

# Nanowell device for the electrical characterization of metal–molecule–metal junctions

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A nanowell device for the electrical characterization of metal–molecule–metal junctions was built using readily available processing tools and techniques. This device consisted of a nanoscale well, with a gold bottom, filled with a self-assembling monolayer of organic molecules, and capped with titanium and gold. Focused ion beam technology was used to fabricate the well with a width less than the grain size of gold. This nanowell improved the device performance dramatically by reducing the chances of pinhole formation in the self-assembling monolayer on the bottom gold electrode. Unlike some established characterization techniques, including conducting probe atomic force microscopy and scanning tunneling microscopy, the nanowell device has the potential for future circuit integration. The effectiveness of the device was confirmed by testing  $I$ – $V$  characteristics of alkanethiols and oligomeric arylthiols. The alkanethiol current was exponentially dependent on chain length with a decay factor ( $\beta$ ) that ranged from 0.7 to 0.75/Å with the applied voltages of 0.1–1.0 V. Additionally, we gained new insight into the electrical behavior of an oligo(phenylene-ethynylene) molecule with a nitro side group. In this work, we present the complete  $I$ – $V$  characteristics observed from the nitro molecule showing electrical switching with memory. Unlike previous reports, we did not observe any reversible negative differential resistance. However, the observed switching with memory behavior may have potential applications in logic and memory devices. © 2005 American Vacuum Society. [DOI: 10.1116/1.1935528]

## I. INTRODUCTION

Current CMOS technology is rapidly approaching size limits due to challenges in lithography and physical limits in transistor scaling. These limits may be overcome using nanometer-size organic molecules as functional units to transfer electrons in nanoscale devices.<sup>1–6</sup> Researchers first proposed using organic molecules in electronic devices in 1974.<sup>7</sup> However, until the 1990s, the field was severely limited by the lack of molecular characterization techniques. The ability to electrically characterize organic molecules was significantly improved by the inventions of the conducting probe atomic force microscope and scanning tunneling microscope. These two probing techniques have been used for much of the electrical characterization of organic molecules to date.<sup>8–11</sup> However, structures relying on probing techniques would not be suitable for commercial device applications. Thus, research groups sought alternative characterization methods with greater potential for integration into CMOS circuits.<sup>1,12–14</sup>

We designed, built, and tested a nanowell molecular device that has potential for circuit integration. Our nanowell device does not rely on a probing technique and has fabrication simplifications when compared to a similar device.<sup>1</sup> These simplifications include the method of lithography, evaporation conditions, and deposition rate. The nanowell is also a planar device as opposed to the through-wafer device.<sup>1</sup> Although processing conditions were simplified, the nanowell device was able to achieve results that agreed with other groups.<sup>1,2,8,9,15–17</sup> The device effectiveness was confirmed by testing the electrical characteristics of both simple alkanethiol molecules and conjugated molecules bearing thiol end groups. Alkanethiol molecules are simple chains of  $sp^3$ -hybridized carbon atoms with relatively low electrical conductivities. We tested both alkane-monothiols (one end of the molecule is terminated with a sulfur atom) and alkanedithiols (both ends of the molecule are terminated with sulfur atoms). Conjugated molecules consist of non- $sp^3$ -hybridized carbon atoms, which have more delocalized electronic states and lower-lying unoccupied molecular orbitals, and are thus more conductive. We tested conjugated molecules with no side groups, as well as conjugated molecules with nitro side groups, commonly referred to as “nitro” molecules. The electrical behaviors of both the alkanethiols and conjugated mol-

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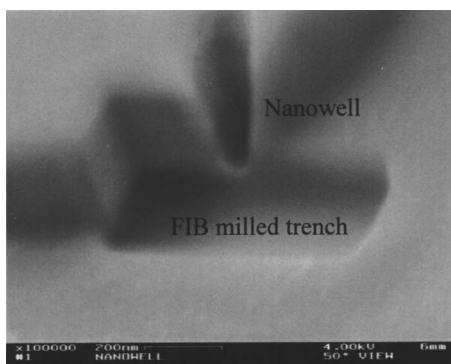


