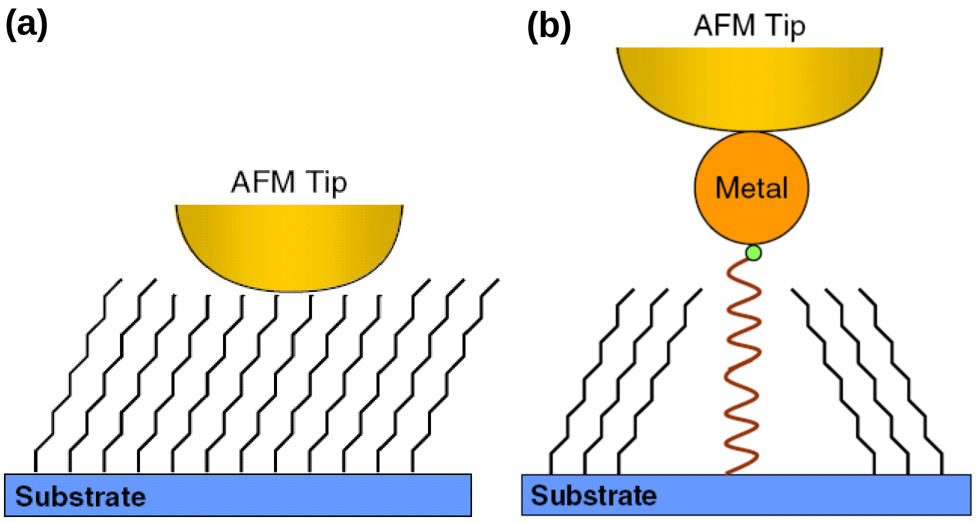


Figure 1.7 **(a)** Schematic representation of a CP-AFM tip in contact with molecules on a substrate. **(b)** Nanoparticle-coupled CP-AFM. Adapted from ref 67.[67]

1.2.2.2 Break junction

The break junction provides another approach to study single molecule junctions. An early example was demonstrated by Reed and Tour et al. in 1997, where experiments were performed with a mechanically controllable break junction (MCBJ, see Figure 1.8).[68] The measurement process is shown in Figure 1.9.[68] A notched Au wire was attached to a flexible substrate. The substrate was bent by a piezoelectric actuator until the notch fractured and produced a gap. The separation of the gap was adjustable by using the actuator. After the gap was formed, molecules of benzene-1,4-dithiol were self-assembled onto the two facing gold electrodes from a solution of tetrahydrofuran (THF). The THF was evaporated and the two electrodes were brought together until one molecule bridged the gap between the two electrodes. By repeatedly opening and closing the gap, statistical data were collected.[68] However, the disadvantage of this technique is that the actual conformation of the electrodes is unknown, while the theoretical studies show that the configuration and compressive stress of the electrodes have an effect on the electronic behavior of single molecule break junctions.[69, 70]

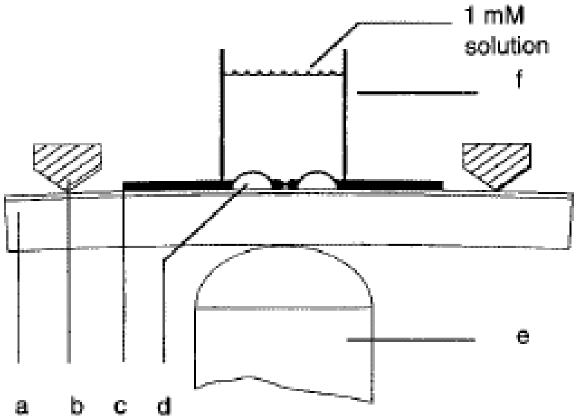


Figure 1.8 A schematic of the mechanically controllable break junction with (a) the bending beam, (b) the counter supports, (c) the notched gold wire, (d) the glue contacts, (e) the pizeo element, and (f) the glass tube containing the solution. Adapted from ref 68.[68]

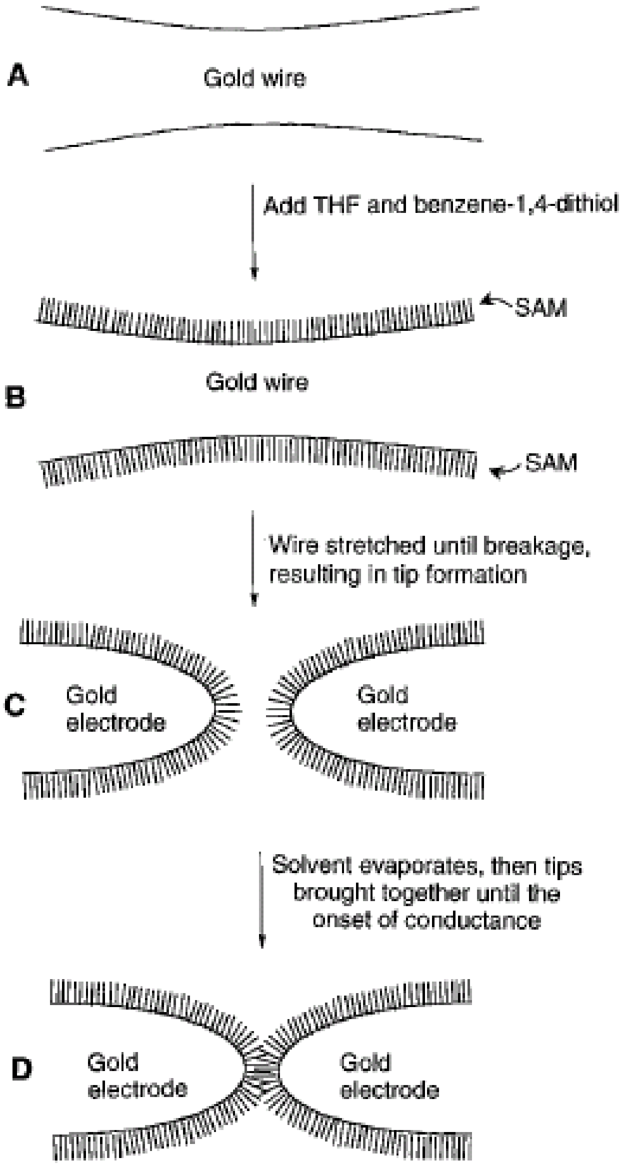


Figure 1.9 Schematic of the measurement process of a MCBJ. (A) The gold wire of the break junction before breaking and tip formation. (B) After addition of benzene-1,4-dithiol, SAMs form on the gold wire surfaces. (C) Mechanical breakage of the wire in solution produces two opposing gold contacts that are SAM-covered. (D) After the solvent is evaporated, the gold contacts are slowly moved together until the onset of conductance is achieved. Steps (C) and (D) (without solution) can be repeated numerous times to test for reproducibility. Adapted from ref 68.[68]

Another similar approach to a break junction was proposed by Xu and Tao using STM.[71] Individual molecular junctions were produced by repeatedly moving a gold STM tip into and out of the gold substrate in a solution of bipyridine or dithiol. When the tip was pulled away from the substrate, the chain of gold atoms was broken and a break junction was formed where a single or a few molecules were assumed to bridge the gap (see Figure 1.10 A, C, E). ~1000 of such experiments were performed and the conductance histogram (see Figure 1.10 B, D, F) was plotted and resistances of various molecules were obtained.

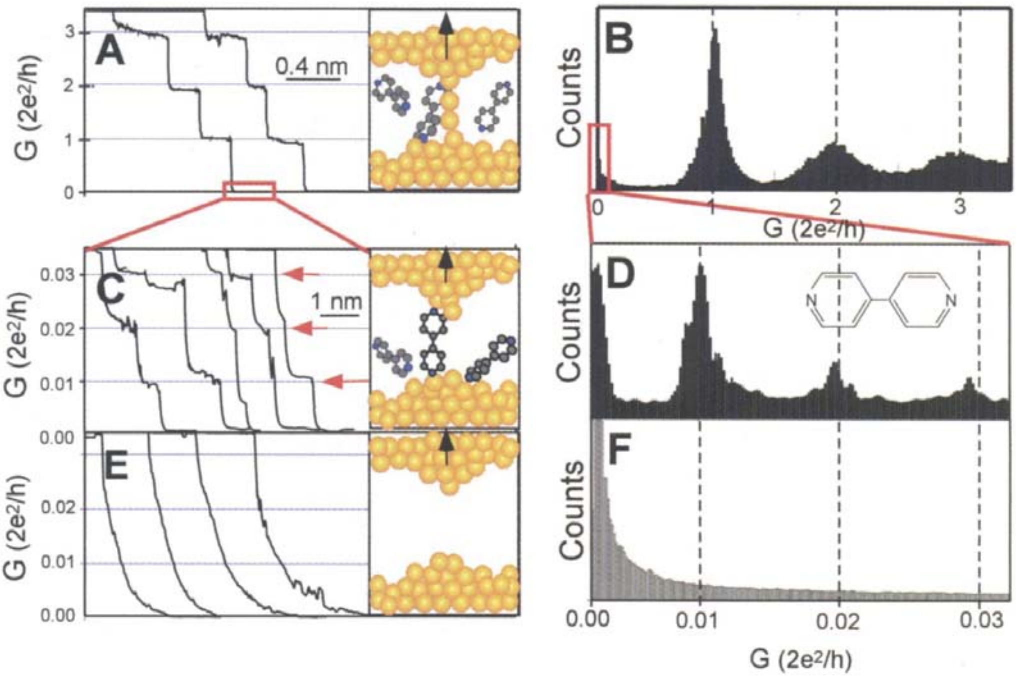


Figure 1.10 (A) Conductance of a gold contact formed between a gold STM tip and a gold substrate decreases in quantum steps near multiples of G_0 (= $2e^2/h$) as the tip is pulled away from the substrate. (B) A corresponding conductance histogram constructed from 1000 conductance curves as shown in (A) shows well-defined peaks near 1 G_0, 2 G_0, and 3 G_0 due to conductance quantization. (C) When the contact shown in (A) is completely broken, corresponding to the collapse of the last quantum step, a new series of conductance steps appears if molecules such as 4,4'-bipyridine are present in the solution. These steps are due to the formation of the stable molecular junction between the tip and the substrate electrodes. (D) A conductance histogram obtained from 1000 measurements as shown in (C) shows peaks near 1 ×, 2 ×, and 3 × 0.01 G_0 that are ascribed to one, two, and three molecules, respectively. (E and F) In the absence of molecules, no such steps or peaks are observed within the same conductance range. Adapted from ref 71.[71]

1.2.2.3 Crossed wire

A molecular junction consisting of a crossed wire (see Figure 1.11[72]) was first used by Kushmerick et al. to study electron transport across organic molecules.[73] To fabricate a crossed wire junction, two 10 μm diameter metal wires were mounted to a test stage in a crossed geometry, and one of the wires, which was perpendicular to an applied magnetic field (B), was modified with a thiolated molecules of interest. A small current passed through this wire, generating the deflection of the wire caused by the Lorentz force which was used to control the junction separation. By slowly increasing the deflection current (i_{def}), the wires were brought together to make contact and then the electrical characteristics could be measured by applying a bias between the two wires. This method allows the change of metal wires, and therefore the effect of work function and junction asymmetry on electron transport can be studied. Using this method, the effect of bond-length alternation in a molecular wire was investigated,[74] and the conductance of scaling of molecular wires in parallel was shown.[72] However, the disadvantage is that the configuration of the molecules at a curved surface is unknown, as well as the geometric area of the junction or the number of conducting molecules.

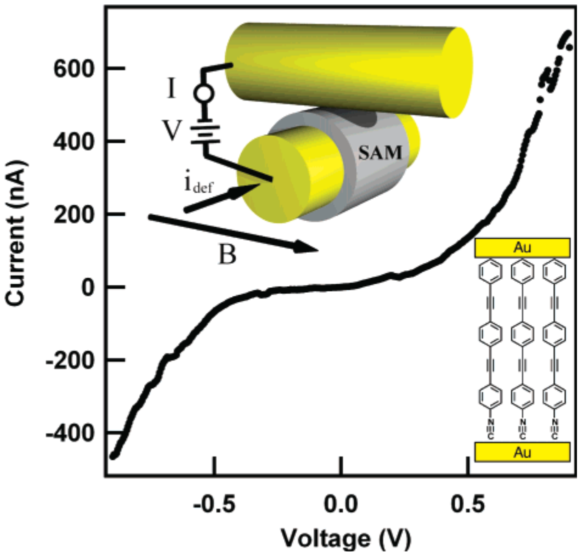


Figure 1.11 Schematic representation of experimental setup and current-voltage (I-V) characteristics of a crossed wire SAMs junction. Adapted from ref 72.[72]

1.2.2.4 Liquid metal

A liquid metal provides a method to fabricate molecular junctions containing an ensemble of molecules. In this technique (Figure 1.12), the junction is formed by making a mechanical contact between a suspended drop of liquid metal and organic molecules, e.g., SAMs. Hg is the most commonly used liquid metal mainly because of the advantages it brings to this junction fabrication approach. First, the junctions are easy to fabricate and no complicated or expensive experimental apparatus is required. Second, the junction area is well defined and the configuration of the molecules is known. Third, the junctions can be fabricated reproducibly due to the chemical and physical properties of Hg. The Hg drop has a high surface tension, greatly reducing the penetration of metals into molecular layers. Hg does not easily form oxide, avoiding the potential influence of another uncontrolled variable. Fourth, various substrates can be used, e.g., Au, Ag, Si, Hg etc. Fifth, many measurements can be performed on different sites of one sample or different samples due to the simplicity of this method. As a result, a large collection of results can be obtained and analyzed statistically generate reliable information about the junctions. However, there are some obvious disadvantages of this technique. Hg is volatile and toxic. Furthermore, Hg can easily form amalgams with Au which can cause short circuits formation when there are defects present in SAMs on an Au substrate. The electrical features of different molecules such as capacitance, conductivity and breakdown voltage, as well as electron transport characteristics on different substrates have been characterized using Hg junctions.[75-77]

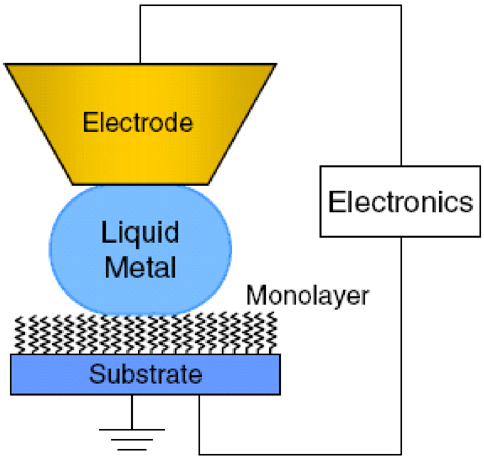


Figure 1.12 Schematic illustration of a liquid metal junction. Adapted from ref 67.[67]

Recently, the Whitesides group reported another liquid metal, Eutectic Gallium-Indium (EGaIn) containing 75% Ga and 25% In by weight, could be used as a top contact to fabricate molecular junctions.[78] Compared to Hg, EGaIn is less likely to form amalgams which can cause short circuits, and a high yield (>80%) of working junctions was obtained. In addition, EGaIn is nonvolatile and thus less toxic than Hg. A disadvantage of EGaIn is that Ga can form oxides easily at the surface and gallium oxide is an n-type semiconductor, which can bring more variables and uncertainties to the system and cause more difficulty in interpreting the results.[78]

1.2.2.5 Physical vapor deposited metal

Physical vapor metal deposition provides a convenient method to fabricate macroscopic scale molecular junctions, which is more suitable for commercial applications compared to other approaches. Furthermore, this method provides a straightforward way for spectroscopic investigation of molecular junctions since it is possible to make junctions large enough for optical spectroscopy. For physical deposition, metal is vaporized by heat, ion bombardment or an electron beam and then the vapor of metal is re-condensed on a cooler substrate. Electron beam evaporation technique is widely used to fabricate molecular junctions because it can produce very pure, smooth and thin films made of a variety of materials such as metal, metal oxide, carbon, etc., in a controllable and reliable way. However, it is known that direct evaporation of noble metals can cause molecular damage, molecular displacement at the substrate/molecules interface, or metal penetration through molecules.[39, 40, 67, 79] Some reactive metals (e.g., Ti, Al, etc.)[38, 80-82] have been reported to react with the terminal group or backbone of the molecules, resulting in damage of molecules. Therefore, the fabricated junctions suffer from issues involving low yield and poor reproducibility. Furthermore, other variables during the metal deposition, e.g., the backpressure of e-beam evaporation chamber, can affect the electrical characteristics of the fabricated junctions.[83]

Attempts to avoid some of the problems described above have involved so called “cold-gold deposition”,[84, 85] soft contact deposition,[86, 87] insertion of a separation layer between molecules and evaporated metal.[88, 89] In “cold-gold deposition”,[84, 85] all the samples are placed on a sample holder cooled by liquid nitrogen and faced away from the metal source container. In this way, heat can be reduced and also radiation emitted from the metal source does not reach the sample. The vacuum chamber is backfilled with Ar and maintained at a controlled pressure during the deposition, typically a few mTorr. The evaporated Au atoms lose some kinetic energy through multiple collisions with Ar atoms, before they land on the molecules. As a result, the molecules show less damage compared to those with direct metal deposition. In soft contact deposition method, a so called lift-off-float-on (LOFO) technique has been reported.[90] In LOFO process,[90] a thin film of metal on a solid substrate is detached in a solvent and then transferred to the target substrate patterned with metal electrodes which are modified with molecules. This technique reportedly caused little damage to the molecular layers and increased the junction yield by reducing the formation of short circuits. However, the residue of solvent and the wrinkles formed during solvent evaporation are a concern when using this technique. By inserting a “buffer” layer between molecules and evaporated metal, the molecules are protected from direct metal deposition and possible damage. The de Boer group successfully manufactured large area molecular junctions up to 100 μm in diameter based on SAMs by inserting a conducting polymer interlayer between the SAM and metal top contact and a high yield up to 100 % was obtained.[88, 91] A similar approach was reported by Preiner and Melosh, using a very thin layer of atomic-layer-deposited Al_2O_3 as protection layer.[89]

1.2.2.6 Conducting polymer

More recently, a new promising technique of top contact fabrication has been demonstrated, which combines conducting polymer as part of top electrode as mentioned in last paragraph.[88] Figure 1.13 schematically describes the whole process.[88] The use of a conducting polymer sandwiched between the molecular layer and top metal electrode reportedly prevents electrical shorts. The yield of fabricated junctions is close to 100% and this technique is compatible with standard integrated fabrication process technology.[88, 91] Furthermore, a shelf life of these devices is more than several months. This technique is simple and possibly compatible with standard integrated circuit fabrication processing. However, the use of conducting polymer can give rise to other issues such as additional tunneling barrier and undefined interface, which could make the system more complicated.

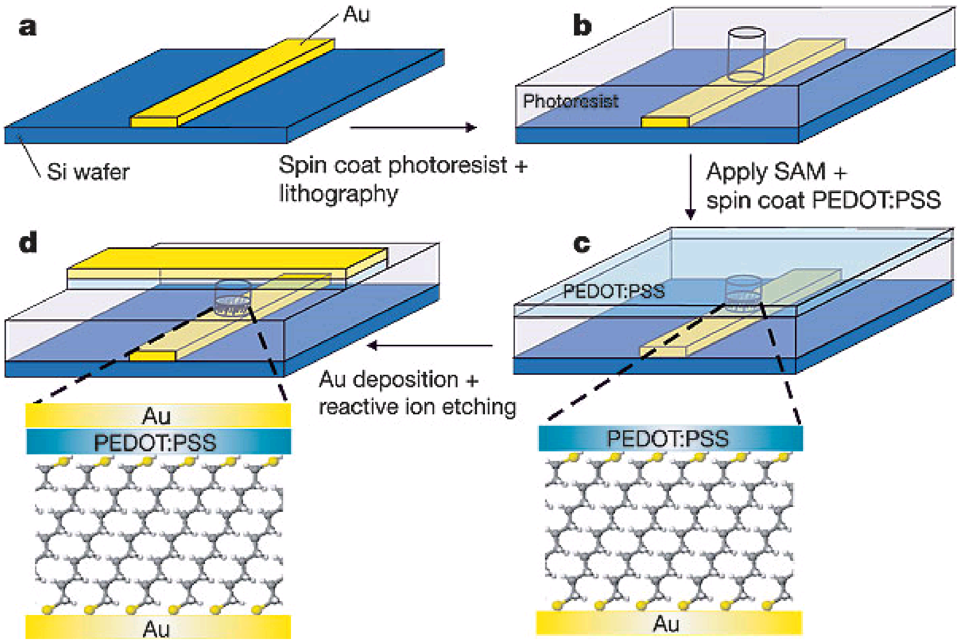


Figure 1.13 Processing steps of a large-area molecular junction. a, Gold electrodes are vapour-deposited on a silicon wafer and a photoresist is spin-coated. b, Holes are photolithographically defined in the photoresist. c, An alkane dithiol SAM is sandwiched between a gold bottom electrode and the highly conductive polymer PEDOT:PSS as a top electrode. d, The junction is completed by vapor deposition of gold through a shadow mask, which acts as a self-aligned etching mask during reactive ion etching of the PEDOT:PSS. Adapted from ref 88.[88]

There are other testbeds in molecular electronics, some of which are beyond the scope of this thesis. More complete discussions on this topic are available in several reviews.[1, 8, 67, 86, 92] Each existing approach of fabrication of molecular junctions has advantages and disadvantages. As a result, there is currently no "best" technique to study the electrical properties of molecules. The choice of technique will depend on the purpose of the work. For example, for fundamental studies single molecule approaches might be a better choice, while for application related research, techniques used for making reproducible and macroscopic devices should be considered.

