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Metal−Molecule−Metal Junctions via PFPE Assisted Nanotransfer Printing (nTP) onto Self-Assembled Monolayers

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As the essential component in molecular electronics, metal−molecule−metal (MMM) junctions have been proposed as cheap, synthetically tunable alternatives to existing semiconductor electronics. A common challenge in self-assembled monolayer (SAM) based MMMs has been reproducibly forming permanent, stable metal electrodes atop molecular layers. For example, electrodes by vapor deposition directly onto SAMs[1a] or on SAMs in defined nanopores[1b] have resulted in a high percentage of shorted devices. To protect fragile molecular layers, SAMs have been coated with conductive polymers prior to vapor deposition of the top metal layer;[2] however, eliminating this additional organic layer may be required to avoid artifacts and device degradation. MMM junctions without this protective polymer layer have been attempted by other methods such as molecular break junctions,[3a] mercury-drop electrodes,[3b] fluid metal eutectic gallium−indium drop junctions (EGaIn),[3c] and crossed-wire junctions.[3d] However, these methods have typically been employed as nonpermanent, analytical techniques and are not suitable for the creation of commercial devices. Consequently, new methods have been pursued to reproducibly form the reliable, long-lasting MMMs that are required for molecular electronic applications.

A soft lithographic method, nanotransfer printing (nTP), has been shown to form permanent and stable metal electrodes on molecular layers without damaging the SAM beneath. Nanotransfer printing operates on the principle that metal films can be transferred from a polymeric stamp to a substrate if the metal film has a higher affinity for the receiving substrate than that of the stamp. Quite often, nTP utilizes covalent attachment between the metal film and the bottom substrate to obtain high quality, reproducible transfer. Most nTP studies use elastomeric poly(dimethylsiloxane) (PDMS) as a patterned stamp since PDMS is cheap, flexible, and easy to fabricate on a variety of surfaces and in a variety of shapes. Work in this area has been quite successful yielding high quality patterns of metal thin films bound to SAMs formed on near atomically smooth surfaces such as silicon,[4a] glass,[4b] and n^+ doped GaAs.[4c,d] However, on rough surfaces via thermal vapor deposition, production of practical Au/SAM/Au[5a] and Co/SAM/Co[5b] MMMs by PDMS based nTP has been limited due to inadequate metal film transfer.

Recently, perfluoropolyether (PFPE) based stamps were used to transfer Au thin films onto silicon substrates.[6] Since the surface energy of PFPE (∼15 mJ/m^2) is significantly lower than that of PDMS (22−25 mJ/m^2), using PFPE eliminated the need for surface functionalization of the receiving surface prior to transfer. This finding suggested that PFPE could be useful for transferring other materials that have thus far been unable to be transferred by PDMS. In addition, PFPE has a higher modulus (∼4 MPa) than PDMS (∼1.5 MPa, *Sylgard 184*) and is less prone to lateral feature collapse during transfer, which is important for transferring nanometer sized, tightly compact arrays. Despite these attractive properties, nTP by PFPE has yet to be thoroughly studied.

Herein, we report a simple method to fabricate MMMs via PFPE based nTP to include the formation of Au/SAM/Au and Co/SAM/Co junctions. Moreover, we report for the first time nTP of Ni films to form Ni/SAM/Ni junctions. Ferromagnetic based MMM junctions such as these are appealing to the emerging field of molecular spintronics.[7] Furthermore, PFPE stamps can be formed directly from PFPE molds, eliminating the need for silicon based masters for stamp replication.[8] We found that each mold could also be reused multiple times without a loss of fidelity.

