

## Supporting Information

# Microfabrication and Integration of Diazonium-based Aromatic Molecular Junctions

Jie Ru<sup>1,2</sup>, Bryan Szeto<sup>1</sup>, Andrew Bonifas<sup>1,3</sup>, Richard L. McCreery<sup>1,2</sup>

<sup>1</sup>National Institute for Nanotechnology, National Research Council Canada,  
Edmonton, Alberta, Canada

<sup>2</sup>Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

<sup>3</sup>Department of Materials Science and Engineering, Ohio State University,  
Columbus, Ohio

Email: [mccreery@ualberta.ca](mailto:mccreery@ualberta.ca)

1. Atomic Force Microscopy of PPF and e-beam carbon
2. XPS results during fabrication
3. Comparison of 45 junctions on five samples of varying area
4. Effect of e-beam carbon on yield and reproducibility
5. SEM images of four junctions with different areas
6. Wiring diagrams for JV curve acquisition
7. Arrhenius plots for carbon/NAB/Cu/Au junctions
8. Detailed fabrication procedure

## 1. Atomic Force Microscopy of PPF and e-beam carbon

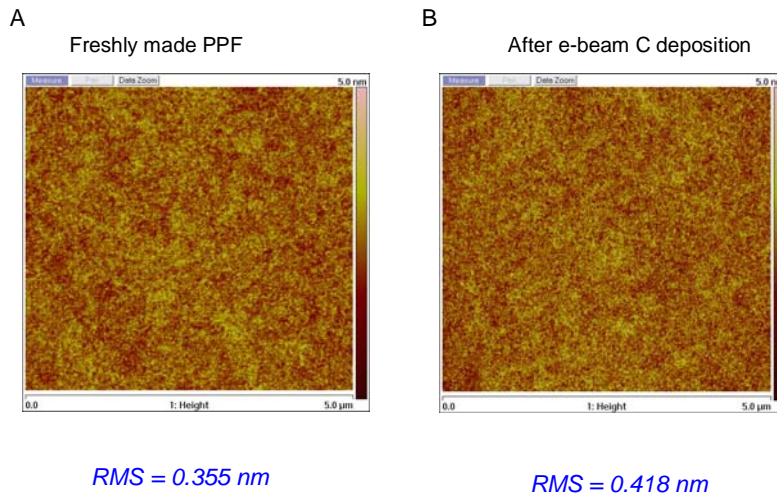


Figure S1. Atomic Force Microscopy scans of microfabricated PPF substrate surface before (A) and after (B) deposition of 10 nm of e-beam carbon. Lateral dimensions are 5 x 5  $\mu\text{m}$ , vertical color scale covers 5 nm.

## 2. XPS results during fabrication

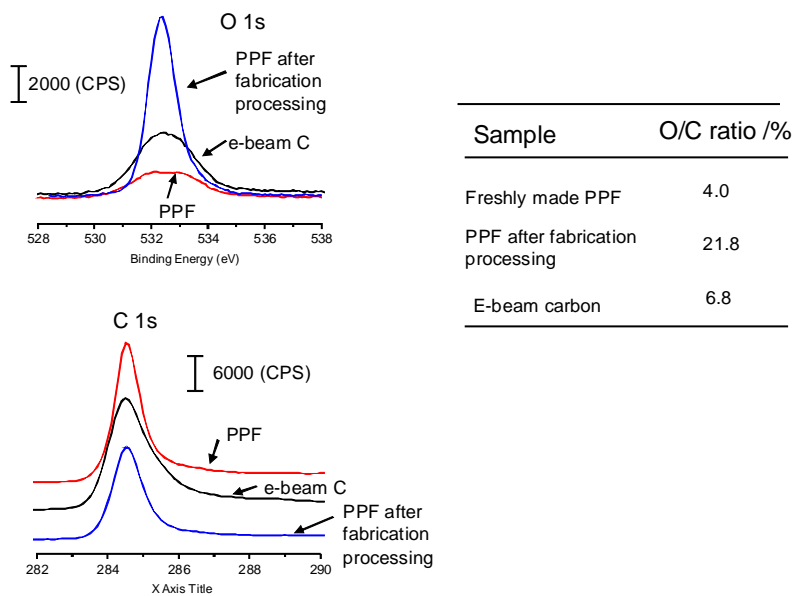


Figure S2. High resolution XPS scans of  $\text{O}_{1s}$  and  $\text{C}_{1s}$  regions for PPF samples subjected to microfabrication process. “PPF” indicates the initial, untreated PPF immediately following pyrolysis, blue curves are after microfabrication, and black curves are after e-beam deposition of 10 nm carbon. Table indicates atomic O/C ratio at each point in the process.