1.3 Integration of molecular junctions

The ultimate goal of molecular electronics is to incorporate different types of functional molecules into integrated circuits. One likely commercial manifestation of molecular electronics involves "hybrid" circuits which integrate the highly refined fabrication techniques of the conventional semiconductor industry with molecular components that enhance function, such as memory devices, photonics, and chemical sensors. The hybrid approach maintains the cost-effective, massively parallel processing of the complementary metal-oxide semiconductor (CMOS) industry, but adds new molecule-based electronic behaviour and functions.[8, 93] For a hybrid approach to be practical, the molecular components must be compatible with CMOS in terms of fabrication and operating temperatures, substrate materials, and fabrication steps such as vapour deposition and photolithography while exhibiting high device yield and reproducible electronic behaviour. Such compatibility has been investigated for Au/SAM/conducting polymer devices containing alkane (di)thiol molecular components.[91] Over 20,000 junctions were fabricated simultaneously on a 6-inch wafer and integration was demonstrated by connecting up to 200 junctions in series (see Figure 1.14).[91] However, the conducting polymer used for the "top contact" is not a common material in semiconductor processing, and the thermal stability study shows that the junctions degraded when temperature exceeded 50 ˚C and the transition temperature was independent of the molecular length of the alkane. This observation could not be explained by either the phase transitions or desorption of alkane thiols on Au. [94] The authors conclude that "The upper limit of 50 ˚C is a strong limitation for the applicability of molecular electronics." Although the paper demonstrated significant progress towards integration with commercial microelectronics, integration of molecular junctions is still a challenge in molecular electronics.

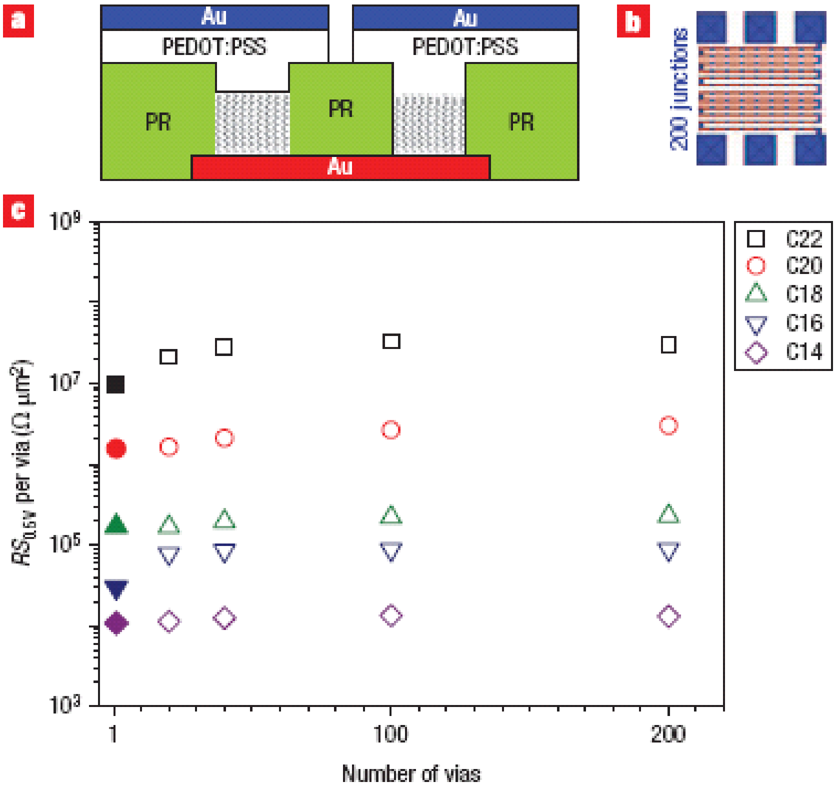


Figure 1.14 Integration of junctions in series. a, Schematic cross-section of a part of a string showing two connected junctions. PEPOT:PSS: poly(3,4-ethylenedioxythiophene) stabilized with poly(4-styrenesulphonic acid). PR: photoresist. b, Layout of strings in which a number of molecular junctions are connected in series. Each section contains two junctions. The red and blue colours represent the bottom and top gold layers, respectively. c, The normalized resistance of alkane-monothiol C_nH_{2n+1}-SH SAM junctions with n=14-22, integrated in strings using the default process flow chart. The junctions are 5 µm in diameter. The normalized resistance per via is presented as function of the number of junctions. Values for discrete single junctions are included as filled symbols for comparison. Adapted from ref 91.[91]

1.4 Research objective

The overall objective of this research is to develop a fabrication procedure to micro-fabricate carbon-based molecular junctions in parallel using semiconductor techniques such as photolithography and physical vapor deposition. Previous carbon-based junctions were fabricated using a Hg drop,[54, 95] a "spot" configuration,[96-98] or a "cross-bar"[99] configuration with large areas (0.0005-0.005 cm^2). The possible future for molecular electronics would be integration of molecule-based electronic functions with the CMOS industry, which requires compatibility of molecular components of the junctions with CMOS in terms of fabrication steps, operating temperatures, substrate materials, etc. Another objective is to explore electron beam deposited carbon as a substrate instead of PPF used previously. Compared to PPF, e-beam deposited carbon is more likely to be used in an industrial environment, since it uses existing physical vapor deposition equipment.

Chapter 2 describes the fabrication procedure of carbon-based microfabricated molecular junctions, including the fabrication of bottom electrode PPF and junction vias (vertical interconnect access), surface modification with aromatic molecules and the evaporation of metal top contacts or top electrodes. The spectroscopic analysis including AFM, SEM, XPS and Raman is described, and preliminary electrical characterization of these molecular junctions is presented.

Chapter 3 describes the electronic properties of the microfabricated carbon/molecule/Cu junctions, including the general junction behavior such as yield and reproducibility, and the compatibility with semiconductor industry such as operating stability at elevated temperature and high voltage. Furthermore, the possible electron transport mechanism is described.

Finally, the thesis closes with a brief summary of all the work presented in Chapter 2 and 3.

CHAPTER 2

FABRICATION OF CARBON/MOLECULE/METAL JUNCTIONS

2.1 Introduction

One of the goals of molecular electronics is to integrate molecular components with new functions into conventional microelectronics devices and circuits.[8] As part of molecular electronics, the fabrication of reliable experimental testbeds is very important. Carbon-based molecular junctions have been investigated intensively by the McCreery group,[6, 8, 83, 87] demonstrating several advantages. As described in section 1.2.1.3, a C-C bond is formed irreversibly with high bond strength (~4 eV) via reduction of aromatic diazonium reagents on conducting carbon substrate. The resulting modified surface is stable up to 500 °C.[53, 100]The fabricated devices show good stability and reliability. Previous work on fabricating carbon-based molecular devices using PPF as bottom electrode includes mercury drop,[54, 95], “spot”[96-98] and “cross-bar” junctions.[83, 99] These previous junctions were relatively large (0.0001-0.0025 cm^2) and exhibited good yield and reproducibility and excellent cycle life (>10^9 voltage cycles to ~1 mA peak current) and temperature stability in a range of 5-450 K.

In this chapter, a new approach to micro-fabricating carbon-based molecular junctions with smaller sizes (3 × 3 to 400 × 400 μm) is described, using techniques compatible with semiconductor technology such as photolithography, vapor deposition, etc. In addition, electron beam deposited carbon is described as an alternative substrate to PPF. A brief overview of the fabrication process followed by a detailed description of each step is provided. The results of microscopic and spectroscopic characterization of the microfabricated devices are illustrated and discussed.

2.2 Experimental

2.2.1 Device fabrication

The micro-fabrication of carbon/molecule/metal devices contains four main steps: (1) fabrication of bottom electrode PPF; (2) fabrication of junction vias (vertical interconnect access), (3) carbon surface modification, (4) deposition of top contact or top electrode. The fabrication procedure is schematically described in Figure 2.1. The details will be described and discussed in a chronological order in the following paragraphs.

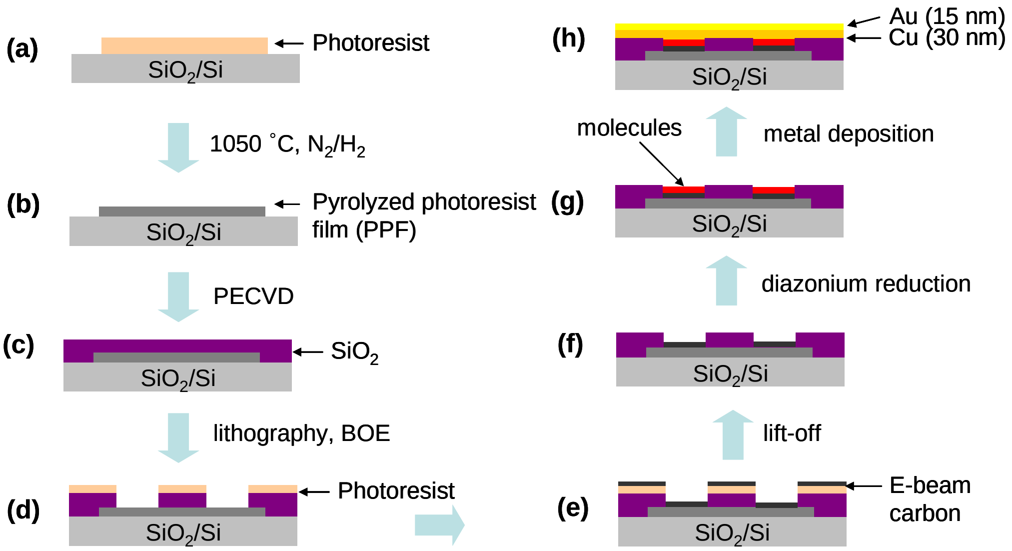


Figure 2.1 Process flow chart for the fabrication of microfabricated carbon/molecule/metal junctions. **(a)** Photoresist AZ P4330-RS is spin-coated and patterned using standard photolithography. **(b)** Pyrolyzed photoresist films (PPF) are formed by pyrolyzing the photoresist in forming gas (95% N_2 + 5% H_2) at 1050 ˚C. **(c)** A ~300 nm SiO_2 layer is deposited as insulating layer using plasma enhanced chemical vapor deposition (PECVD). **(d)** Vertical junction holes are defined in the PECVD SiO_2 layer by optical lithography and buffered oxide etching (BOE). **(e)** A 10 nm of carbon film is deposited by electron beam evaporation. **(f)** The photoresist used in step (d) is stripped by rinsing with acetone. **(g)** A molecular layer is covalently attached to the carbon surface in the junction holes using electrochemical methods. **(h)** The junction is completed by electron beam deposition of copper and gold as top contacts through a shadow mask.

2.2.1.1 Preparation of PPF

A 4-inch single side polished wafer (0.5 mm thick, <100> oriented, boron doped, 5-10 Ω·cm, Cemat Silicon S.A.) with 300 nm thick thermally grown silicon oxide was used as a substrate. The wafer was cleaned with a hot piranha solution (concentrated H_2SO_4/30% H_2O_2, 3:1 v/v) for 15 min, rinsed with copious deionized water, and dried with nitrogen in a spin rinse drier. *(Warning: Piranha solution is a strong oxidizer and can react with many organic materials* *explosively. Extreme caution must be taken when preparing, handling and disposing of piranha solution. All work must be done in a fume hood.)* The wafer was passivated with hexamethyldisilazane (HMDS), which acted as an adhesion layer between the photoresist and the oxide surface of the substrate. Positive photoresist AZ 4330-RS (AZ Electronic Materials, NJ) was spin-coated on the wafer at a speed of 500 rpm for 10 s followed by 2500 rpm for 60 s, and soft baked on a hotplate at 110 ˚C for 180 s in air, resulting in a thickness of ~4.5 μm measured by a profilometer. The photoresist was left in air to rehydrate for ~30 min before UV exposure was carried out. A Quintel Q-4000 mask aligner was used to expose the photoresist using the pressure contact mode. The average UV intensity was a combination of ~10 mW/cm^2 at 365 nm and ~25 mW/cm^2 at 405 nm and the exposure time was 20 s. After the UV exposure, the photoresist was developed in a mixture of AZ400K developer (AZ Electronic Materials, NJ) and deionized water (1:2 v/v) for ~30 s, then rinsed with deionized water and dried with a stream of nitrogen. The patterned photoresist was pyrolyzed as follows.[55, 56] The wafer was transferred to a quartz tube furnace (Carbolite model GHA 12/600) and the furnace was flushed with forming gas (5% H_2 and 95% N_2) for 15 min to make the furnace atmosphere inert before the start of pyrolysis. The patterned photoresist was pyrolyzed by ramping the temperature to 1050 ˚C at a rate of 10 ˚C/min and holding at 1050 ˚C for 1 hour with forming gas flowing at ~1200 sccm (standard cubic centimeter per minute). The forming gas was kept flowing until the sample was cooled down to room temperature. After pyrolysis, the thickness of PPF films were ~1 μm as determined by a profilometer and the resistivity was ~0.006 Ω cm as measured by a four point probe.

2.2.1.2 Definition of junction vias (vertical interconnect access)

In order to electrically isolate the junctions, a process of fabricating junction holes (or vias) was performed.

(1) ~300 nm thick SiO_2 was deposited on the wafer as insulating layer by a Trion plasma enhanced chemical vapor deposition system (PECVD). The deposition temperature was 291-295 ˚C. The SiO_2 film thickness varied depending on the deposition conditions, e.g., deposition temperature, chamber pressure and deposition time. Therefore, the thickness of PECVD SiO_2 layer was always verified with a thin film thickness measurement system (Filmetrics).

(2) The wafer was passivated with HMDS before optical lithography was carried out.

(3) Positive photoresist HPR 504 (MicroChem) was spin-coated at 500 rpm for 10 s and 3000 rpm for 40 s and the thickness was ~1.4 μm as confirmed by a profilometer. The photoresist was soft baked at 115 ˚C in vacuum for 90 s and left in air at room temperature to absorb moisture for ~15 min before UV exposure.

(4) The photoresist was exposed under UV (365 nm, 400 W) in a vacuum contact mode for 2.6 s with a mask aligner (ABM).

(5) The development was performed in a developer 354 (MicroChem) for ~30 s. Then the wafer was rinsed with deionized water and dried with a stream of nitrogen gas.

(6) The PECVD SiO_2 unprotected by the photoresist was etched to expose PPF by a buffered oxide solution (buffered oxide etch, 10:1, J.T. Baker). The observed etching rate was ~70 nm/min. The etching process yielded junction via-holes in the SiO_2 layer with areas ranging from 3 × 3 to 400 × 400 μm. Note: junction areas are stated by their nominal dimensions (e.g. 3 × 3 μm), but were determined by inspection with an optical microscope or scanning electron microscope (SEM).

(7) The wafer was diced into chips using a dicing saw (DAD 321, Disco). The photoresist was not stripped but left as a lift-off mask for the subsequent electron beam deposition of carbon films.

(8) For each chip, a 10 nm thick electron beam carbon film was deposited using an electron beam evaporator (PVD 75, Kurt J. Lesker). Briefly, the chips were loaded into the evaporation chamber, facing down towards the graphite source (graphite rods, 32 mm in diameter and ~10 mm in length, spectroscopic purity, SPI supplies). The chamber was pumped down to ~8×10^{-7} torr before e-beam carbon evaporation. The chamber pressure was monitored by a residual gas

analyzer (RGA/200, Stanford Research Systems). For all the e-beam carbon depositions, unless noted otherwise, the total pressures observed were in a range of 0.5-1.5 × 10^{-5} torr. A 10 nm thick electron beam carbon film was deposited at a rate of 0.02-0.1 nm/s, where the rate and thickness were monitored using a quartz crystal microbalance.

(9) The photoresist was stripped with acetone (HPLC grade, Fisher) and the chips were then cleaned thoroughly with isopropanol (HPLC grade, Fisher) and deionized water (>18 MΩ, TOC<4 ppb, Millipore), and blown dry with nitrogen.

2.2.1.3 Carbon surface modification

Electrochemical deposition of molecular layers. A BASi Epsilon-EC potentiostat (Bioanalytical Systems, IN) was used to carry out the electrochemical derivatization of the carbon surfaces in junction vias. A standard three-electrode system was applied, where the microfabricated sample was working electrode, Ag/Ag^+ was reference electrode and a coiled platinum wire was counter electrode. As shown in Figure 2.6 (b), a large rectangular contact pad on each chip permitted contact with all the exposed carbon areas simultaneously. The Ag/Ag^+ reference electrode was prepared by immersing an Ag wire into a solution of 0.01 M $AgNO_3$ (Aldrich) and 0.1 M *n*-tetrabutylammonium tetrafluoroborate ($TBABF_4$, Aldrich, 99%) in acetonitrile (ACN) (Aldrich, Caledon, anhydrous HPLC grade).

The Ag/Ag$^+$ electrode was calibrated using $E_{1/2}$ of ferrocene (Fc) (Aldrich) in ACN.[101] The $E_{1/2}$ of Fc obtained from cyclic voltammogram was 89 mV vs. the Ag/Ag$^+$ reference electrode and the E° of Fc is +0.31 V vs. aqueous standard saturated calomel electrode (SCE). Therefore, the potential of the Ag/Ag$^+$ reference electrode was +0.22 V vs. aqueous SCE.

The modification of carbon surfaces in junction vias was carried out by electrochemical reduction of 1 mM solution of the corresponding diazonium salts in 0.1 M $TBABF_4$ in ACN. The 4-nitroazobenezene (NAB) and fluorene (FL) tetrafluoroborate diazonium salts were synthesized using the procedure described previously.[102, 103] Diazonium tetrafluorborate solutions were freshly prepared and purged with Ar for ~15 min before use. The cyclic voltammetry method was employed for growing the molecular film. Figure 2.2 shows the reaction mechanism of diazonium reduction on carbon surface.[6] The formation of radicals indicates that the reaction is robust whereas prone to multilayer formation. However, it is possible to control or increase the film thicknesses by controlling the potential sweep conditions, e.g., scanning rate and range, and number of scans.[58] For NAB film, the obtained thicknesses were 2.2 ± 0.2, 3.8 ± 0.2, 5.2 ± 0.2 nm and 2.4 ± 0.2 nm when the applied potential was scanned from +0.4 V to -0.6 V (vs. Ag/Ag$^+$, 0.01 M) for 1 cycle, 4 cycles, 10 cycles and from +0.4 V to -0.2 V for 4 cycles, respectively, all at 0.2 V/s (see table 2.1). For FL film, the applied potential was scanned from +0.4 V to -0.8 V (vs. Ag/Ag$^+$, 0.01 M) for 4 cycles at 0.2 V/s, and the film thickness was 2.8 ± 0.2 nm. Figure 2.3 (a) shows a cyclic voltammogram of NAB attachment on e-beam carbon surface and (b) shows the molecular structures of NAB and FL. As shown in Figure 2.3 (a), a broad irreversible reduction peak is observed on the first scan, indicating the reaction is irreversible. On the second scan, the peak disappears which indicates the surface is blocked by the molecules attached to the surface. The molecular film thickness is controlled by the total charge passed during the grafting electrolysis to form mono- or multilayers. In the case of CV method, the total charge can be obtained from the integration of cyclic voltammogram. Given constant concentration and other conditions, additional CV scans yield thicker molecular films. After surface modification, the chips were rinsed with acetonitrile thoroughly. Molecular film thicknesses were determined with the AFM scratching method as reported previously[103] and details of the procedure will be given in the next paragraph.