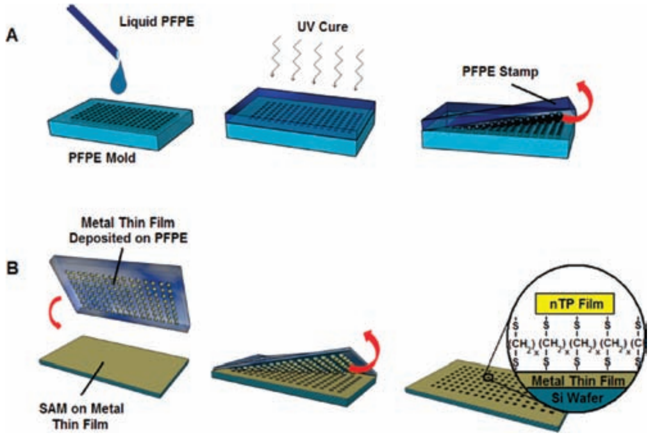

Figure 1. Fabrication procedure. (A) Liquid PFPE is drop-casted onto a PFPE mold with predefined features, cured, and then peeled away to reveal the negative of the mold. This process can be repeated on the same mold. (B) A metal thin film is thermally deposited on the PFPE stamp, and an SAM is formed on a metal thin film electrode. They are brought into intimate contact, and then the stamp is peeled away leaving a pattern of covalently bound metal thin films.

Figure 1a shows the method by which the PFPE stamps were produced.[10] It is known from literature that liquid PFPE can be molded from silicon masters, and in a similar process, liquid PFPE can be replicated from PFPE molds.[8] Replication was done by drop-casting liquid PFPE onto the mold and then curing it under UV illumination. The PFPE stamp can then be separated from the mold (∼1 mm thick) revealing the negative of the mold's features. This process can be repeated multiple times with the same mold without noticeably hindering the quality of the features or nTP.

To form the bottom metal thin film electrode, Au, Ni, or Co metal was deposited by thermal vapor deposition onto a silicon wafer.[10] Immediately following deposition, the wafer was transferred to a 30 mM solution of decanedithiol (DDT) and soaked for 24−48 h. Since Co and Ni are known to form an unwanted native oxide rapidly in air, this step was done in a glovebox with an inert N_2 atmosphere.[9] After soaking, the substrate was removed from the solution, sonicated in tetrahydrofuran (THF) to remove physisorbed SAM molecules, dried under N_2, and further dried by vacuum (1 mbar, >1 h).

The rate of deposition of the bottom electrode greatly affects the root-mean-square roughness (rms) of the final surface. Since DDT is considerably short (∼1.4 nm), relatively smooth bottom electrodes were required

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to maximize the number of thiolated ends accessible for covalent attachment during transfer. By elevating the rate of deposition from 1 to >6 Å/s, the rms decreased from 1.163 to 0.704 nm for Au, 1.242 to 0.470 nm for Ni, and 1.139 to 0.387 nm for Co.[10] Only the smooth surfaces yielded reproducible transfer. Similarly, a densely packed SAM is critical; therefore, transfer printing onto surfaces soaked in solutions less than 30 mM resulted in incomplete transfer.

Separately, a thin metal film was deposited on a patterned PFPE stamp by vapor deposition (Figure 1b). For Au transfer, 10 nm of Au were thermally deposited starting at 1 Å/s for the first nanometer of thickness and then increasing to 15 Å/s for the final duration of the deposition. The elevated rate of deposition is required since the particle adsorption on PFPE is low due to its low surface energy. For Ni and Co transfer, 10 nm of Au were deposited as above, followed by 10−30 nm of Co or 10 nm of Ni.

Following vapor deposition, the stamp was brought into contact with the SAM coated electrode under N_2 inside a glovebox. The whole arrangement, bottom metal film/DDT/top metal film/PFPE stamp, was placed under vacuum (1×10^{-6} mbar) for 1 h to remove any air trapped between the SAM and the metal film to be transferred. After removing the system from the vacuum, the stamp was peeled from the bottom electrode revealing a patterned substrate. In the case of Ni and Co, the Au transferred along with the Ni and Co. Figure 2 shows 200 nm features of Au on Au/DDT (2a) and Ni onto Ni/DDT (2c) electrodes. Figure 2b and 2d show an inverse wafer “honeycomb effect” from transferring Co using a PFPE stamp replicated from another PFPE stamp. Figure 2d shows the inverse honeycomb of Co cross-transferred onto a Ni/DDT electrode. Samples showed no evidence of degradation after sonicating in THF for 60 s or after the scotch tape test, which suggests strong covalent bonding to the SAM surface.