### 3. Comparison of 45 junctions on five samples of varying area

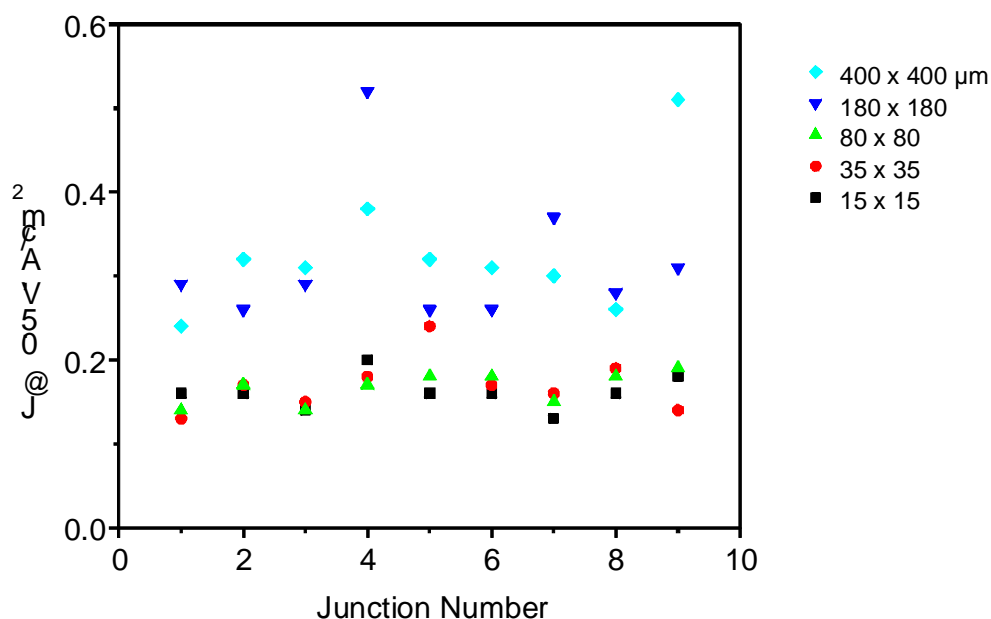


Figure S3. Individual J(0.5 V) values for 9 junctions selected randomly from each one of 5 samples with different areas. Junction type was PPF/e-carbon/NAB(3.8)/Cu.

### 4. Effect of e-beam carbon on yield and reproducibility

Table S-1 Comparison of junctions fabricated with and without e-beam carbon

dimension (μm)	area(um <sup>2</sup> )	PPF/NAB(3.8)/Cu			PPF/e-C/NAB(3.8)/Cu		
		J at 0.5 V (A/cm <sup>2</sup> )	rsd(%)	yield	J at 0.5 V (A/cm <sup>2</sup> )	rsd(%)	yield
400x400	156000	0.308	29.7	8/9	0.325	24.2	9/9
180x180	31000	0.238	25.4	9/10	0.321	24.9	10/10
80x80	6400	0.132	53.0	10/10	0.173	10.6	10/10
35x35	1300	0.138	41.7	6/10	0.173	18.8	10/10
16x16	250	0.106	31.9	8/10	0.162	11.6	10/10
7x7	50	0.105	68.6	6/10	0.145	87.2	10/10
3x3	10	0.039	84.0	7/10	0.040	106.6	8/10