FIG. 1. SEM image of the cross section of the nanowell. A FIB milled trench was added for viewing purposes to expose the cross section of the nanowell. The bottom diameter of the well is about 50 nm as seen in the picture.

ecules tested with the nanowell device were comparable to results from other groups.<sup>1,2,8,9,15–17</sup> We also gained new insight into the electrical behavior of nitro molecules. Different groups have reported a variety of electrical behaviors from nitro molecules including: reversible negative differential resistance,<sup>18,19</sup> stochastic switching,<sup>20</sup> bias dependent switching,<sup>21</sup> and voltage dependent switching with memory.<sup>2,4,13</sup> We observed electrical switching with memory from nitro molecules in our nanowell test device. However, reversible negative differential resistance was not observed.

## II. EXPERIMENTAL PROCEDURE

The devices were fabricated on silicon chips that had pre-patterned gold electrodes covered with silicon dioxide. Although our nanowell device design was similar to a previously reported device,<sup>1</sup> fabrication was simplified. Simplifications included: using the focused ion beam (FIB) technique instead of electron beam lithography to mill the holes for the molecules, evaporating at a faster deposition rate, performing the evaporation on an uncooled substrate, and the elimination of backside processing.<sup>1</sup> Performing the evaporation on an uncooled substrate differed from the low temperature method reported by Reed *et al.*<sup>1</sup> This method was used by Reed *et al.*<sup>1</sup> to minimize damage to the molecules during the evaporation. However, recently, Reed *et al.* actually reported a higher yield of working devices for uncooled evaporation than for cooled evaporation.<sup>22</sup> Thus, whether substrate cooling improves or worsens the yield of working devices is unclear. Similarly, the effects of small changes in evaporation rate are still unknown. Our evaporation method simplifications allowed us to use readily available unaltered equipment and thus, should make the fabrication process easier for other research groups to reproduce.

A gallium focused ion beam (FEI FIB 200) with a 8 nm diam was used to mill a 100 nm sized well through a 100 nm thick silicon dioxide layer. This silicon dioxide layer covered a prepatterned 200 nm thick gold layer. The milling time was determined based on the intensity of secondary electron emissions from the well. As the ion beam milled through the oxide and reached the bottom gold surface, the intensity of secondary electron emissions increased, and the milling was

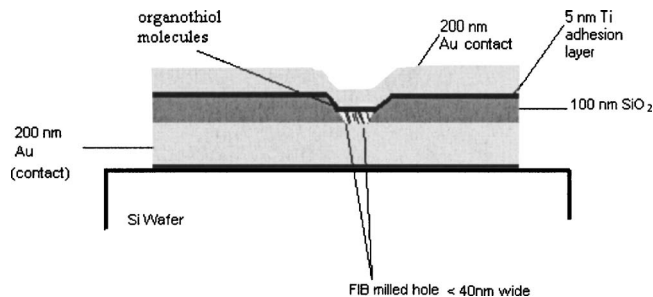


FIG. 2. Cross section of the nanowell test device.

stopped. The ion beam's Gaussian profile, along with the redeposition of the sputtered material, resulted in a diameter smaller than 100 nm at the bottom of the well. Figure 1 shows the scanning electron microscopy image of a cross section of a milled well. From this image, the bottom diameter is estimated to be 50 nm. Additional estimations obtained from alkanethiol  $I$ - $V$  data found the active molecular area in the well to have a diameter between 10 and 40 nm.