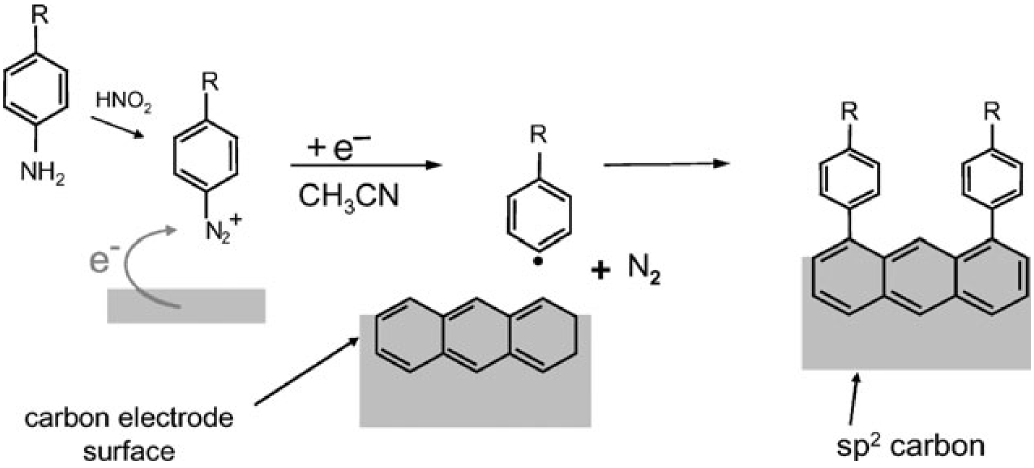


Figure 2.2 Covalent bonding of aromatic molecules to a graphitic carbon surface via reduction of aryl diazonium reagents. Phenyl radicals can bond to an unsatisfied surface valence or across a double bond. Adapted from ref 6.[6]

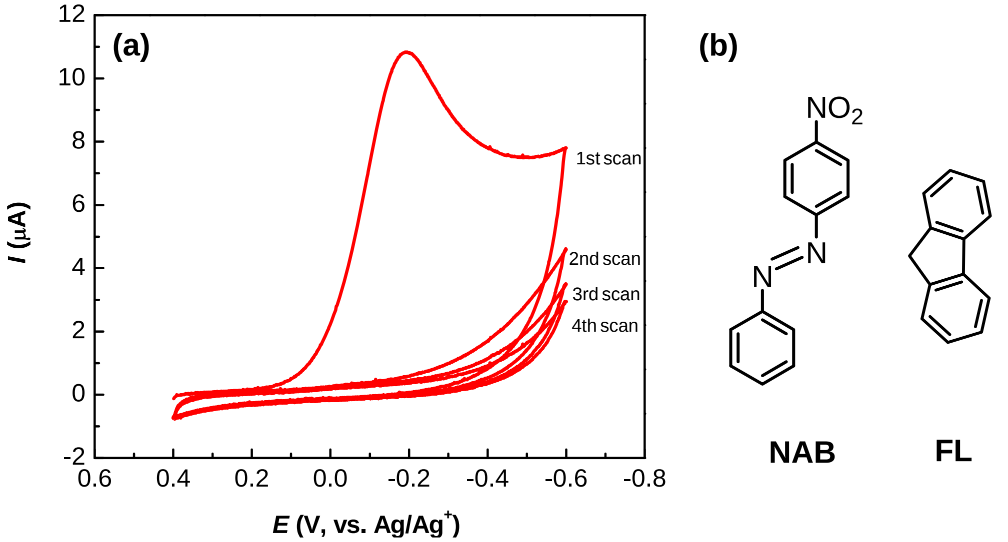


Figure 2.3 **(a)** Cyclic voltammogram of reduction of 1mM $NO_2C_6H_4N_2^+$ BF_4^- in ACN at e-beam carbon surface. Scan rate is 200 mV/s. **(b)** Molecular structures of nitroazobenzene (NAB) and fluorene (FL).

Molecular film thickness measurement. An AFM scratching technique[103] provides a reliable and direct way to measure the organic molecular film thickness, which is an important parameter for studying the electronic behavior of molecular junctions. In this technique, a trench was created by intentionally scratching the molecular film attached on a carbon surface in contact mode AFM using an AFM tip loaded by a constant force. The force was large enough to completely remove the organic film while causing little damage to the underlying substrate. The trench and surrounding area were then imaged in tapping mode and a line profile across the trench and outside surface was obtained. The depth or height of the trench analyzed by the AFM software was the corresponding thickness of the molecular film. A statistical analysis of the results of trench depths was used to determine the molecular film thickness to avoid bias by the observers.

For the experiments described in this thesis, the thickness measurement was carried out in air with a DI3100 atomic force microscope (Digital Instruments, Santa Barbara, CA) and silicon AFM tips (NSC15/ALBS, MikroMasch, Wilsonville, OR) with a resonant frequency of ~300 kHz were used for imaging and scratching the surface. A set-point voltage of 0.25 V in contact mode AFM was applied to scratch the surface and the scan rate was kept at ~1-2 Hz during the scratching process. After the scratching, the AFM image was acquired in tapping mode at a scan rate of 0.5-1 Hz. All the image analysis was performed by the AFM software "Nanoscope version 6.13". Figure 2.4 shows an example of AFM scratching measurement on e-beam carbon surface modified by NAB film. As shown in Figure 2.4 (a), a 0.5 µm × 0.5 µm trench was created in the contact mode AFM. In Figure 2.4 (b), a horizontal line was drawn across the trench and a line profile was obtained. The depth calculated between the two vertical lines (one inside the trench area and the other one in the unscratched area) determined the thickness of the NAB film. The statistical analysis of the trench depth is illustrated in Figure 2.4 (c). Instead of using a single horizontal line across the trench to calculate the depth, a rectangular box which can cover a larger area of the trench was applied to calculate the depth. The rectangular box included both the scratched and unscratched areas. A pair of lines across the trench (one inside the trench and the other one outside) was randomly chosen in the rectangular box. The depth was determined by calculating the difference of the average height of each line which was calculated by the AFM software. Generally, 10-14 line pairs within the rectangular box were generated and thus 10-14 depth values of the trench were obtained. By calculating the average and standard deviation of the depth values, the molecular layer thickness was determined statistically. As listed in Table 2.1, all the thickness values were averaged from 2-3 scratches on each corresponding sample.

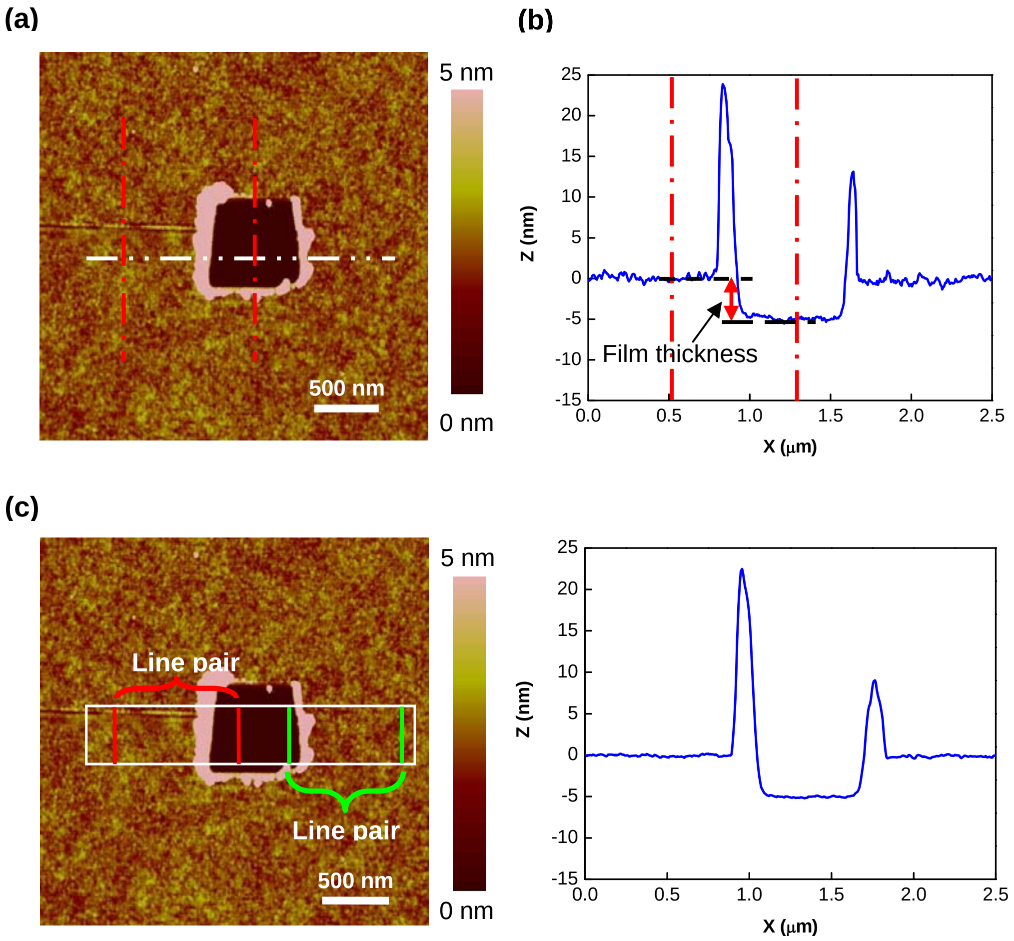


Figure 2.4 **(a)** AFM image of a NAB film with a 0.5 μm × 0.5 μm trench generated by "scratching" technique. **(b)** A line profile for the image in (a). **(c)** Statistical method used to determine the molecular film thickness.

Molecule	AFM thickness (nm)	Electrochemical deposition conditions
NAB	2.2 ± 0.2	CV, +0.4V to -0.6V, 1 cycle @ 0.2 V/s
NAB	2.4 ± 0.2	CV, +0.4V to -0.2V, 4 cycles @ 0.2 V/s
NAB	3.8 ± 0.2	CV, +0.4V to -0.6V, 4 cycles @ 0.2 V/s
NAB	5.2 ± 0.2	CV, +0.4V to -0.6V, 10 cycles @ 0.2 V/s
FL	2.8 ± 0.2	CV, +0.4V to -0.8V, 4 cycles @ 0.2 V/s

Table 2.1 Molecular film deposition conditions and thicknesses measured by AFM scratching technique.

2.2.1.4 Deposition of top contacts

Following the surface modification, the chips were rinsed thoroughly with ACN, blown dry with nitrogen gas and then transferred to a PVD 75 electron beam evaporator (Kurt J. Lesker). The evaporation chamber was pumped down to a base pressure of ~2.0×10^{-6} torr prior to metal deposition. 30 nm of copper followed by 15 nm of gold was deposited onto the modified vias to complete the junctions through a shadow mask. The deposition rate and thickness were monitored using a QCM. The chamber pressure was monitored by a RGA. For all the metal depositions, unless noted otherwise, the total pressures observed during deposition were in a range of $3\text{-}10 \times 10^{-6}$ torr.

Copper was deposited at ~0.01 nm/s for the first 2 nm and ~0.02 nm/s for additional 3 nm, then ~0.05 nm/s for another 10 nm, finally ~0.1 nm/s for the rest of 15 nm. Gold was deposited at ~0.05 nm/s for the first 5 nm and ~0.1 nm/s for the following 10 nm.

For the convenience of illustration, the notation of a molecule junction follows a layer format, stating each layer from bottom to top, and the thickness of the molecule film in nanometers is indicated in parentheses. For example, PPF/e-beam C/NAB(3.8)/Cu/Au describes a junction with a 3.8 nm NAB film on e-beam carbon deposited on PPF, and a Cu and Au top contact which is 30 nm of Cu on the molecules and 15 nm of Au on top of Cu. Unless stated otherwise, the film thicknesses of e-beam carbon, Cu and were always 10, 30 and 15 nm, respectively.

2.2.2 Device characterization

Atomic force microscopy (AFM). AFM was carried out with a DI3100 atomic force microscope (Digital Instruments, Santa Barbara, CA). The AFM images were collected in tapping mode at scan rates of 0.5-1 Hz using silicon AFM tips.

Scanning electron microscopy (SEM). SEM images were taken with a Hitachi S4800 SEM. Cross-sectional samples were prepared by cleaving the sample through the junctions. To reduce charging effects and increase the conductance of the samples, 3 nm Cr was sputtered on the cross sectional surfaces of the samples.

Raman spectroscopy. Raman spectra were collected with a custom built spectrometer equipped with an Ar ion laser (514.5 nm), a 50 mm f/1.8 lens (Nikon), a holographic reflection grating (2000 groove/mm), and a back-thinned charge coupled device (CCD) detector (Andor) cooled to -80 °C. The incident laser power was 100 mW and the integration time was 30 s.

X-ray photoelectron spectroscopy (XPS). XPS analysis was performed with an AXIS 165 spectrometer (Kratos Analytical) equipped with a monochromatic Al Kα source (1486.6 eV) in the Alberta Center for Surface Engineering and Science. The base pressure in the analytical chamber was lower than 1.5×10^{-10} torr.

Electrical characterization. The electrical measurements of the junctions were performed in ambient air using a potentiostat (Reference 600, Gamry Instruments) in a 3-wire configuration (Figure 2.5). A voltage was applied through two tungsten probes between the exposed carbon electrode (wire 1, labeled as "V^{+}_{drive}") and metal electrode (wire 2, labeled as "V^{-}_{drive}"), and the third probe labeled as ''V^{+}_{sense}'' (wire 3) was used to compensate the ohmic losses in carbon electrode due to the non-negligible resistance of PPF. For all the current density-voltage (J-V) curves, the voltage was plotted as carbon relative to metal top contact, and positive current corresponds to electron transport from Cu through the molecular layer to PPF.

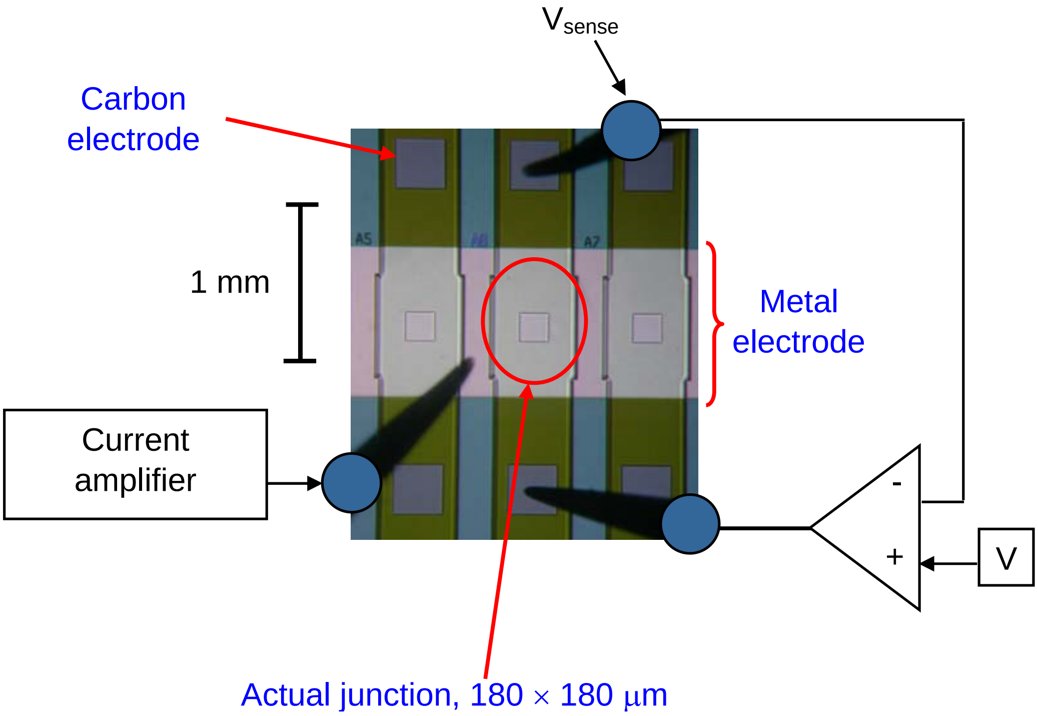


Figure 2.5 Electrical measurement setup in a 3-wire configuration. Bias is applied between V^{+}_{drive} and V^{-}_{drive}, and V^{+}_{sense} is used to correct the applied bias for ohmic losses in the carbon electrode.

2.3 Results and Discussion

2.3.1 Microscopy characterization

A photograph of a 4-inch wafer before dicing is presented in Figure 2.6 (a). After lithography and e-beam carbon deposition was complete, the wafers were diced to yield samples similar to that shown in Figure 2.6 (b). Each chip had 3 rows of junction vias, and each row had 9 or 11 vias except that there were 8 or 10 vias on the first row with a "blank" one on the left. Therefore, one chip could produce 26 or 32 molecular junctions. As shown in Figure 2.6 (b), a large pad at the top of the chip was used for electrochemical deposition from diazonium solution, allowing electrical contact to all 32 the junction vias on one chip. Following the electrochemical deposition of molecules and metal top contact deposition, the sample was cleaved to isolate the individual junctions, a necessary process to eliminate “crosstalk” between the molecular junctions. Although molecular layer formation was performed on each diced chip in this study, it is certainly feasible to perform the electrochemical deposition at the full wafer level. For example, Cu plating of full 200-300 mm diameter wafers via the “Damascene” process is common in commercial semiconductor processing.[104, 105] Similar process is likely adaptable to molecular layer formation via diazonium reduction. PPF contact pads on top and bottom sides of the junction vias were used for contact with tungsten probes during the electrical testing.

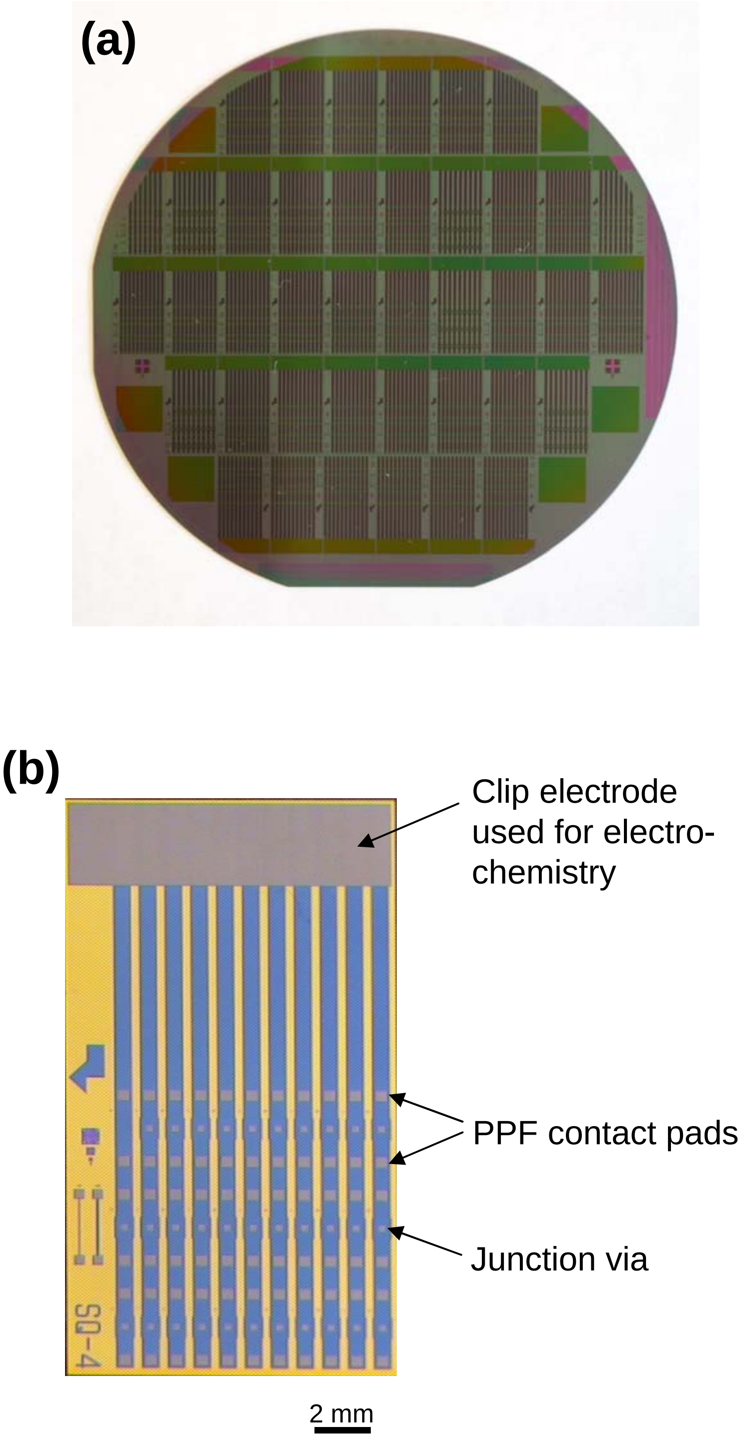


Figure 2.6 **(a)** Photograph of a fabricated wafer. Each wafer contains 36 chips and the size of each chip is 0.9 × 1.7 cm. **(b)** Photograph of a diced chip.