## 5. SEM images of four junctions with different areas

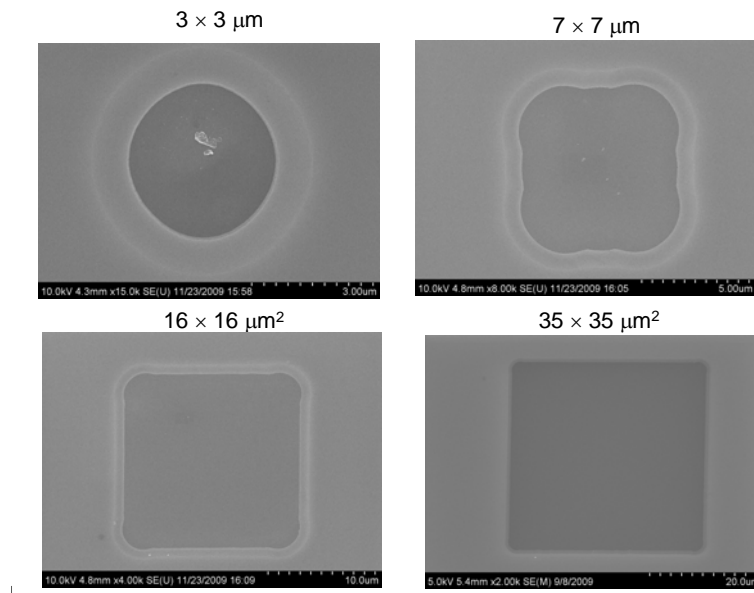


Figure S4. Top view SEM micrographs of junction vias with four areas, showing changes in shape and the incidence of defects for the smaller dimensions.

## 6. Wiring diagrams for JV curve acquisition

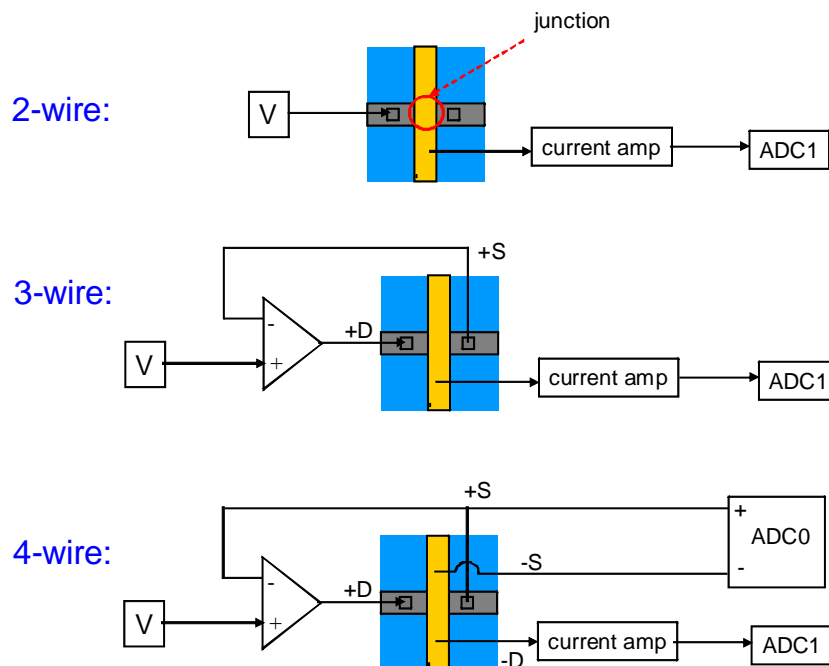


Figure S5. Wiring schematics for 2,3, and 4 wire configurations.  $V$  is bias voltage from a digital to analog converter, ADC1 is the analog to digital channel for current. ADC0 monitors voltage, and has a differential input in the case of the 4-wire arrangement. “D” and “S” denote “drive” and “sense”, with the “sense” leads corresponding to high impedance voltage monitors.