After milling wells, the chips were cleaned with piranha solution (30% hydrogen peroxide added to 66% sulfuric acid in a ratio of 1:3) before being placed in a solution of self-assembling molecules. The milli-molar solution of molecules was prepared in an inert atmosphere of nitrogen gas inside a glove box. The solutions for molecules 1, 2, 3, and 4 were prepared by dissolving the molecules in ethanol to form the milli-molar solution. The solution for molecule 5 was prepared by dissolving the molecules in ethanol and then treating the solution with sulfuric acid to remove the acetyl group.<sup>23</sup> The chips were left in the solution for 48 h for the self-assembling monolayer (SAM) of molecules to assemble on the gold surface exposed by the milled well. The chips were then transferred to an electron beam evaporator while minimizing exposure to the atmosphere. A 5 nm layer of titanium followed by 200 nm of gold were deposited on top of the molecules inside the e-beam evaporator. Ti was deposited at a rate of 1 Å/s. The cross section of the nanowell device is shown in Fig. 2.

The first molecules assembled in the nanowell device were simple alkanethiols (molecule 1 and 2 in Fig. 3). These molecules, as well as different types of conjugated molecules (molecule 3, 4, and 5 in Fig. 3), were tested to confirm that the nanowell device could effectively measure the electrical characteristics of the inserted molecules. Molecules 1 and 2 were purchased commercially, molecules 3 and 4 were synthesized at the University of Virginia, and molecule 5 was synthesized at Rice University according to literature protocols.<sup>24</sup> Cyclic voltammetry, an electrochemical characterization technique, was used to ensure full coverage of the self-assembling monolayers on gold substrates.<sup>25</sup>

## III. RESULTS

### A. Alkanethiol $I$ - $V$ characteristics

The first step to confirming the effectiveness of the device was to test the simple alkanethiol molecules. The  $I$ - $V$  char-

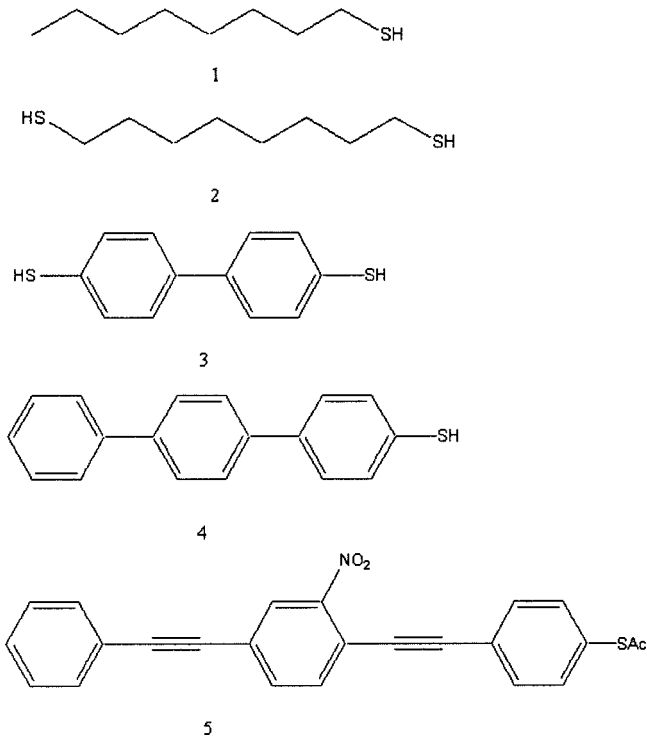


FIG. 3. Chemical structures of the molecules tested in the nanowell device. Molecule 1: C8 alkanethiol, Molecule 2: C8 alkanedithiol, Molecule 3: 4,4'-biphenyldithiol, Molecule 4: terphenylthiol, Molecule 5: 4-ethynylphenyl-4'-ethynylphenyl-2'-nitro-1-benzenethiol, the nitro molecule, prepared by the *in situ* deprotection of the acetate-protected thiol.