A photograph of a finished chip after deposition of molecular layers and metal top contacts is shown in Figure 2.7 (a) and a micrograph of a finished junction is shown in (b). SEM cross sections of cleaved junctions are shown in (c) and (d). As indicated in the SEM images, the layer structure of the junction is observed: from bottom to top, there are SiO_2/Si substrate, PPF, Cu and Au top contacts in sequence. The molecular layer (2-5 nm thick) is not visible due to the resolution limitation of the instrument. The e-beam deposited Cu and Au are continuous and homogenous. The edge of the junction via shows a slope angle of ~20°, resulting from the BOE etching of PECVD SiO_2. This slope ensures a good continuity of the Cu/Au deposit from the SiO_2 to the molecular layer.

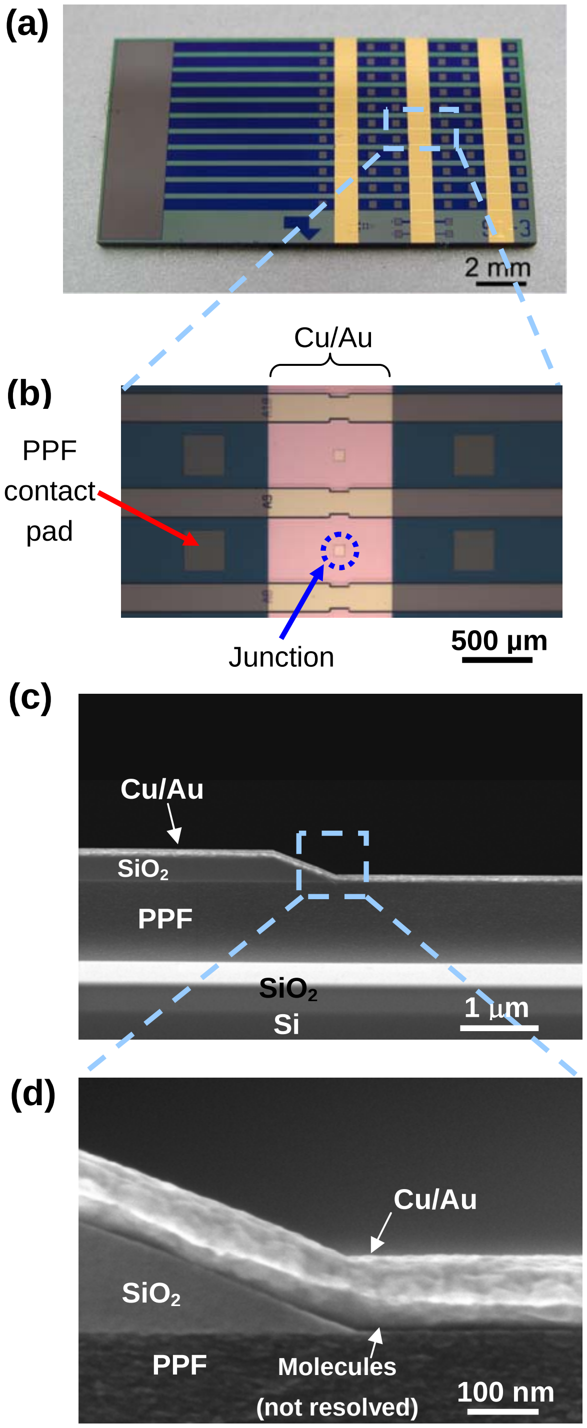
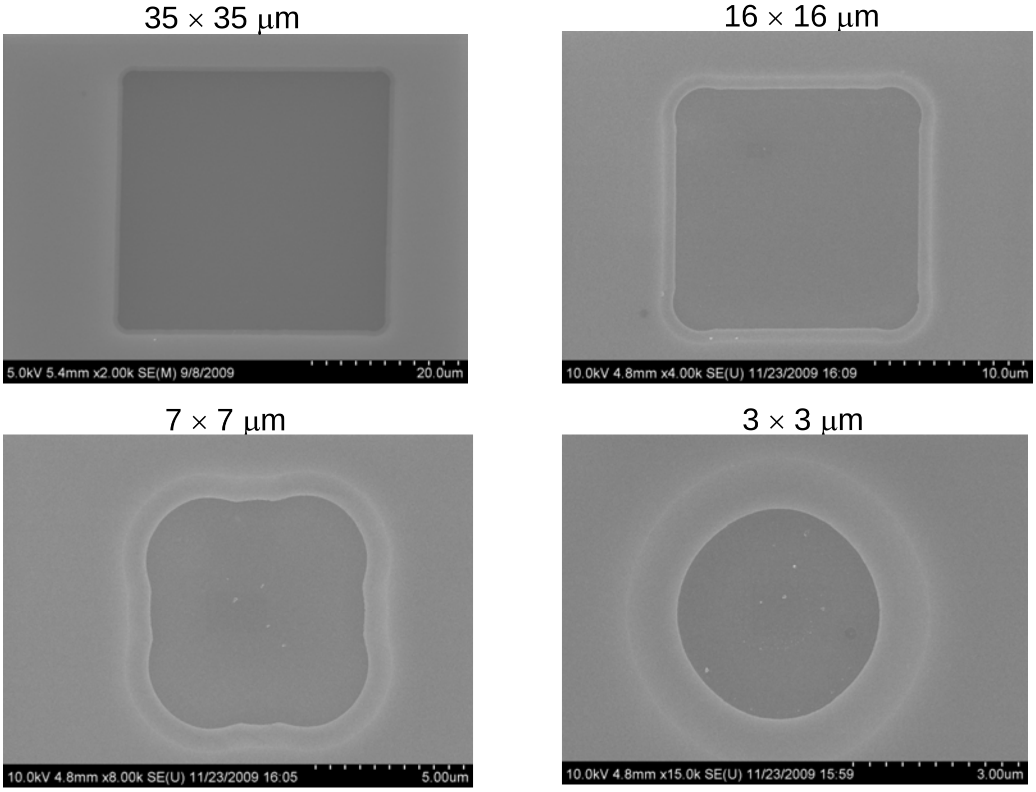


Figure 2.7 **(a)** Photograph of a finished chip with metal top contacts. **(b)** A micrograph of a finished junction from the chip shown in (a)**.** **(c)** SEM image of cross section of a junction. **(d)** Magnified view of (c).

Figure 2.8 shows top view SEM images of the junction vias with four different areas. Due to the limitation of photolithography, the shape of the via becomes rounded for sizes below 16 × 16 μm, and the smallest via is circular rather than square.


35 × 35 μm

16 × 16 μm

7 × 7 μm

3 × 3 μm

Figure 2.8 Top view SEM images of completed junction vias with four different areas.

Due to the nanometer length scale of the molecules, the surface topography and roughness of the substrate for a molecular junction strongly affect electrical behavior of the molecular junction. To reduce the possibility of short circuits caused by the direct contact between the rough surface of the substrate and top contact layer, the substrates are required to be very flat. AFM was applied to investigate the surface roughness of the substrate. Figure 2.9 shows AFM images of carbon surfaces at different points during fabrication. Figure 2.9 (a) shows the freshly fabricated PPF surface after pyrolysis, which has a root-mean-square roughness (rms) of 0.36 nm for a 5 μm × 5 μm area. Figure 2.9 (b) shows the surface of the 10-nm thick e-beam carbon film on PPF which has an rms roughness of 0.42 nm. Figure 2.9 (c) shows the line profiles of the two samples in (a) and (b). After all the microfabrication steps and e-beam carbon deposition, the rms roughness of carbon surface was nearly unchanged, indicating that the fabrication process has a very small effect on the roughness of carbon surface. Such flatness is comparable to or less than the thickness of the molecular layer studied in this thesis (2-5 nm).

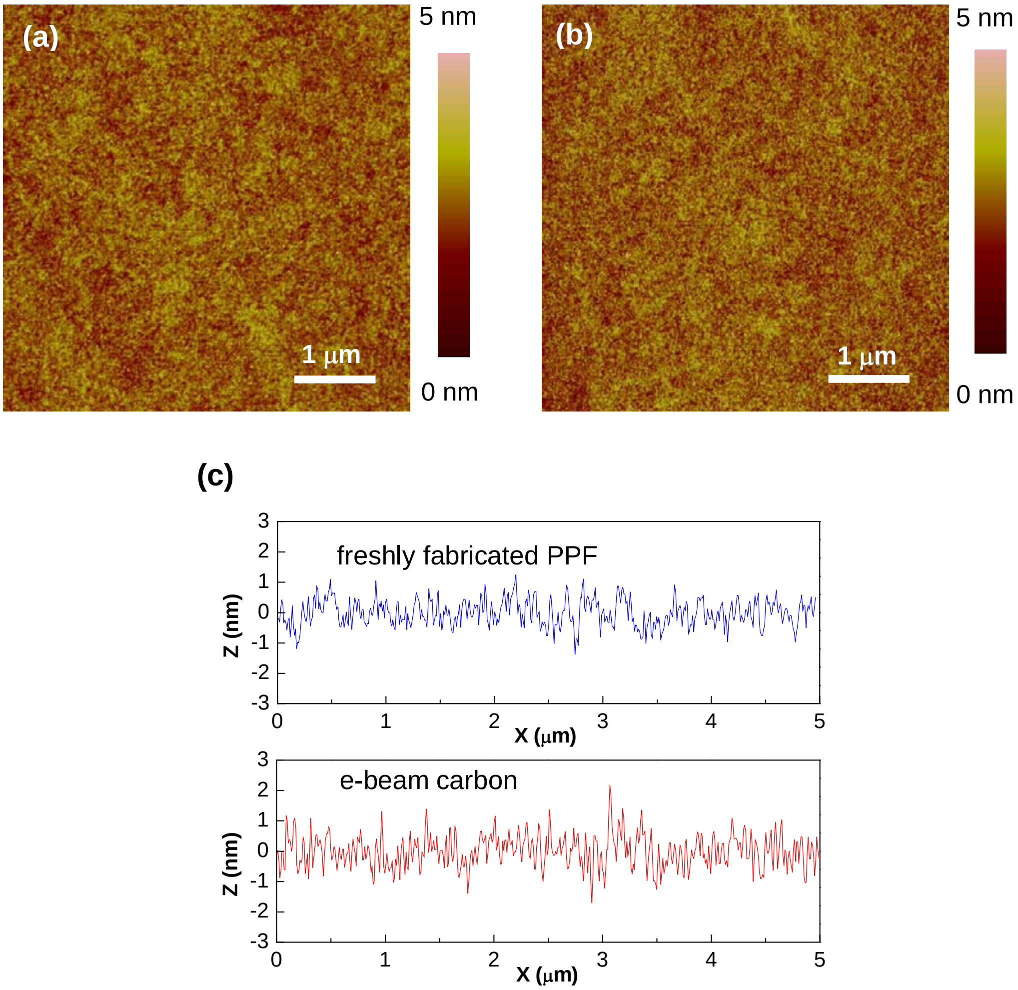


Figure 2.9 AFM analysis of carbon surfaces. **(a)** Freshly fabricated PPF with an rms roughness of 0.36 nm (5 μm × 5 μm area). **(b)** 10-nm e-beam carbon film on PPF with an rms roughness of 0.42 nm. **(c)** Depth profiles of the samples in (a) (blue line) and (b) (red line).

2.3.2 Spectroscopy characterization

XPS was used to analyze the chemical composition of different carbon surfaces. Figure 2.10 (a) and (b) are high resolution XPS spectra of O_{1s} and C_{1s} for three different carbon samples, which are freshly made PPF immediately following pyrolysis (step (b) in Figure 2.1), PPF after microfabrication (step (d) in Figure 2.1), and 10-nm e-beam carbon film on PPF (step (e) in Figure 2.1). In Figure 2.10 (a), the peak at 284.5 eV is attributed to graphite-like carbon. In Figure 2.10 (b), the freshly made PPF shows a small oxygen peak at 532.7 eV which increases significantly after microfabrication processing. However, after depositing 10 nm thick e-beam carbon films, the oxygen peak intensity decreases to a value comparable to that of freshly made PPF. The atomic oxygen to carbon ratio (O/C) is the parameter often used to determine the oxygen coverage of the carbon film.[57, 106] The O/C ratio for the three carbon samples are listed in Table 2.2. The O/C ratio for PPF surface increased from 4.0% to 21.8% after microfabrication, which is likely due to oxidation by the oxygen plasma in the step of PECVD SiO_2 deposition. After e-beam carbon deposition, the O/C ratio was reduced to 6.8%.

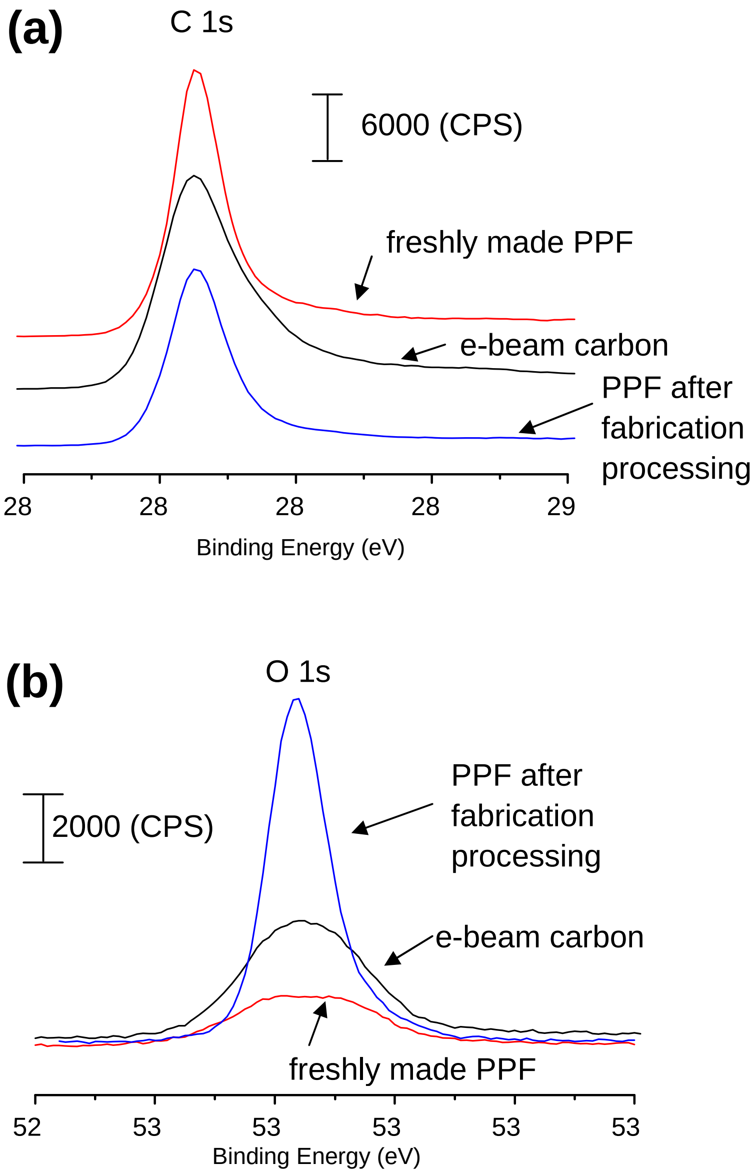


Figure 2.10 High resolution XPS spectra of **(a)** C_{1s} and **(b)** O_{1s} regions for different carbon films.

Sample	O/C ratio (%)
freshly made PPF	4.0
PPF after fabrication processing	21.8
e-beam carbon	6.8

Table 2.2 Atomic O/C ratios of different carbon films, from XPS.

Raman spectroscopy was used to characterize the microstructure of carbon films. Figure 2.11 shows the representative Raman spectra of freshly prepared PPF, PPF after fabrication processing and e-beam carbon films (10 nm in thickness) in the region of 1000-2000 cm^{-1}. The spectrum of e-beam carbon shows a broad peak centered at ~1500 cm^{-1} which is characteristic of amorphous carbon. The spectra of PPF films for both freshly fabricated PPF and PPF after fabrication processing contain two distinct bands at 1350 cm^{-1} and 1600 cm^{-1}. The band at 1600 cm^{-1} assigned as G-band is commonly observed in graphitic materials, and the band at 1350 cm^{-1} assigned as D-band is diagnostic of disorder in carbon materials.[107] The Raman spectrum of freshly prepared PPF is similar to that of PPF after fabrication, indicating that the fabrication process has minor effect on microstructure of PPF. The broad spectrum for e-beam carbon indicates significantly greater disorder than that in PPF.

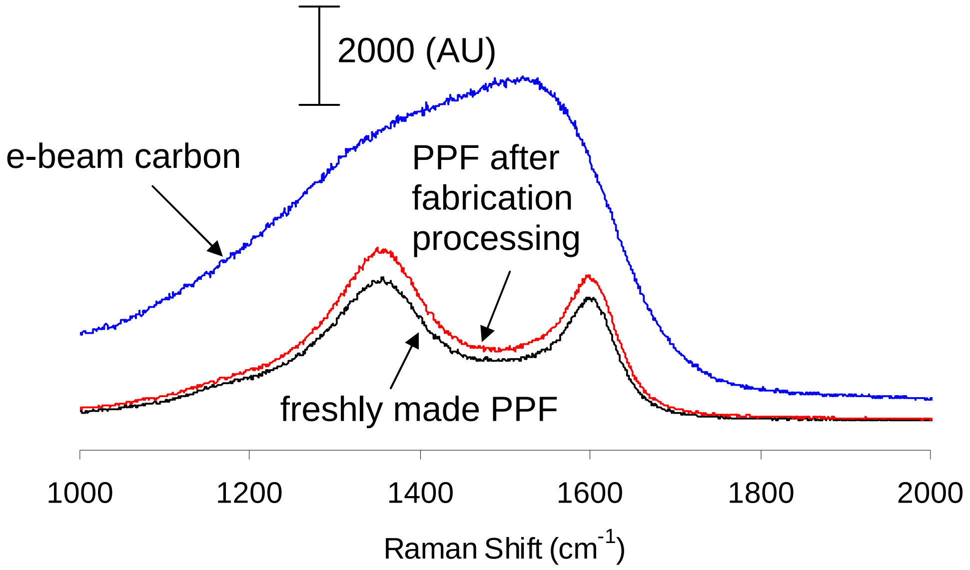


Figure 2.11 Raman spectra of freshly made PPF, PPF after fabrication processing and 10 nm of e-beam carbon film.

2.3.3 Comparison of electronic behavior of junctions fabricated with and without e-beam carbon

In this thesis, a "working" device is defined as a junction showing voltage-current density (J-V) characteristics significantly different from the control junction (i.e. carbon/Cu without molecules) or open circuit.

Figure 2.12 (a) and (b) show overlays of 32 J-V curves of all the carbon/NAB/Cu junctions (80 × 80 μm) on one chip using PPF and e-beam carbon as substrates respectively. As described in the experimental section, PPF/e-beam carbon/NAB/Cu junctions were fabricated following the steps shown in Figure 2.1, while PPF/NAB/Cu junctions were fabricated in the same way but without a 10 nm of e-beam carbon film between molecules and PPF. To make a direct comparison, both chips shown in Figure 2.12 were prepared from one wafer, and surface modification and top contact deposition were performed at the same time under same conditions. The NAB film thicknesses were both 3.8 ± 0.2 nm as measured by AFM. Although both samples showed 100% yield (32/32), PPF/NAB/Cu exhibited less reproducible behavior than PPF/e-beam carbon/NAB/Cu. The relative standard deviation (rsd) of J at 0.5 V was 71% for PPF/NAB/Cu junctions while the rsd was 10% for PPF/e-beam carbon/NAB/Cu junctions. In addition, most of the JV curves for PPF/NAB/Cu show higher J values than those of PPF/e-beam carbon/NAB/Cu at the same voltages. XPS analysis of different carbon surfaces (Table 2.2) shows that the atomic O/C ratio increased from 4.0% to 21.8% after microfabrication process, and was reduced to 6.8% after deposition of a 10 nm thick e-beam carbon film on PPF surface. The high O/C ratio implies a high oxygen coverage on carbon surface, which might affect the surface modification reaction of diazonium reduction and thus the quality of molecular film. Variations in surface coverage and packing density may result in more scattered and higher J-V characteristics of PPF/NAB/Cu junctions than those of PPF/e-beam carbon/NAB/Cu junctions.