## 7. Arrhenius plots for carbon/NAB/Cu/Au junctions

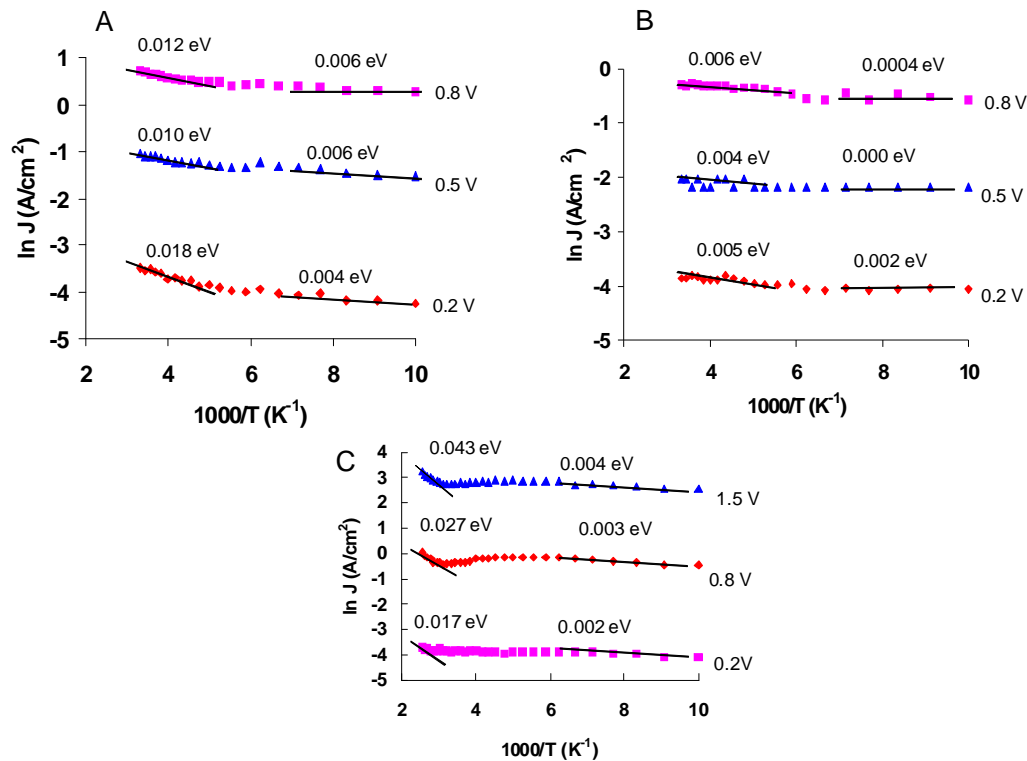


Figure S6. Arrhenius plots of  $\ln J$  at three biases (0.2, 0.5, 0.8 V) for 35 x 35  $\mu\text{m}$  junctions as follows: A. NAB(3.8), 100-300 K; B. NAB(5.2), 100-300 K; C. NAB(5.2), 100-390 K. Slopes are indicated for low and high temperature ranges. Junction of panel C failed at 400 K.

## 8. Detailed fabrication procedure

### (1) Fabrication of PPF

The fabrication process steps of microfabricated carbon/molecule/metal junctions are shown schematically in Figure 1 of the main text. A 4" silicon (100) wafer with 300 nm thick thermally grown silicon oxide was used as substrate. The wafer was cleaned with a hot piranha solution (concentrated H<sub>2</sub>SO<sub>4</sub>:30% H<sub>2</sub>O<sub>2</sub>, 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, which acted as an adhesion layer between the photoresist and the oxide surface of the substrate. Positive photoresist AZ P4330-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 (thickness ~4.5 μm). 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 pressure contact mode. The average UV intensity was a combination of ~10 mW/cm<sup>2</sup> at 365 nm and ~25 mW/cm<sup>2</sup> 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<sup>1,2</sup>. The wafer was transferred to a quartz tube furnace (Carbolite model GHA 12/600) and the furnace was flushed with forming gas (5% H<sub>2</sub> and 95% N<sub>2</sub>) 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) Fabrication of junction vias

In order to electrically isolate the junctions, a process of fabricating junction holes (or vias) was performed. ~300 nm thick SiO<sub>2</sub> was deposited on the wafer as insulating layer by a Trion plasma enhanced chemical vapor deposition system (PECVD). Positive photoresist HPR 504 (MicroChem) was spin-coated and patterned by optical lithography. The PECVD SiO<sub>2</sub> unprotected by the photoresist was etched to expose PPF by a buffered oxide solution (40%NH<sub>4</sub>F:49%HF, 10:1 v/v, J.T. Baker). The observed etching rate was ~70 nm/min. The etching process yielded junction via-holes in the SiO<sub>2</sub> layer with sizes ranging from 3 × 3 to 400 × 400 μm. 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. For each chip, a 10 nm thick electron beam carbon film was deposited using an electron beam evaporator (PVD 75, Kurt J. Lesker). The photoresist was stripped with acetone and the chips were then cleaned thoroughly with isopropanol and deionized water (TOC <4 ppb), and blown dry with nitrogen.