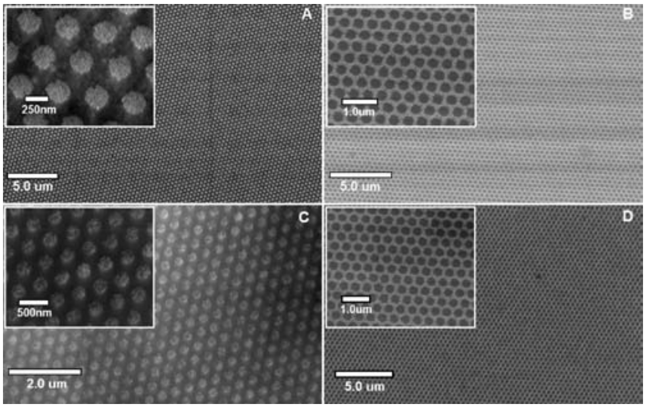

Figure 2. Scanning electron micrographs of devices fabricated via nTP. (A) 200 nm Au/DDT/Au junctions. (B) Inverse “honeycomb” of 200 nm Co/DDT/Co junctions. The stamp used was replicated from another PFPE stamp. (C) 200 nm Ni/DDT/Ni junctions. (D) Honeycomb of Ni/DDT/Co from Co nTP onto a Ni/DDT surface.

Conductivity measurements were carried out on 200 nm MMMs by c-AFM. Figure 3a shows a full scan of a Au/DDT/Au junction, and Figure 3b shows the average of 42 $I-V$ curves over 1.0 V. The linear, zero-crossing region was used to calculate a resistance of 5.05 MΩ.[10] The nonlinearity seen is typical of tunneling seen in similar systems, and the resistance is similar to values seen in Au MMMs formed by other methods.[2] In contrast to Au, the Ni and Co bottom electrodes have a lower SAM density as well as a possible residual surface oxide.[9] In addition, transferred Ni and Co features can potentially oxidize in air despite being shielded by a Au layer. As a result, the resistances observed through these junctions were high, which is apparent in the representative $I-V$ curve of a Ni/DDT/Ni junction (Figure 3c). Though there is evidence of tunneling in these systems, the resistances gathered were variable, due to additional oxide tunneling barriers.[10] Full electrical characterization will be the focus of future studies.

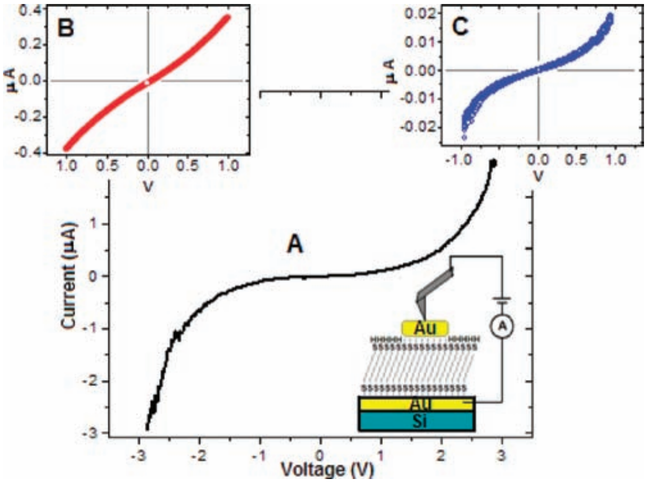

Figure 3. Conductive atomic force microscopy. (A) Full scale $I-V$ curve of a 200 nm Au/DDT/Au feature. (B) Average $I-V$ of 42 Au/DDT/Au junctions. (C) $I-V$ curve from a single 200 nm Ni/DDT/Ni junction.

In summary, we present a simple method to construct functional MMMs with high density and high fidelity by nanotransfer printing Au, Ni, and Co electrodes onto SAMs using PFPE stamps. The devices were well ordered and showed reproducible tunneling $I-V$ characteristics. This new method not only offers a unique test bed to investigate the electrical properties of molecules in an ensemble in MMMs with different metal contacts but also makes a significant step toward the utilization of MMMs at the device level.

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Supporting Information Available: Device fabrication details. This information is available free of charge via the Internet at http://pubs.acs.org.

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