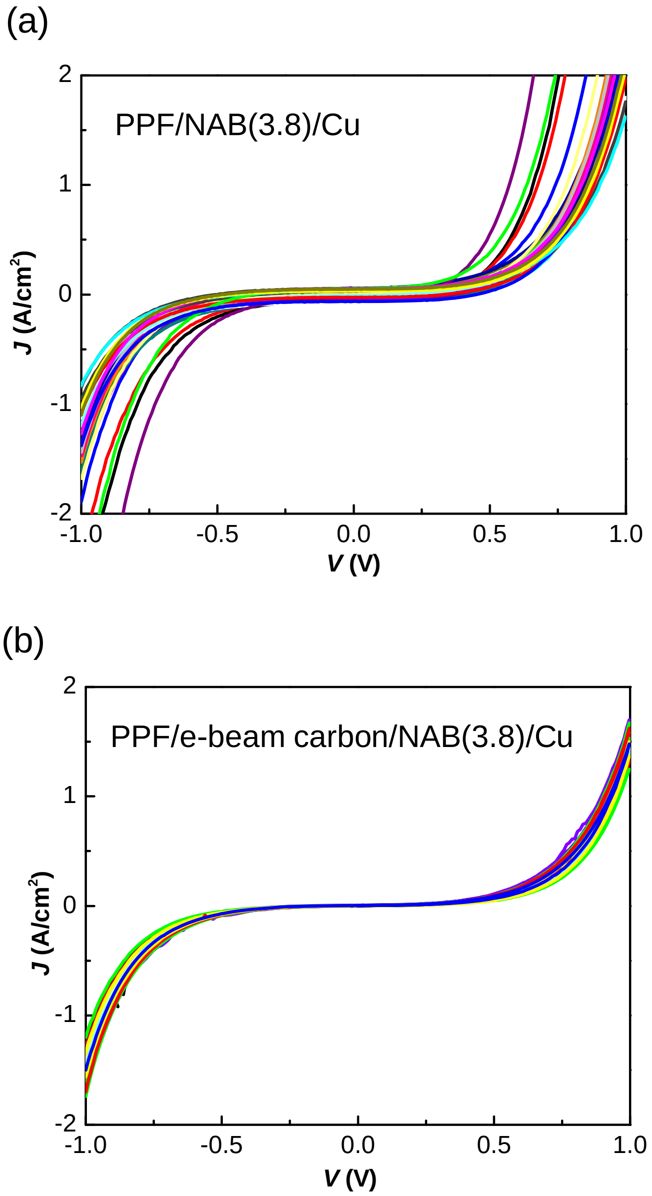


Figure 2.12 Overlays of 32 J-V curves for microfabricated molecular junctions **(a)** PPF/NAB(3.8)/Cu and **(b)** PPF/e-beam carbon/NAB(3.8)/Cu. Device size was 80 × 80 μm, and the scan rate was 1 V/s.

Figure 2.13 (a) shows the overlays of the average J-V curves of 32 junctions from each chip in Figure 2.12. Figure 2.13 (b) shows the same J-V curves plotted on a logarithmic scale. Both J-V curves for junctions fabricated with and without e-beam carbon show similar characteristics in shape and current density. Although e-beam carbon has a higher resistivity (~0.015 Ω·cm)[59, 108] than PPF (~0.006 Ω·cm), the e-beam carbon added negligible resistance to the PPF/NAB/Cu junction. Table 2.3 lists the data of yield, average J (V=0.5 V) and rsd of J (0.5V) for junctions (3 × 3 to 400 × 400 μm) fabricated with and without e-beam carbon. The average values of J (0.5V) for PPF/NAB/Cu and PPF/e-beam carbon/Cu with same areas were quite similar. The yield and reproducibility of junctions made with e-beam carbon were superior to those without e-beam carbon, indicating that the addition of 10 nm of e-beam carbon film can significantly improve junction quality in terms of yield and reproducibility. Furthermore, compared to PPF, e-beam deposited carbon is a more suitable substrate in an industrial environment. Therefore, the e-beam carbon was included in all junctions in the following sections in this thesis.

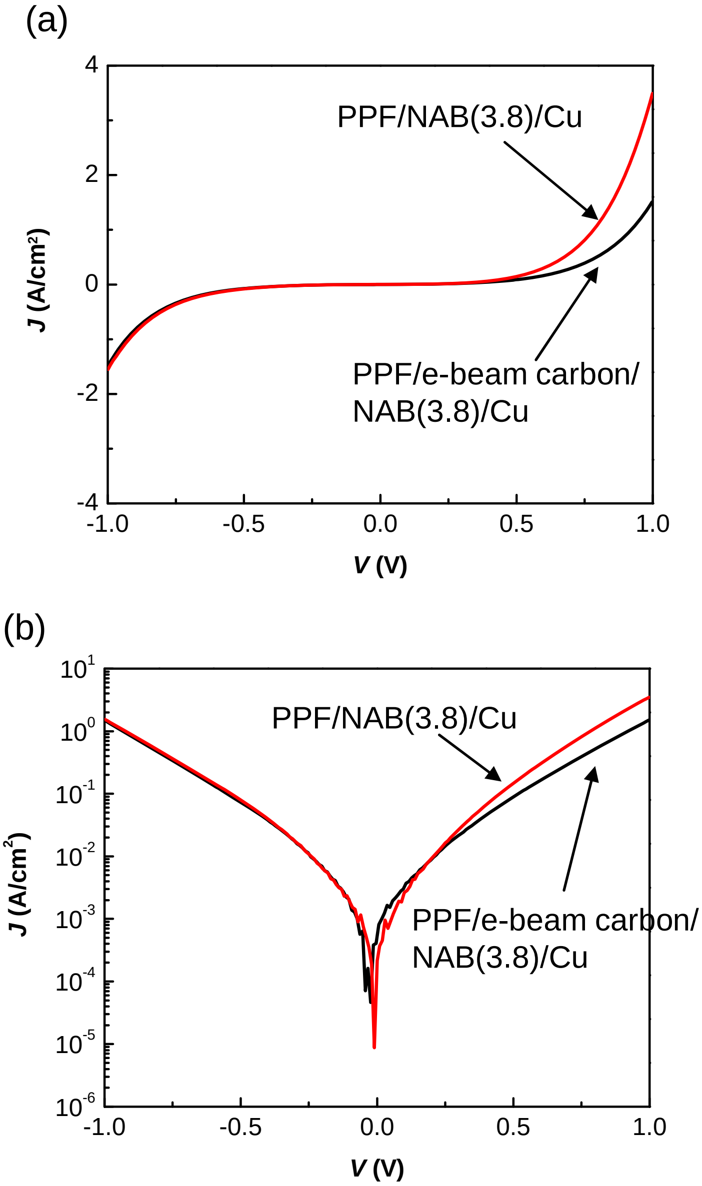


Figure 2.13 **(a)** Average J-V curves for PPF/NAB(3.8)/Cu and PPF/e-beam carbon/NAB(3.8)/Cu and each curve is an average of 32 junctions shown in Figure 2.12. **(b)** Same plot in (a) in log scale.

		PPF/NAB(3.8)/Cu			PPF/e-beam C/NAB(3.8)/Cu		
Dimension (μm)	Area[a] (μm^2)	Jave[b] at 0.5 V (A/cm^2)	rsd (%)	Yield[c]	Jave[b] at 0.5 V (A/cm^2)	rsd (%)	Yield[c]
400 × 400	156000	0.308	30	8/9	0.325	24	9/9
180 × 180	31000	0.238	25	9/10	0.321	25	10/10
80 × 80	6400	0.132	53	10/10	0.173	11	10/10
35 × 35	1300	0.138	42	6/10	0.173	19	10/10
16 × 16	250	0.106	22	8/10	0.162	12	10/10
7 × 7	50	0.105	69	6/10	0.145	87	10/10
3 × 3	10	0.039	84	7/10	0.040	110	8/10

a. determined with optical or SEM microscopy of completed junctions.
b. average value of all the "working" junctions which did not show short or open circuits.
c. number of junctions showing J-V characteristics significantly different from short or open circuits.

Table 2.3 Comparison of junctions fabricated with and without e-beam carbon.

2.4 Summary

In this chapter, a new approach to microfabricate carbon-based molecular junctions using conventional semiconductor processing technologies has been demonstrated. The fabrication process is applied on 4-inch wafers using simple steps and techniques that are compatible with standard CMOS fabrication techniques.

The microfabricated junction vias were characterized with a variety of microscopic and spectroscopic techniques. The comparison of microfabricated junctions made with e-beam carbon and PPF as substrate shows that the electronic properties of the junctions are similar to each other, but junctions have better yield and reproducibility when e-beam carbon is used.

CHAPTER 3

ELECTRICAL CHARACTERIZATION OF MICROFABRICATED CARBON/MOLECULE/METAL JUNCTIONS

3.1 Introduction

In Chapter 2, a new micro-fabrication process to fabricate carbon-based molecular junctions is demonstrated, using simple techniques compatible with CMOS industry. The goal of this chapter is to evaluate the reproducibility, stability and reliability of the electronic behavior of these microfabricated devices, since they are basic requisites before molecular electronic devices can be integrated with commercial microelectronics. In this chapter, the electronic properties of the carbon/molecule/Cu junctions on the yield and reproducibility, the area scaling, and the operational stability are investigated. Furthermore, the electron transport mechanism is probed and the electronic behavior is compared among junctions with similar structure but made with various fabrication methods.

3.2 Experimental

3.2.1 Device fabrication

The procedure used to fabricate the carbon/molecule/metal junctions was described in detail in Chapter 2. As discussed in chapter 2, electron beam deposited carbon films as substrate improved the junction yield and reproducibility, since PPF was oxidized after the fabrication process, leading to a degradation of yield and reproducibility. Therefore, e-beam carbon films were included in all the junctions discussed in this chapter.

3.2.2 Electronic characterization

Unless stated otherwise, current density-voltage (J-V) curves were obtained at 1 V/s in a 3-wire arrangement at room temperature as described in Chapter 2. Junctions were also tested in 2-wire and 4-wire configurations in some cases. A detailed wiring diagram for 2-, 3-, and 4- wire configurations is illustrated in Figure 3.1. In a 2-wire configuration, the bias was applied between one probe placed on carbon and the other one on metal top contact, and current was monitored with a current amplifier (Model 570, Stanford Research Systems). In a 3-wire configuration, the third probe labeled as “S+” was used to compensate the ohmic losses in carbon electrode due to the non-negligible resistance (10^2-10^3 Ω) in carbon leads and associated contacts. The resistance of the metal lead was significantly lower (<20 Ω), but could be corrected with a fourth probe (labeled as “S-”) on the opposite end of the metal lead if necessary. A potentiostat (Reference 600, Gamry Instruments) was used for 3-wire measurement since a wide current range could be obtained (600 mA to 60 pA). The 4-wire configuration was implemented with Labview software and a National Instruments 6110 multifunction data acquisition board. For all the obtained current density-voltage (J-V) curves, the voltage was plotted as carbon relative to metal top contact.

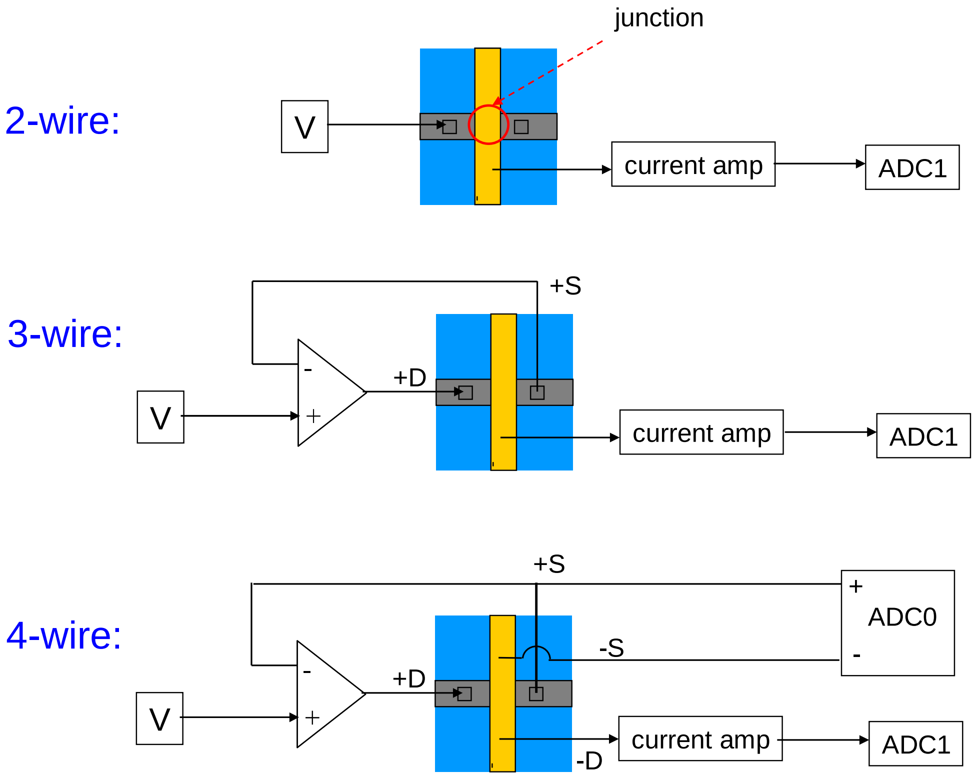


Figure 3.1 Wiring schematics for 2-, 3-, and 4-wire configurations. V is bias voltage from a digital to analog converter; ADC1 is the analog to digital channel for current. ADC0 monitors voltage, and has a differential input in the case of the 4-wire arrangement. “D” and “S” denote “drive” and “sense”, with the “sense” leads corresponding to high impedance voltage monitors.

For J-V curves obtained above and below room temperature, the samples were measured in a cryogenic probe station (Janis ST-500). The samples were placed on a copper stage in the vacuum chamber and the chamber was pumped to 2×10^{-6} torr by a turbo pump. The chamber was cooled down to 100 K by flowing liquid nitrogen. J-V curves were collected in a range from 100-390 K every 10 K by heating the sample stage with a temperature controller (Scientific Instruments model 9700).

As stated in Chapter 2, a "working" device is defined as a junction showing voltage-current density (J-V) characteristics significantly different from the control junction (i.e., carbon/Cu without molecules) or open circuit. Junctions are denoted from bottom to top with the molecular layer thickness in nm determined by AFM in parentheses, for example, PPF/e-beam carbon/NAB(3.8)/Cu/Au. The thicknesses of e-beam carbon, Cu and Au were 10 nm, 30 nm and 15 nm, in all cases.

3.3 Results and discussion

3.3.1 Yield and reproducibility

For technological applications, high yield and reproducibility are basic requisites for molecular junctions. Here "yield" indicates the percentage of working devices out of all the devices measured, and "reproducibility" is defined as the relative standard deviation (rsd) of the current density at V=0.5 V for all the working devices of the same type.

Figure 3.2 (a) shows an overlay of 32 J-V curves of all the PPF/e-beam carbon/NAB(3.8)/Cu junctions (80 × 80 μm) on one chip and (b) shows the same plot on a logarithmic scale. The molecular structure of NAB is also indicated in Figure 3.2 (a). The relative standard deviation is 10% for current density (J) at V=0.5 V and is less than 20% in the entire voltage range.

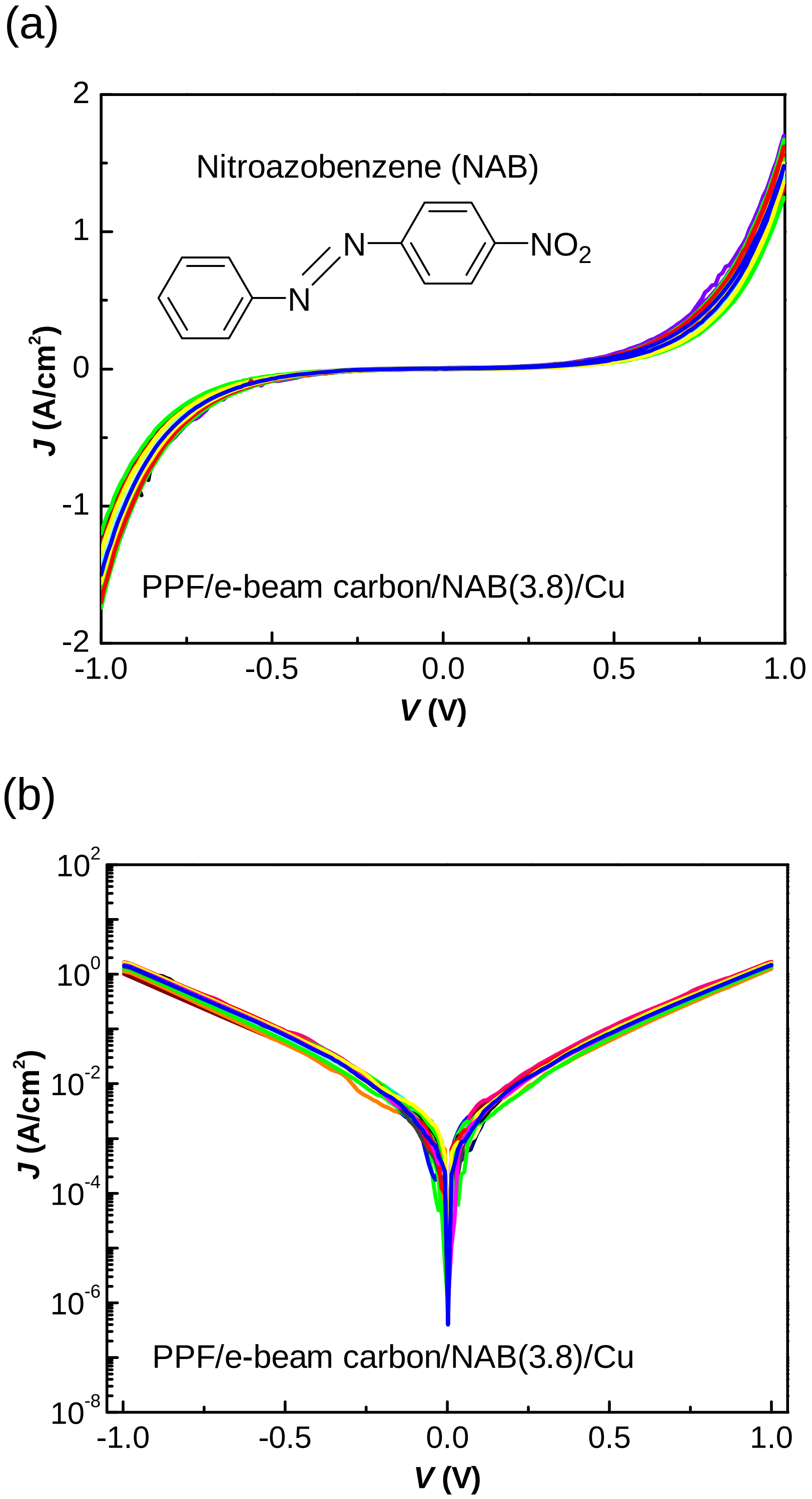


Figure 3.2 **(a)** Overlay of J-V curves for all the 32 PPF/e-beam carbon/NAB(3.8)/Cu junctions on one chip. **(b)** Results of (a) plotted on a logarithmic scale. Device area was 80 × 80 μm. Yield was 100% (32/32), and relative standard deviation for J (0.5 V) was 10%.