## (3) Carbon surface modification

The modification of carbon surfaces in junction vias was carried out by electrochemical reduction of 1 mM solution of the 4-nitroazobenzene (NAB) diazonium ion in 0.1 M *n*-tetrabutylammonium tetrafluoroborate in acetonitrile. The NAB tetrafluoroborate salt was synthesized using the procedure described previously<sup>3,4</sup>. Diazonium tetrafluoroborate solutions were freshly prepared and purged with Ar for ~15 min before use. The cyclic voltammetry method was employed for

growing the molecular film. The films with different thicknesses were obtained by controlling the potential sweep conditions, e.g., scanning rate and range, and number of scans. The resulting NAB thicknesses were  $2.2 \pm 0.2$ ,  $3.8 \pm 0.2$ ,  $5.2 \pm 0.2$  nm and  $2.4 \pm 0.2$  nm when the applied potential was scanned from +0.4 V to -0.6 V (vs.  $\text{Ag}/\text{Ag}^+$ , 0.01 M) for 1 cycle, 4 cycles, 10 cycles and from +0.4 V to -0.2 V for 4 cycles at 0.2 V/s respectively. After surface modification, the chips were rinsed with acetonitrile thoroughly. Molecular film thicknesses were determined with the AFM scratching method as reported previously<sup>4</sup>.

#### (4) Top contact deposition

Following the surface modification, the chips were immediately transferred to a PVD 75 electron beam evaporator. The evaporation chamber was pumped down to a base pressure of  $\sim 2.0 \times 10^{-6}$  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 quartz crystal microbalance. The chamber pressure was monitored by a residual gas analyzer (RGA/200, Stanford Research Systems). For all the metal depositions, unless noted otherwise, the total pressures observed were in a range of  $0.3\text{-}1.0 \times 10^{-5}$  torr. Copper was deposited at  $\sim 0.01$  nm/s for the first 2 nm and at  $0.03\text{-}0.1$  nm/s for the remaining of 28 nm. Gold was deposited at  $\sim 0.05$  nm/s for the first 5 nm and  $\sim 0.1$  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 nanometer 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.

### **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, unless indicated otherwise. A voltage was applied between the bottom carbon electrode and the metal top contact through tungsten probes, with the reference (i.e. “sense”) electrode lead connected to the PPF lead opposite the “drive” electrode contact. The 3-wire configuration was used for the compensation of non-negligible ohmic losses in the carbon lead. 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. As noted in the main text and figure 7, a 3-wire arrangement compensated for most of the ohmic voltage losses, but a 4<sup>th</sup> wire corrected for the much smaller ohmic losses in the metal lead on large junctions (>80 x 80  $\mu\text{m}$ ). Where noted, the 4-wire configuration was implemented with Labview software and a National Instruments 6110 multifunction data acquisition board.

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  $2 \times 10^{-6}$  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).

### **Spectroscopic characterization:**

#### (1) AFM

Atomic force microscopy (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. Thickness measurements of molecular films were performed using the AFM scratching technique as reported previously<sup>4</sup>. A trench was created on the sample surface in contact mode and imaged in tapping mode. The molecular film thickness was determined by the height or depth of the obtained trench.

#### (2) SEM

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

#### (3) XPS

X-ray photoelectron spectroscopy analysis was performed with the AXIS 165 spectrometer (Kratos Analytical) equipped with a monochromatic Al K $\alpha$  source (1486.6 eV). The chamber pressure during the sample analysis was maintained at  $\sim 1.5 \times 10^{-10}$  torr.

### **References:**

- (1) Ranganathan, S.; McCreery, R. L.; *Anal. Chem.* 2001, 73, 893.
- (2) Ranganathan, S.; McCreery, R. L.; Majji, S. M.; Madou, M.; *J. Electrochem. Soc.* 2000, 147, 277
- (3) Solak, A. O.; Eichorst, L. R.; Clark, W. J.; McCreery, R. L.; *Anal. Chem.* 2003, 75, 296.
- (4) Anariba, F.; DuVall, S. H.; McCreery, R. L.; *Anal. Chem.* 2003, 75, 3837.