The yield and reproducibility among different samples were investigated by comparing J-V characteristics of junctions fabricated from three wafers, each of which was fabricated on different days independently, including the fabrication of PPF and junction via, molecular layer and metal top contact deposition, and device measurement. Figure 3.3 shows the average J-V curves for 9-10 junctions from each of three wafers on a log scale, and the error bars stand for one standard deviation. The results showed a good overlap of the three J-V curves and no obvious differences in curve shape or symmetry. The data in Figure 3.3 are summarized in Table 3.1, where the values of low voltage resistance and current density at 0.5 V are shown for all the junctions fabricated from three samples. Both sample 1 and 2 showed a yield of 100% (10/10), and sample 3 showed a yield of 90% (9/10) with one junction shorted. The relative rsd for J at 0.5 V for a total of 29 junctions on three samples was 38% and the variation of low voltage resistance was within a factor of 2, indicating a good yield and reproducibility from wafer to wafer.

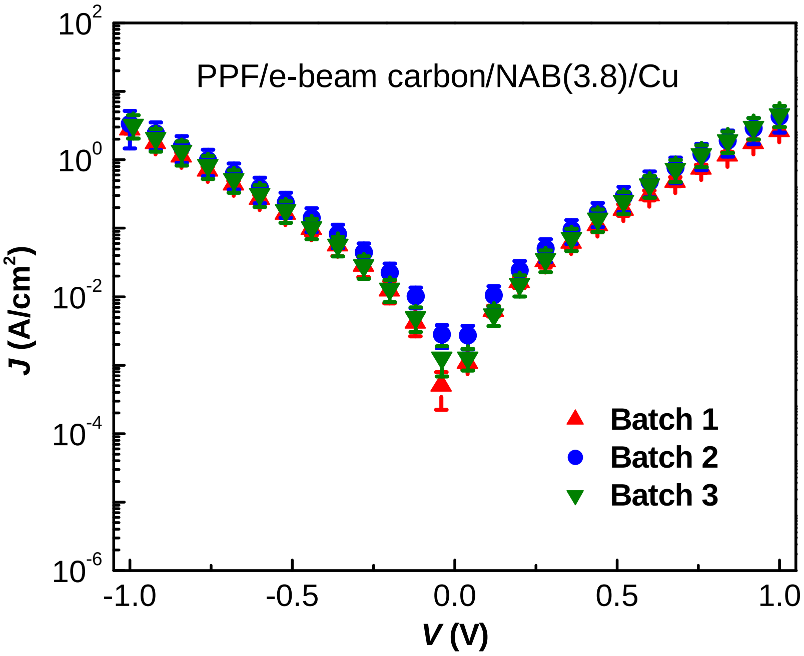


Figure 3.3 Average J-V responses for three batches of PPF/e-beam carbon/NAB(3.8)/Cu junctions (35 × 35 μm) fabricated on different days on different wafers, with error bars shown for one standard deviation of 9-10 junctions in each batch.

	Sample 1		Sample 2		Sample 3	
Junction number	R (±0.1V, MΩ)	J (0.5 V, A/cm^2)	R (±0.1V, MΩ)	J (0.5 V, A/cm^2)	R (±0.1V, MΩ)	J (0.5 V, A/cm^2)
1	1.43	0.130	0.918	0.291	1.36	0.332
2	1.59	0.142	0.766	0.337	2.79	0.158
3	1.77	0.165	0.784	0.350	2.59	0.170
4	1.91	0.153	0.936	0.331	2.14	0.243
5	1.97	0.175	1.060	0.241	1.75	0.240
6	1.04	0.250	0.803	0.290	2.35	0.206
7	1.80	0.168	1.190	0.235	3.73	0.179
8	2.44	0.158	0.837	0.305	1.48	0.314
9	1.89	0.183	1.630	0.109	2.83	0.097
10	2.37	0.138	3.640	0.048	-	-
Average	1.82±0.41	0.166±0.034	1.26±0.88	0.254±0.101	2.34±0.75	0.216±0.075

Table 3.1 Low voltage resistances and current densities for three samples of PPF/e-beam carbon/NAB(3.8)/Cu shown in Figure 3.3.

The high yield and reproducibility of the microfabricated junctions is partially due to the strong C-C covalent bond between the substrate and aromatic molecular layer, presumably preventing the penetration of electron beam deposited Cu atoms. Furthermore, previous XPS analysis of PPF/NAB/Cu shows that Cu-N bond was formed after Cu deposition and the formation of Cu-N bond is likely to anchor the evaporated Cu atoms and reduce penetration of Cu into the NAB film.[109] Figure 3.4 shows overlays of 10 J-V curves on linear (a) and logarithmic (b) scales for PPF/e-beam carbon/FL(2.8)/Cu junctions (80 × 80 μm) from one sample. The yield was 100% (10/10) and the rsd values for J were within 20% in the entire voltage range (±1 V). Obviously, there are no Cu-N bonds formed in the case of FL (structure shown in Figure 3.4), indicating that the structure of the molecular end group has minor effect on the electronic behavior of carbon/molecule/Cu junctions in terms of yield and reproducibility. Furthermore, the results for junctions based on NAB and FL demonstrate that the high yield (>90%) and reproducibility (rsd<40% for J at 0.5 V) occurs for both cases, implying that electron beam deposited Cu is a reliable top contact for carbon-based molecular junctions.

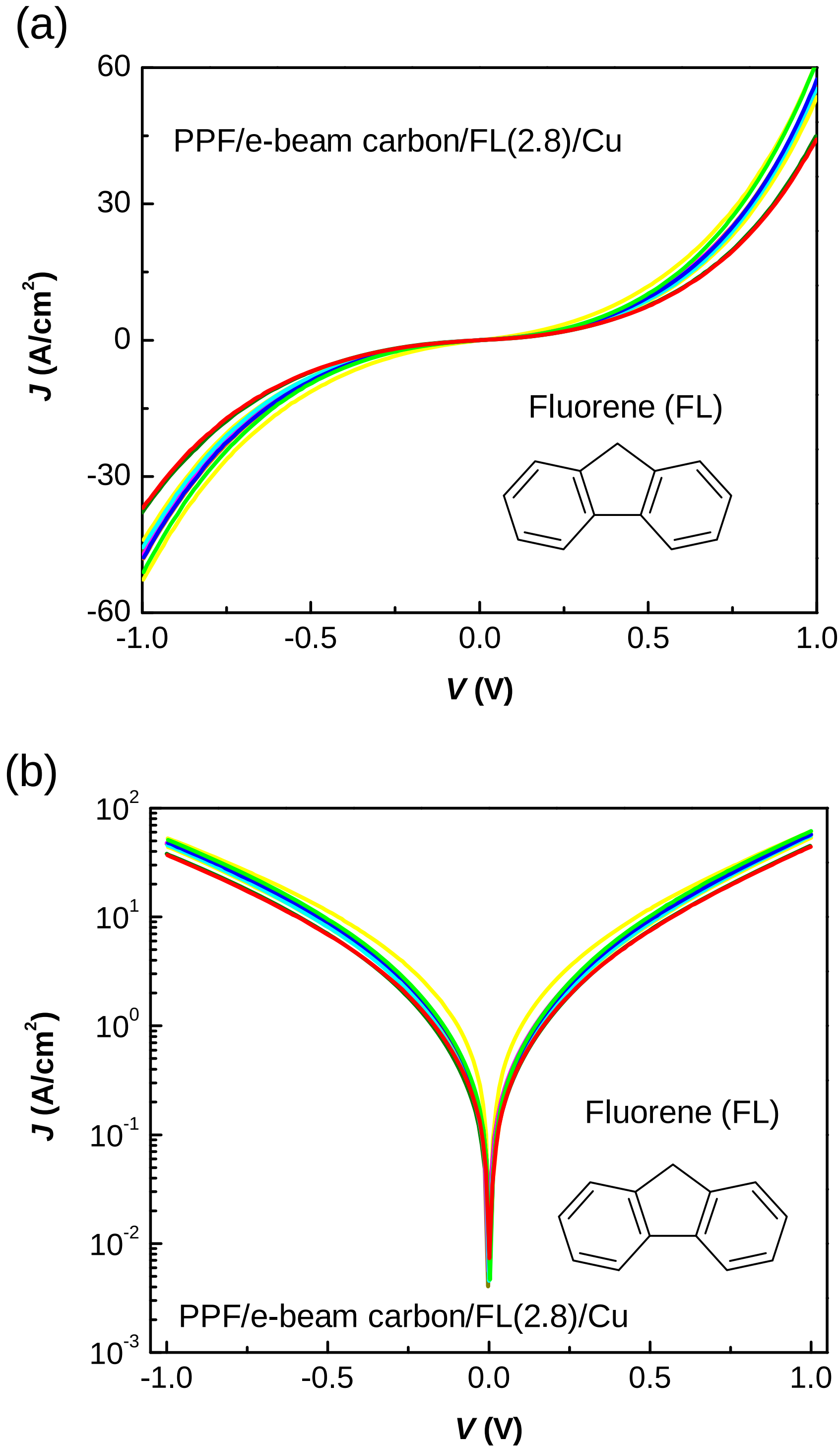


Figure 3.4 Overlay of J-V curves for 10 junctions of PPF/e-beam carbon/FL/Cu from one chip for **(a)** linear and **(b)** logarithmic scales.

3.3.2 Scalability

Current-voltage (I-V) curves for microfabricated PPF/e-beam carbon/NAB/Cu junctions with a range of areas from 16 × 16 to 400 × 400 μm are plotted in Figure 3.5 (a). Each curve is obtained by averaging I-V curves from 9-10 junctions, representing the I-V characteristics of junctions with corresponding area. The error bars represent one standard deviation unit. As expected, the current increases with increasing junction size and there are no obvious differences in shape or symmetry for all the I-V characteristics. When the current is divided by the junction area, the current density-voltage (J-V) curves are obtained, as shown in Figure 3.5 (b). The five curves approximately overlap, indicating that the JV curves are independent of junction area over a factor of 600 in both curve shape and magnitude. Table 3.2 summarizes the data of PPF/e-beam carbon/NAB(3.8)/Cu junctions with varying area from 3 × 3 to 400 × 400 μm. The average values of current density at 0.5 V range within one order of magnitude, while the junction areas range over four orders of magnitude, indicating that current scales with area for these microfabricated junctions. However, as junction size decreases, the current density at 0.5V shows a minor decrease. The decrease in current density is likely a result of an increase in molecular film thickness. Due to the nonlinear diffusion effect on small-area electrodes, there will be more current flowing on the carbon surface per unit area of the small devices than large ones during the diazonium reduction, resulting in the growth of thicker molecular films on small devices. The device yield and reproducibility degrade for 3 × 3 and 7 × 7 μm junctions, but the reasons are unclear. SEM images of junction vias with different areas shown in Figure 2.8 reveal that the junction shape becomes rounded when the size is smaller than 16 × 16 μm, and debris or defects are apparent for the smaller sizes. Since the parameters used in lithography are not optimized, the rounded features are probably caused by the overexposure of the photoresist to the UV light during the lithography and can be eliminated by using proper dosage of the UV exposure. Figure 3.6 shows SEM images of top view of a junction via deposited with (a) and without (b) e-beam carbon film and cross section (c) of a junction via after BOE etching. The e-beam carbon film did not completely cover the surface of the junction hole and formed a distinctive edge between covered and uncovered areas as shown in Figure 3.6 (b). Such “edge effect” was caused by the “overhang” of the photoresist shadow mask after etching of PECVD oxide by BOE as shown in Figure 3.6 (c). As discussed in Chapter 2, junctions made with and without e-beam carbon showed similar behavior, suggesting that the “edge effect” did not affect the average junction behavior. However, as shown in Table 3.2, when the junction size decreased, the ratio of the area of uncovered surface with e-beam carbon over the total junction area became non-negligible, which could partially explain the lower precision observed for 3 × 3 and 7 × 7 μm junctions. To eliminate such “edge effect” while keeping a low O/C ratio of carbon surface, an Ar or H_2 plasma can be applied to reduce the O/C ratio without using e-beam carbon. It is possible that the PPF surface will become rougher due to the use of plasma. However, by controlling the operational conditions of the plasma such as power, time, gas concentration, etc., the increase of surface roughness can be minimized so that the change of roughness should have a minor effect on the resulting IV characteristics of the microfabricated junctions.

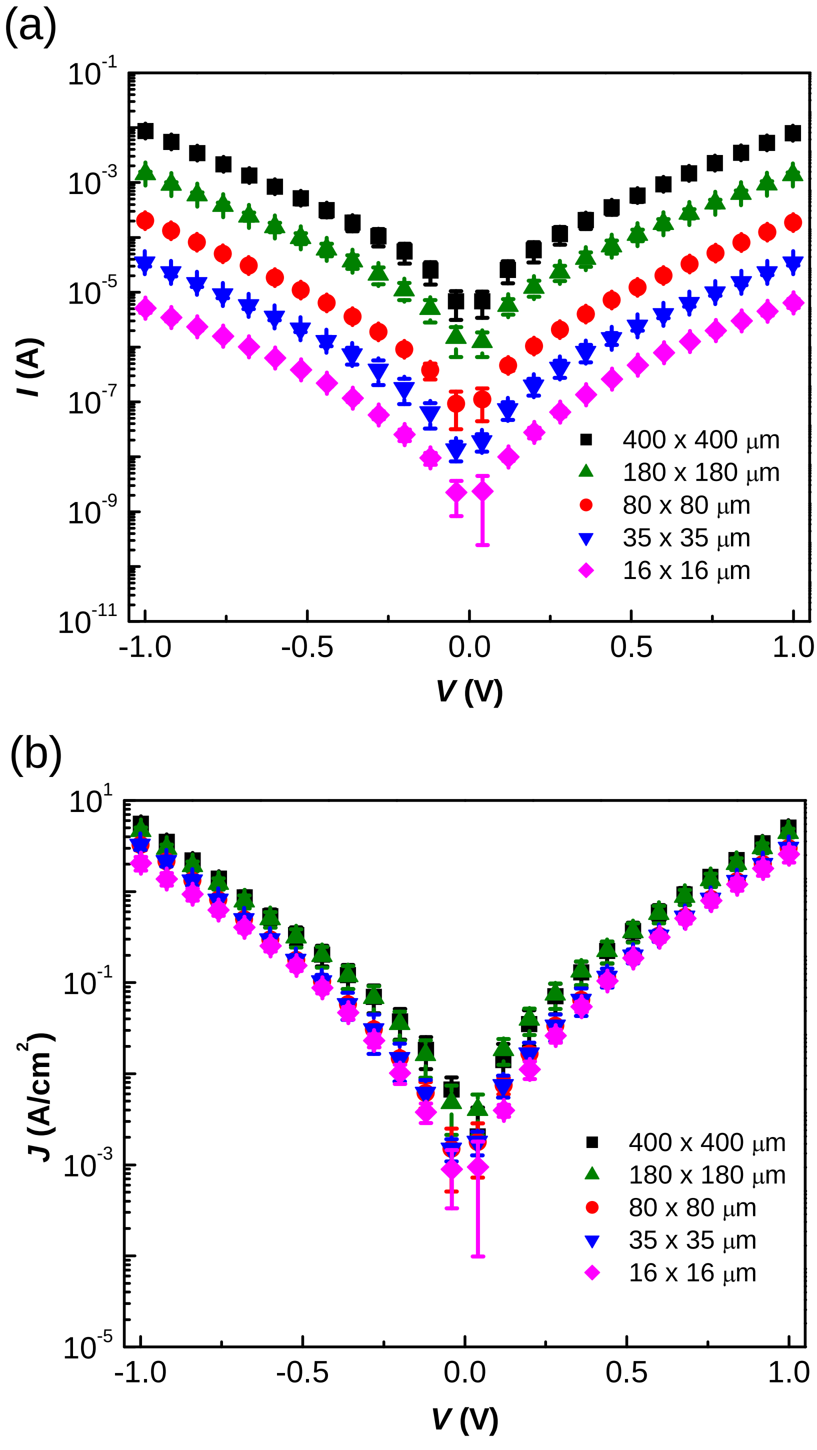


Figure 3.5 **(a)** I-V curves for PPF/e-beam carbon/NAB/Cu junctions with five different areas (legend shows the size of the junction). The error bar shows the standard deviation on averaging 9-10 junctions for each area. **(b)** J-V curves obtained by dividing the current of junction shown in (a) by the corresponding areas.

Dimension (μm)	Area[a] (μm^2)	E-beam carbon surface coverage[b] (%)	Jave[c] at 0.5 V (A/cm^2)	rsd (%)	Yield
400 × 400	156000	99	0.325	24	9/9
180 × 180	31000	98	0.321	25	10/10
80 × 80	6400	97	0.173	11	10/10
35 × 35	1300	94	0.173	19	10/10
16 × 16	250	90	0.162	12	10/10
7 × 7	50	74	0.145	87	10/10
3 × 3	10	51	0.040	110	8/10

a. the total area of the junction via determined with optical or SEM microscopy of completed junctions.

b. the ratio of e-beam carbon covered junction area over the total junction area.

c. average value of all the “working” junctions which did not show short or open circuits.

Table 3.2 Comparison of PPF/e-beam carbon/NAB(3.8)/Cu junctions with varying area.

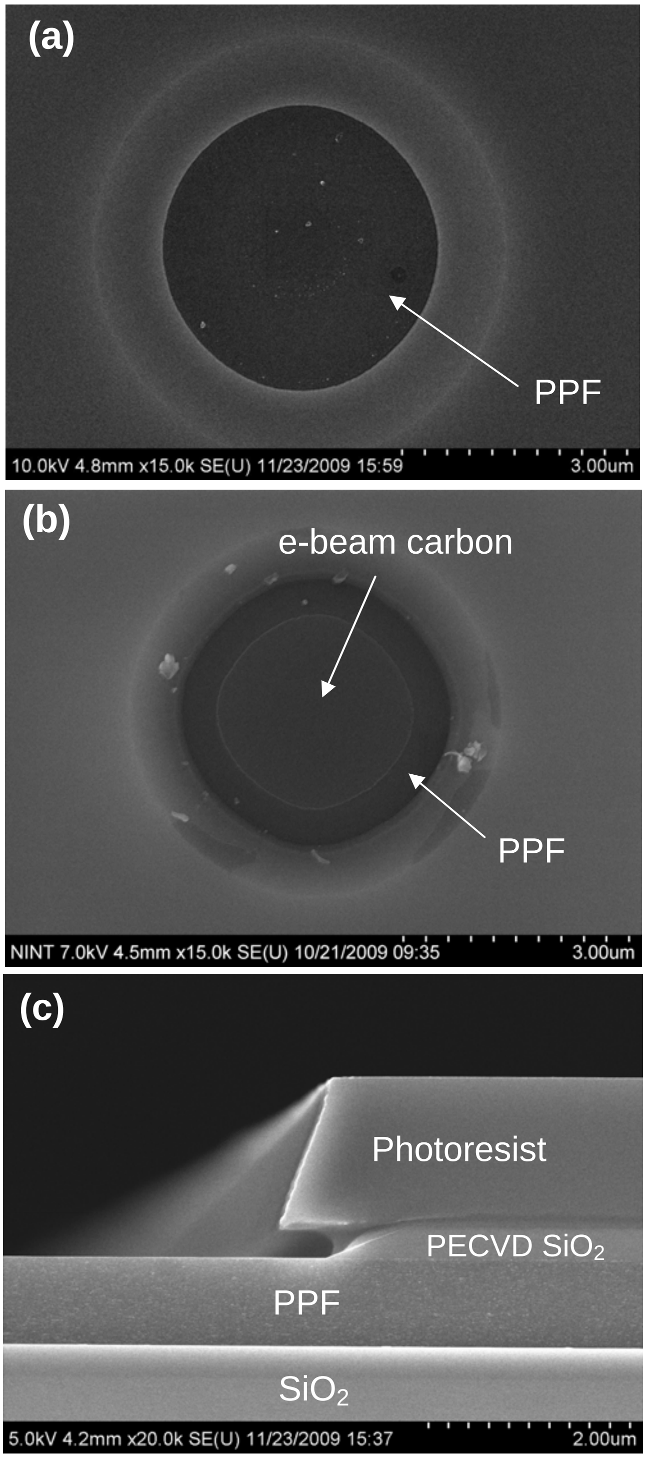


Figure 3.6 **(a)** Top view SEM image of a PPF junction via (3 × 3 μm) without deposition of e-beam carbon film. **(b)** Top view SEM image of a PPF junction via (3 × 3 μm) after deposition of 10-nm of e-beam carbon film. **(c)** SEM image of cross section of a junction via after BOE etching and before e-beam carbon deposition (step (d) in Figure 2.1).

3.3.3 Effect of ohmic potential drop on large and small devices

As described in Chapter 2, PPF films have a lower conductivity than that of most metals. Therefore, a high current (e.g., mA magnitude) can cause significant ohmic potential drop through the PPF leads of the molecular junctions, leading to some distortion of the resulting J-V response. To compensate ohmic losses in PPF and metal leads, the "3-wire" and "4-wire" measurement techniques were used as described in section 3.2.2. The effect of uncompensated resistance on junction electronic behavior obtained from the three measurement configurations is shown in Figure 3.7 (a) for the case of a large (400 × 400 μm) and (b) a small (16 × 16 μm) NAB junction. For the case of large device, there are significant differences in curve shape and current value among the three measurements, while the differences are minor for the small device. For example, the measured current values at 1 V were 2.03 mA for 2-wire, 14.6 mA for 3-wire, and 35.0 mA for 4-wire measurement in Figure 3.7 (a), while for the small device shown in (b), the current values at 1 V were 2.11, 2.99 and 2.88 μA for 2-, 3- and 4-wire measurements respectively. These results indicate that the resistance error caused by PPF, metal and associated contact resistances can be significantly reduced by decreasing the junction size. Furthermore, it is clear that lead and contact resistance is a consideration in any practical devices containing PPF, but the problem is less severe as the junction size decreases.

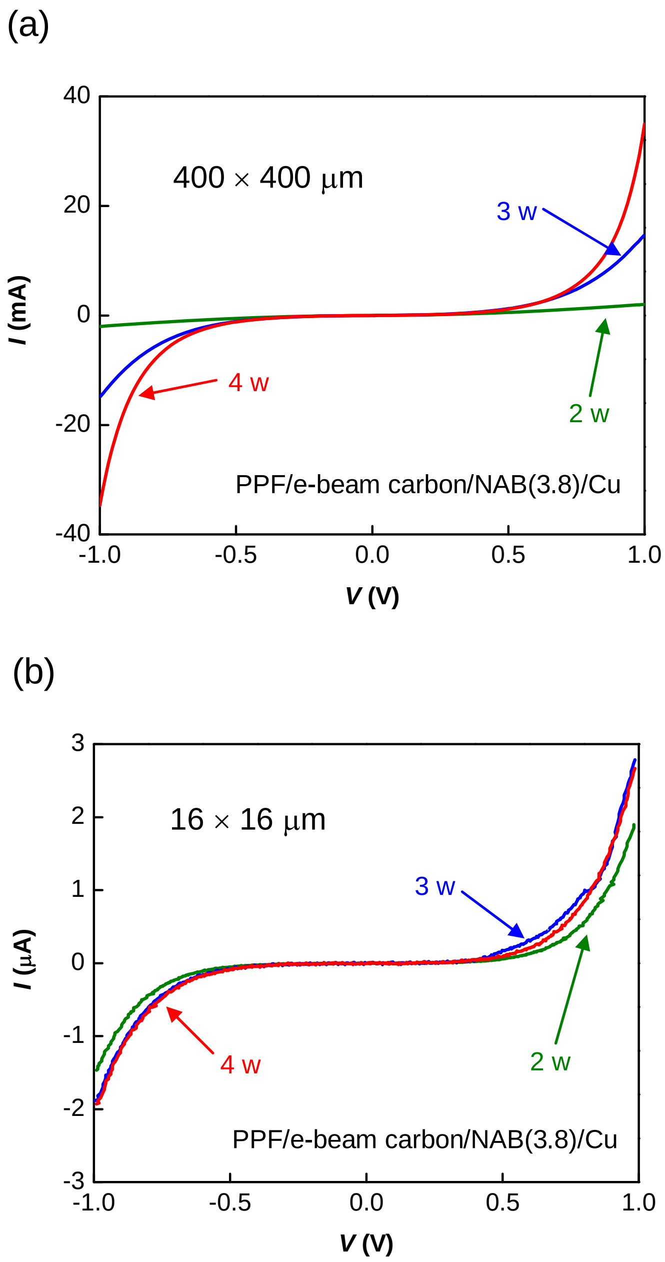


Figure 3.7 Effect of contact and lead resistance on observed current-voltage curves for NAB(3.8) junctions of different sizes. 3-wire (3 w) geometry corrects for PPF resistance, while 4-wire (4 w) corrects for both PPF and Cu/Au resistance. Note large difference in current scales.

3.3.4 Operational stability

In addition to high yield and reproducibility, the device stability is also important for practical applications of molecular devices. To assess the device stability under consecutive voltage cycling, a single PPF/e-beam carbon/NAB(3.8)/Cu junction was scanned using 3-wire mode for 25 hours at 50 Hz, with a triangle wave of ±0.5 V amplitude applied continuously. Figure 3.8 shows the I-V curves for initial scan, after scanning for 3 hours (5.4×10^5 cycles) and 25 hours (4.5×10^6 cycles). There are no obvious differences among the consecutive scans, indicating good stability of these microfabricated devices under repetitive cycling.

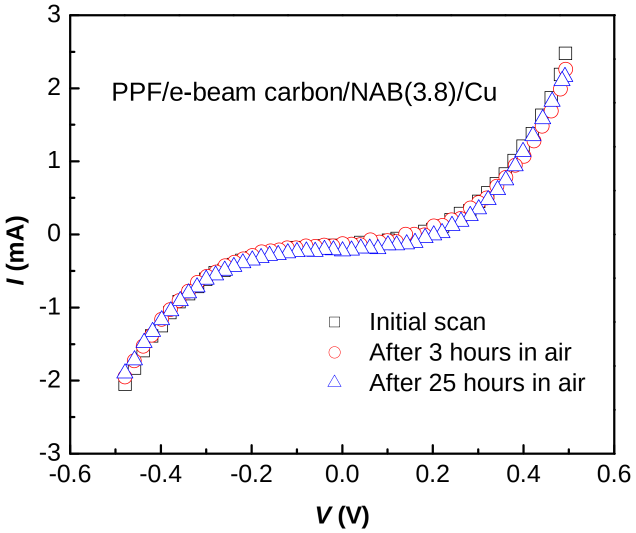


Figure 3.8 Current-voltage curves for a single PPF/e-beam carbon/NAB(3.8)/Cu junction (80 × 80 μm) at initial scan, after 3 hours (5.4×10^5 cycles) and after 25 hours (4.5×10^6 cycles) in air at 50 Hz.

The thermal stability of microfabricated junctions was also tested. A PPF/e-beam carbon/NAB(3.8)/Cu junction (180 × 180 μm) was first heated to 100 °C in a vacuum system (~5 × 10^{-6} torr) for 22 hours, with I-V curves recorded periodically. The results are presented in Figure 3.9. Figure 3.9 (a) shows the I-V characteristics obtained at room temperature before and after heating for 22 hours. There are no observable changes in shape or current magnitude, indicating that the junction can survive at temperature of at least 100 °C in vacuum. I-V curves recorded at 100 °C for 3 hours, 6 hours and 22 hours in Figure 3.9 (b) show only minimal changes in current, indicating that the devices can be operated at 100 °C without having apparent damage. The same junction was then heated to 150 °C in vacuum and the resulting I-V curves are shown in Figure 3.10. Heating at 150 °C caused a gradual increase in current by ~50% with no change in shape after 20 hours, and the current then remained constant for at least another 24 hours. It is reported that the deposited metal films have a large concentration of point, linear and planar defects, which are formed during the vapor, chemical or electrochemical deposition process of metal films. Since the defect movement can be thermally activated, the annealing process at low temperature (100-200 °C) can cause great changes in the electron transport, mechanical and microstructural properties of the deposited metal films.[110] Therefore, it is likely that the copper atoms in the electron beam evaporated copper film are annealed at 150 °C, resulting in the electrical or microstructural change of the copper film and thus the conductance increase of the junction at the first 20 hours during the heating process. However, the annealing process is completed after 20 hours, resulting in constant IV responses of the same junction.

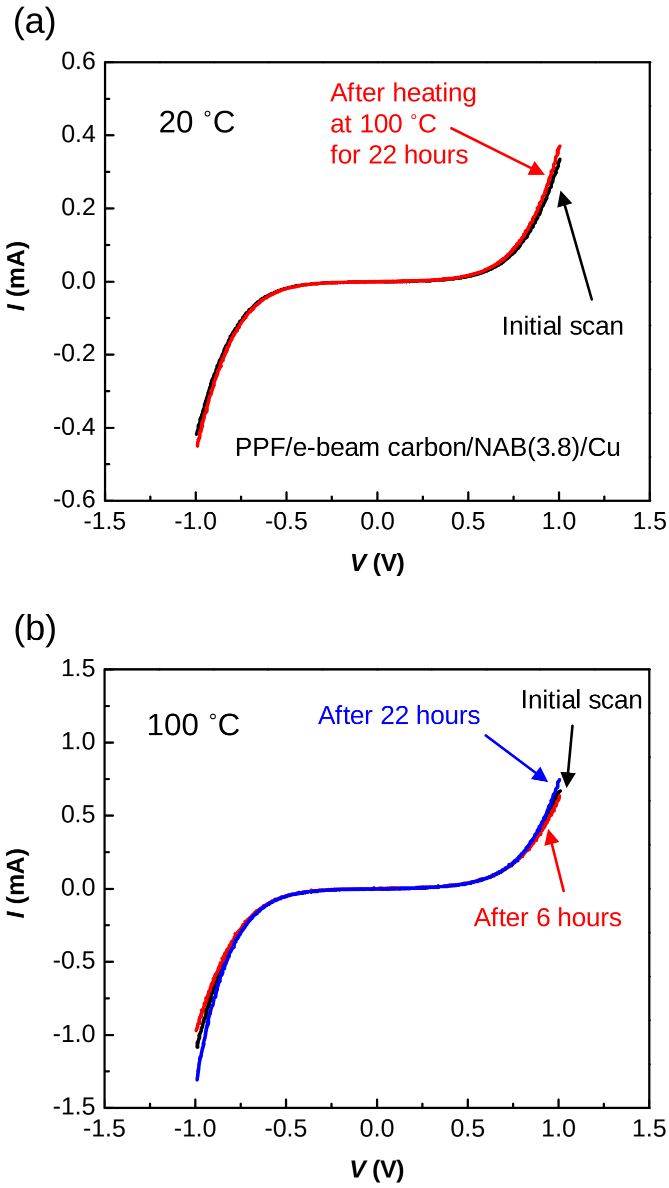


Figure 3.9 **(a)** J-V characteristics of a single PPF/e-beam carbon/NAB(3.8)/Cu junction (400 × 400 µm) measured in vacuum at room temperature initially and after heating at 100 ˚C for 22 hours continuously. **(b)** J-V characteristics of the same junction shown in (a) recorded during the heat treatment at 100 ˚C in vacuum for initial scan, after 6 hours and after 22 hours. The scan rate was 100 V/s in both (a) and (b).

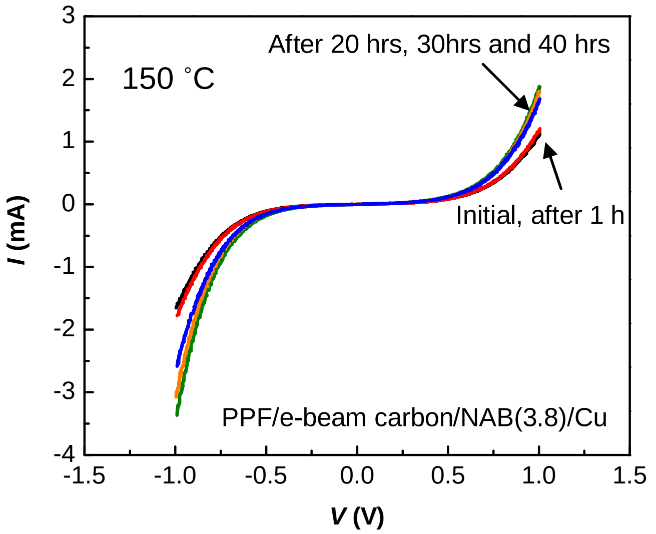


Figure 3.10 J-V curves of the same junction shown in Figure 3.9 recorded during the heat treatment at 150 ˚C in vacuum for initial scan, after 1 hour, 20 hours, 30 hours and 44 hours. The scan rate was 100 V/s.

The McCreery group demonstrated previously that PPF/NAB/Cu “cross-bar” junctions are stable for over 10^9 repeated voltage cycles with peak current densities of ~0.6 A/cm^2 (~1 mA for a 0.0017 cm^2 device).[111] Given the much smaller areas of the microfabricated junctions reported here, it was possible to subject the junctions to higher voltages and current densities than studied previously. Figure 3.11 shows the J-V curves of a microfabricated PPF/e-beam carbon/NAB/Cu junction (16 × 16 μm) obtained at three voltage ranges of ±1.5, ±2 and ±2.5 V. Current density of ~470 A/cm^2 at 2.5 V did not cause any observable changes in the J-V behavior of the junction. A negative bias of -2 V produced a current density of ~90 A/cm^2, but more negative bias resulted in irreversible breakdown and very high currents. Breakdown always occurred more readily for negative bias, when the Cu/Au is at positive potential. Breakdown for negative bias is likely due to the oxidation of Cu to a mobile Cu^+ ion, which is driven by the applied field to the carbon surface where it is reduced to form a filament. This destructive process for junctions containing either Ag or Cu contacts was described by the McCreery group previously.[112]

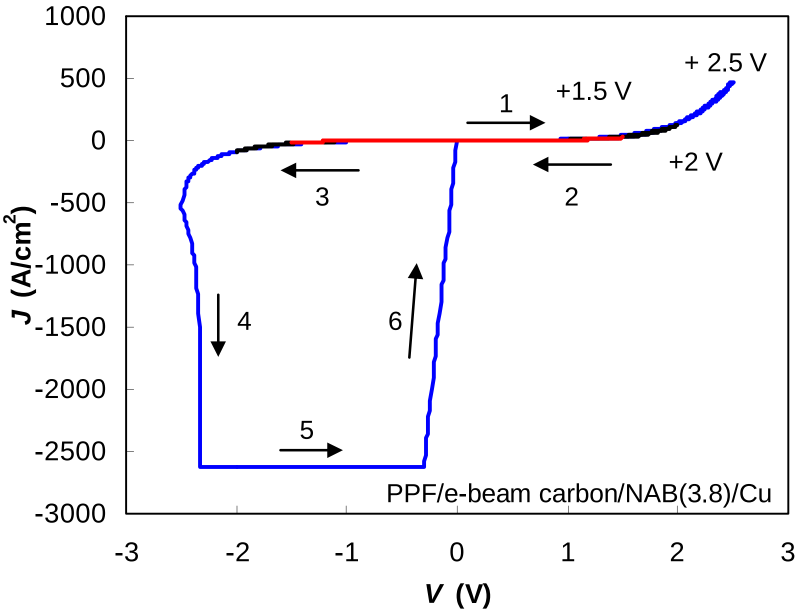


Figure 3.11 J-V curves for a single junction PPF/e-beam carbon/NAB(3.8)/Cu (16 × 16 μm) obtained at three voltage scans ±1.5, ±2 and ±2.5 V. All the scans were initiated from 0 V to a positive direction, as indicated by the numbered arrows. The scan rate was 1 V/s for all the J-V curves.

Acceptance of molecular junctions as practical devices requires that their behavior is reproducible across many laboratories or fabrication sites. Resistance of the same molecules reported by different groups, however, can vary by several orders of magnitude, due to differences in junction paradigms, measurement techniques, fabrication conditions, etc.[1] Therefore, it is difficult to make direct comparisons of electronic characteristics for molecular junctions made from different labs. Herein, we compare the current results of microfabricated carbon/NAB/Cu/Au junctions to those reported previously for junctions with similar structure.[83, 87, 111] These results were obtained over a period of ~3 years, and the junctions with a wide range of areas were fabricated in three different ways. For example, Bergren et al. utilized a "cross-bar" junction format with "direct" e-beam deposition of top contact, and the junction area was defined by the contact area between metal top contact and PPF, ranging from 0.0001 to 0.0025 cm^2.[83, 111] Bonifas et al. deposited the metal top contact with a "soft" deposition method based on surface diffusion of Cu atoms and the junction area was 1.5 μm^2.[87] In the current study, Cu was deposited with "direct" e-beam evaporation technique and junction areas varied from 10 to 156,000 μm^2. The yield for each fabrication technique was over 90%, and rsd for J (0.5 V) within each batch of junctions was 10-30%. The average J (1 V) values for carbon/NAB/Cu/Au junctions made by various fabrication methods and geometries are compared in Table 3.3. Although the junction areas span 5 orders of magnitude, the variation in J value at 1 V is less than a factor of 5. The small remaining variation is at least partially attributed to fabrication and measurement variables, such as metal deposition backpressure, junction age, and uncompensated resistance of PPF. These results show a good consistency of device behavior for a wide range of fabrication methods and junction areas. Hence, the microfabrication of carbon-based devices provides a reliable technique to make molecular junctions, which should find applications in the future.

Junction structure	Junction geometry and area (μm^2)	Top contact deposition[a]	J at 1 V (A/cm^2)	Ref
PPF/NAB(4.5)/Cu/Au	Cross bar 10,000-250,000	Direct	1.06	83
PPF/NAB(4.5)/Cu/Au	Sidewall 1.5	Soft deposition by metal diffusion	0.66	87
PPF/NAB(4.5)/Cu/Au	Sidewall 1.5	Direct	0.78	87
PPF/e-beam carbon(10)/ NAB(3.8)/Cu/Au	Microfabricated via-hole 10-156,000	Direct	0.60[b]	This work

a. top contact including Cu and Au deposited by electron beam evaporation.
b. current density adjusted to 4.5 nm of NAB using β=2.6 nm^{-1}.

Table 3.3 Comparison of carbon/NAB/Cu/Au junctions fabricated with different methods.

3.3.5 Molecular layer thickness dependence of J-V characteristics

As described in chapter 2, the reduction of diazonium ions is a radical reaction and therefore is prone to multilayer formation. By controlling the reaction conditions, molecular layers with various thicknesses can be obtained. Figure 3.12 (a) shows the J-V curves of PPF/e-beam carbon/NAB/Cu junctions with a series of NAB thicknesses. As indicated in the figure, the measured NAB thicknesses were 2.2±0.2, 2.4±0.2, 3.8±0.2, and 5.2±0.2 nm. The error bars represent one standard deviation determined from 8-10 junctions for each thickness. There is very little change in curve shape with NAB thickness, while the junction conductance is strongly dependent on film thickness. For example, at 0.5 V, the current density decreased from 10.1 A/cm^2 for NAB(2.2) to 4.87 A/cm^2 for NAB(2.4), 0.298 A/cm^2 for NAB(3.8) and 0.00251 A/cm^2 for NAB(5.2). Therefore, an increase in thickness by a factor of 2.4 caused a decrease in current density by a factor of over 4000. The plots of ln J at 0.1, 0.3, 0.5 and 0.7 V as a function of NAB thicknesses are presented in Figure 3.12 (b) and the linear fits indicate that the current density depends exponentially on molecular layer thickness. The slopes at V=0.1, 0.3, 0.5 and 0.7 V are 0.26, 0.24, 0.23 and 0.22 Å^{-1} respectively. Because current density for a tunneling mechanism should follow a relation $J \propto \exp(-\beta d)$ where d is molecular layer thickness and β is attenuation coefficient,[113] β can be deduced from the slope of the plot of ln J as a function of d. The β values reported in literature range from 0.2 to 0.6 Å^{-1} for conjugated molecules [99, 114, 115] and from 0.8 to 1.5 for alkane molecules[1]. The obtained β value of 0.26 Å^{-1} at 0.1 V is very close to that reported recently for "cross-bar" junctions with larger areas (0.25 Å^{-1} at 0.1 V)[111]. It is also similar to the tunneling constant value of 0.22 Å^{-1} reported previously for electron transfer through diazonium-derived monolayers modified glassy carbon to redox-active molecules in electrolyte solution[116] and 0.21-0.22 Å^{-1} observed for "cross-bar" junctions containing biphenyl and nitrobiphenyl[99]. As shown in Figure 3.12 (b), β slowly decreases with increasing bias and this is also expected from theory.[117] A similar observation was reported by Anariba et al. for nitrobiphenyl devices[99] and Akkerman et al. for alkanethiol devices[88].

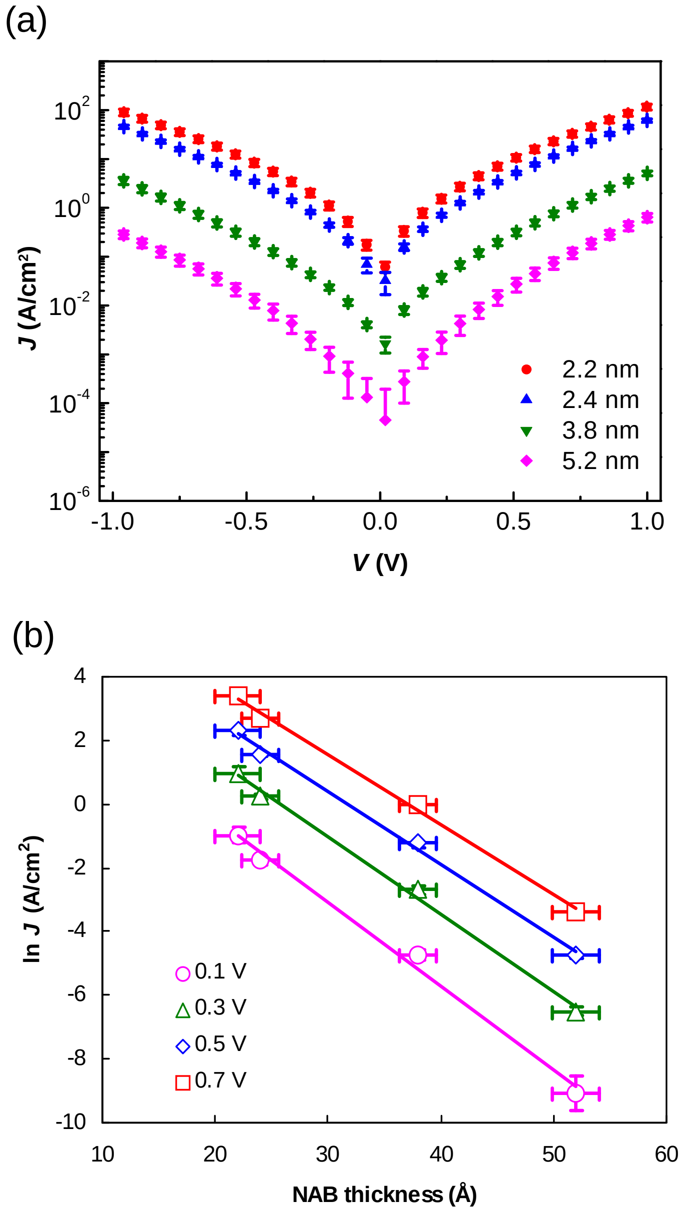


Figure 3.12 **(a)** J-V curves for 35 × 35 μm molecular junctions with varying NAB thicknesses from bottom to top: 5.2, 3.8, 2.4, 2.2 nm. **(b)** Plot of ln(J) at V=0.1, 0.3, 0.5 and 0.7 V as a function of NAB thickness in Å.

3.3.6 Temperature dependence of J-V characteristics

The temperature dependence of J-V curves for PPF/e-beam carbon/NAB/Cu microfabricated junctions was examined over a range of 100-300 K for NAB(3.8) and 100-390 K for NAB(5.2) devices as shown in Figure 3.13 and 3.14. The corresponding Arrhenius plots at three different voltages are also shown. In the temperature region below 200 K, the junction conductance was independent of temperature, with a very small slope corresponding to 1-6 meV for the apparent activation energy. In higher temperature region (>250 K), the conductance slowly increased with temperature, showing a slope of 20-40 meV. This behaviour is quite similar to that of previously reported “cross-bar” junctions made without microfabrication which were studied over the temperature range of 5-450K.[83, 111] The temperature independence below 200 K is likely due to tunneling transport through the highest occupied molecular orbital (HOMO) of NAB (-6.65 eV) since the HOMO is closer to the Fermi level of the contacts (-4.90 eV) than the lowest unoccupied molecular orbital (LUMO) (-3.03 eV). The energy level diagram for a PPF/NAB/Cu junction is shown in Figure 3.15. The greater likelihood of hole transport is not very obvious for NAB since the offset between the HOMO level and the Fermi level of PPF is not significantly smaller than that between the LUMO and the Fermi level. However, most of the aromatic molecules usually have higher LUMO energy, e.g., -0.71 eV for fluorene. The temperature dependence observed at higher temperature is consistent with effects resulting from the broadening of the Fermi function in the contacts and is not related to thermal activation of molecular reorganization or configuration changes.[111]

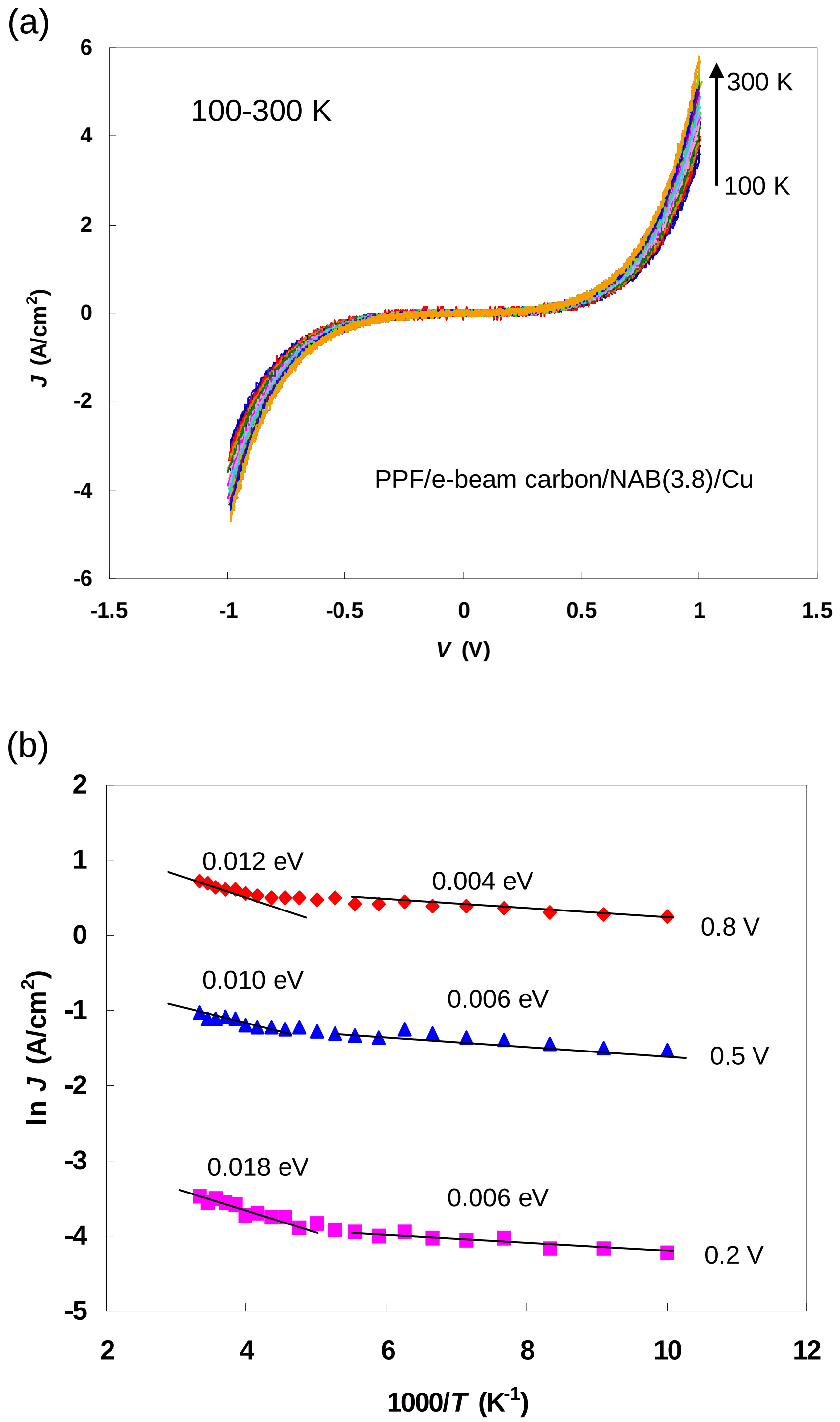


Figure 3.13 **(a)** J-V curves for PPF/e-beam carbon/NAB(3.8)/Cu junction (35 × 35 μm) at different temperatures in the range of 100-300 K. The scan rate was 1000 V/s. **(b)** Arrhenius plots for data in (a) at 0.2 V, 0.5 V and 0.8 V with the slopes indicated in low and high temperature regions.

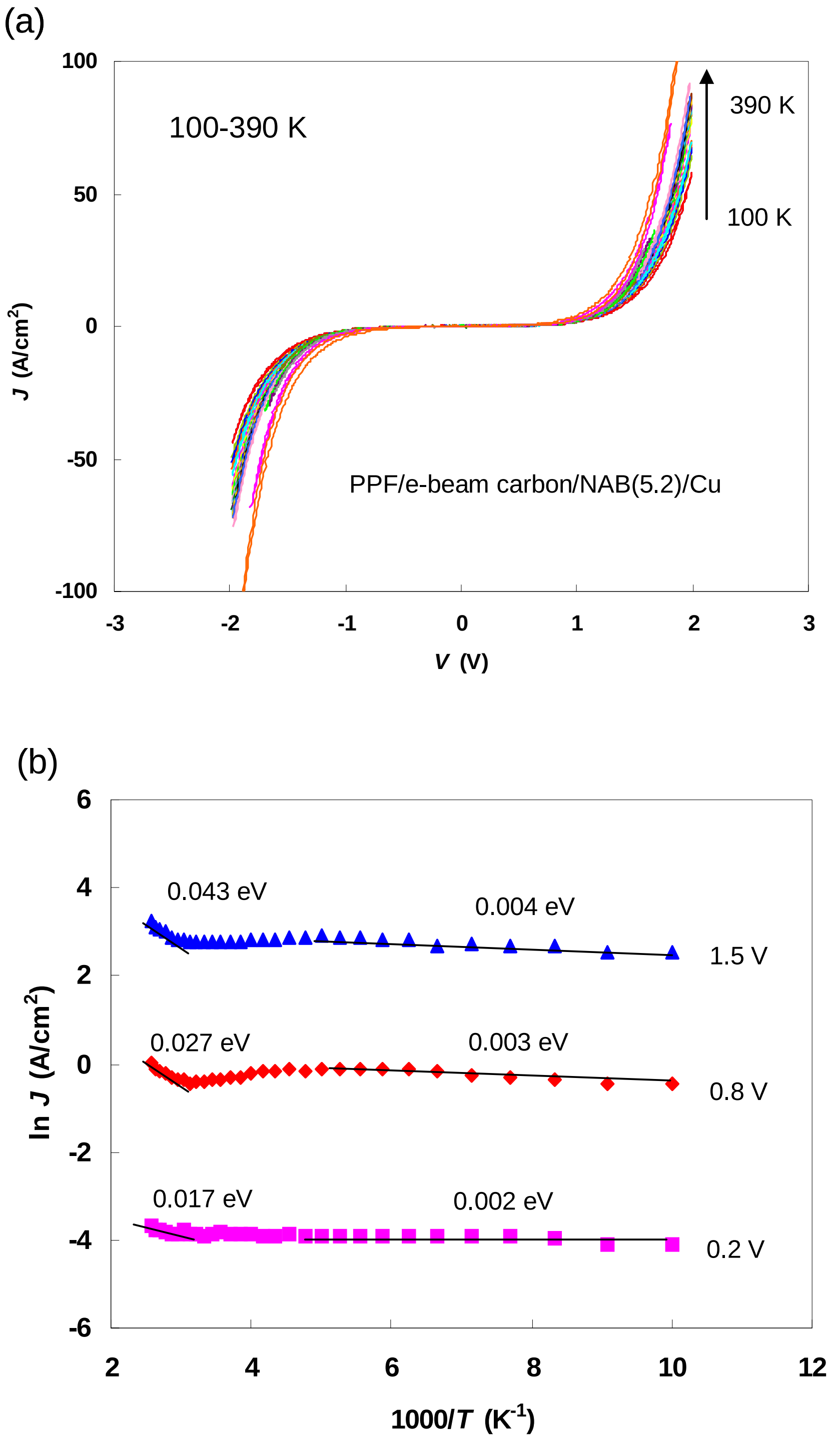


Figure 3.14 **(a)** J-V curves for PPF/e-beam carbon/NAB(5.2)/Cu junction (35 × 35 μm) at different temperatures in the range of 100-390 K. The scan rate was 100 V/s. **(b)** Arrhenius plots for data in (a) at 0.2 V, 0.8 V and 1.5 V with the slopes indicated in low and high temperature regions.

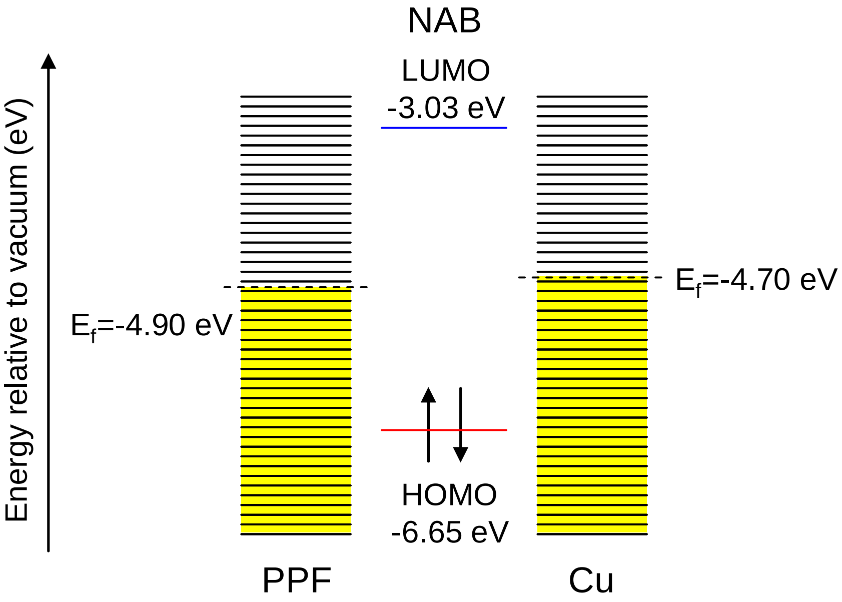


Figure 3.15 Energy level diagram for a PPF/NAB/Cu junction. HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; E$_f$, Fermi level of the contacts. The HOMO and LUMO values of NAB molecule were calculated with density function theory and the work functions of PPF and Cu were measured with a Kelvin probe.

3.3.7 Electron transport mechanism

Bergren et al. has recently investigated the charge transport mechanisms of PPF/NAB/Cu "cross-bar" junctions by analysis of current density-voltage curves as a function of the molecular layer thickness and temperature. The results showed that current density decreased exponentially with thickness, giving a β value of 0.25 $Å^{-1}$ at 0.1 V. In addition, J-V curves obtained at temperatures from 5 to 450K showed temperature independence below ~250 K and a weak temperature dependent response at more elevated temperatures.[111] These results are similar to those observed for microfabricated junctions described in this thesis, which had a strong thickness dependence with β of 0.26 Å at 0.1 V and weak temperature dependence in the range of 100-390 K. The observed transport is consistent with quantum mechanical tunneling of holes through a barrier represented by the difference between the Fermi level of the contacts and the HOMO energy of the molecular layer, with no thermal activation of molecular layer involved.[111] Our β value is significantly smaller than that observed for alkanes (0.8-1.5 $Å^{-1}$)[1] due to the extensive electron delocalization in aromatic molecular layers with conjugated structures as well as the smaller Fermi level/HOMO offset. Furthermore, electron delocalization results in a HOMO energy, dielectric constant, and effective carrier mass which depend strongly on molecular layer thickness.[111] The temperature dependence of the J-V curves is a result of the electron distribution by the Fermi function at the contacts, instead of any "activation" process. Another important conclusion in the paper is that although nonresonant tunneling is likely the electron transport mechanism, the existence of resonant tunneling can not be ruled out. As the HOMO energy approaches that of the contact Fermi level, the resonant tunneling should become dominant. As shown in Figure 3.15, the Fermi levels of PPF and Cu are close to -5 eV relative to vacuum, and a variety of molecules have HOMO energies close to -5 eV. Theory predicts that for the "resonant" case corresponding to zero Fermi level/HOMO offset β should approach zero[118, 119] and the device will behave essentially as a “short circuit” with high conductance. The microfabricated junctions have small areas, which can essentially reduce the magnitude of junction current. Therefore they should allow testing the theory over a wider range of voltages and current densities.

3.4 Summary

In this chapter, we demonstrated that the microfabricated carbon/molecule/metal junctions with areas from 3 × 3 μm to 400 × 400 μm had high yield, reproducibility, and good stability and reliability. The yield of these molecular devices was over 90% and the relative standard deviation for current density at 0.5 V was within 20% for junctions made in one batch and 40% for junctions made from different batches. The current scaled with device area over a factor of 600. Junction stability investigations reveal that these devices can survive under potential cycling for several millions of times, and elevated temperatures up to 100 ˚C in vacuum. A ~50% increase in current density was observed after 20 hours at 150 ˚C, but then the current density remained constant for an additional 24 hours. With high yield and reproducibility, thermal stability, the reported results provide important steps to integration of molecular electronic devices with commercial microelectronic processes. Furthermore, the electronic characteristics were similar to previously reported junctions with similar structure made by other techniques, showing weak temperature dependence in the range of 100-390 K and a strong thickness dependence with β of 0.26 Å at 0.1 V. These results are consistent with a tunneling mechanism through a low barrier without any thermal activation process.

CONCLUSIONS AND FUTURE WORK

Molecular electronics seeks to use organic molecules as active components in electronic devices and one likely route to practical applications of molecular electronics is “hybrid” circuits which combine the fabrication techniques of the traditional semiconductor industry with molecular components. For a hybrid approach to be practical, the fabrication techniques of molecular electronic devices must be compatible with the complementary metal-oxide semiconductor (CMOS) industry. Furthermore, massively parallel fabrication, high yield and reproducibility, and operational stability are essential before molecular electronic devices can be integrated with commercial microelectronics. In this thesis, carbon/molecule/Cu/Au molecular junctions were microfabricated using techniques compatible with semiconductor industry and exhibited good yield, reproducibility, cycle life and thermal stability, demonstrating significant steps toward practical applications of molecular electronics.

In chapter 2, a new approach to microfabricate carbon-based molecular junctions using conventional semiconductor processing technologies has been demonstrated. The fabrication process is applied on 4-inch silicon wafers using simple steps and techniques that are compatible with standard CMOS fabrication processing, yielding more than 30 chips with each containing 26 or 32 devices with sizes from 3 × 3 μm to 400 × 400 μm. Electron-beam deposited carbon films were introduced as substrates instead of previously studied PPF and the comparison of junctions made with e-beam carbon and PPF shows that both junctions have similar electronic characteristics, but e-beam carbon improves the electronic behavior in both yield and reproducibility. In chapter 3, the current density-voltage characteristics of microfabricated junctions based on e-beam carbon are further described in terms of yield and reproducibility, scalability, temperature and molecular layer thickness dependence. Furthermore, the cycle life and thermal stability of the junctions were also tested. The yield of these devices was over 90% and the relative standard deviation for current density at 0.5 V was within 20% for junctions made in one batch and 40% for junctions made from different batches. The current scaled with device area over a factor of 600. Junction stability test reveals that these devices can survive under potential cycling for several millions of times, and elevated temperatures up to 150 ˚C in vacuum. The current density increased by ~50% after 20 hours at 150 ˚C, but then remained constant for an additional 24 hours. The devices showed electronic characteristics quantitatively and qualitatively close to previously reported junctions with similar structure made by other techniques, including a weak temperature dependence in the range of 100-390 K and a strong thickness dependence with β of 0.26 Å at 0.1 V. These results are consistent with a tunneling mechanism through a low barrier without any thermal activation process.

As a preliminary attempt to microfabricate small carbon-based molecular devices using photolithography, the current work can be improved regarding the fabrication process, such as optimizing the parameters of lithography, e.g., the UV exposure time and intensity, the thickness of the photoresist film, the time of development, using a mild method to remove oxide on PPF instead of applying a lift-off procedure to deposit e-beam carbon, and eliminating impurities on junction vias by doing all the process in the cleanroom.

ENDNOTES

A version of Chapter 2 and Chapter 3 has been published. Ru, J.; Szeto B.; Bonifas, A.; McCreery, R. L. *Appl. Mater. Interfaces*, 2010, ASAP.

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