acteristics of these molecules are well known and it is easy to establish whether measured current is a result of molecular tunneling. The nanowell devices were probed with voltages from  $-1.5$  V to  $1.5$  V in a HP 4145B semiconductor parameter analyzer for the  $I$ - $V$  characteristics of the alkanethiol molecules. The  $I$ - $V$  characteristics found were exponential and symmetric about  $0$  V for all of the alkanethiol molecules tested. The measured data was fit to the Simmons tunneling equation<sup>26</sup> [Eq. (1)] using the nonlinear curve fitting software Microcal Origin 6.1. The Simmons equation calculates current density based on the tunneling probability of electrons through a potential barrier. The tunneling probability through a potential barrier is found using the quantum mechanical WKB approximation. The Simmons equation has been used by different research groups<sup>8,9,15</sup> to characterize metal-alkanethiol-metal junctions. The equation expresses the current density through a barrier in the tunneling regime of voltage  $< \phi_b$  as

$$J = \left( \frac{e}{4\pi^2 \hbar d^2} \right) \left\{ \left( \phi_b - \frac{eV}{2} \right) \exp \left[ - \frac{2(2m)^{1/2}}{\hbar} \alpha \left( \phi_b - \frac{eV}{2} \right)^{1/2} d \right] - \left( \phi_b + \frac{eV}{2} \right) \exp \left[ - \frac{2(2m)^{1/2}}{\hbar} \alpha \left( \phi_b + \frac{eV}{2} \right)^{1/2} d \right] \right\}, \quad (1)$$

where  $m$  is electron mass,  $d$  is barrier width,  $\phi_b$  is the potential barrier height,  $V$  is the applied bias, and  $\alpha$  is a unitless

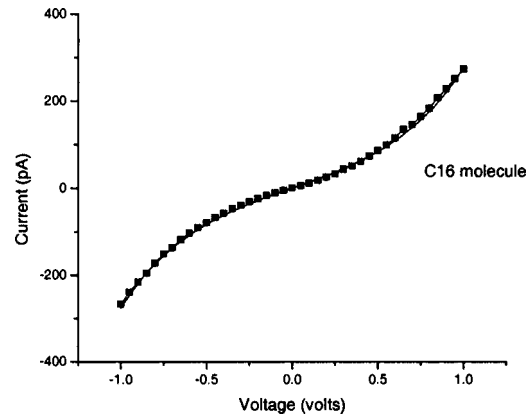


FIG. 4.  $I$ - $V$  characteristics of hexadecanethiol (C16) tested in the nanowell test device. The solid line indicates the best-fit curve to the experimental data.

parameter that may be used to differentiate between potential barrier shapes. The values of the unknown  $\phi_b$ ,  $\alpha$ , and area parameters for the molecules tested in the nanowell were determined by finding a curve of best fit for the Simmons equation with the experimental  $I$ - $V$  data. The unknown parameters were found using a three-parameter fit to the curve; their values were used as an approximation to compare with established results.<sup>8,9,15</sup> Figure 4 shows an  $I$ - $V$  curve for a hexadecanethiol (C16) molecule tested in the nanowell device. The curve of best fit for the C16 data is plotted as a solid line in Fig. 4 and was used to determine the  $\alpha$  and  $\phi_b$  values of  $0.54$  and  $2.2$  V, respectively. This curve matches the experimental data quite closely.

We also tested octane mono and dithiol (C8), decanethiol (C10), dodecanethiol (C12), and hexadecanethiol (C16) molecules in the nanowell device. We obtained an average potential barrier height ( $\phi_b$ ) and  $\alpha$  value for each of these molecules. Table I lists  $\phi_b$  and  $\alpha$  values for these molecules obtained experimentally as well as literature values.<sup>8,9,15</sup>

It was important to establish that the current transmission was due to tunneling through the alkanethiol molecules, not through silicon dioxide or air. The value of the  $\alpha$  parameter signifies the shape of the potential barrier. A rectangular barrier, such as air or silicon dioxide, should have an  $\alpha$  value close to unity.<sup>15</sup> Molecular tunneling barriers have  $\alpha$  values

TABLE I. Summary of barrier height ( $\phi_b$ ) and barrier shape ( $\alpha$ ) values found for C8 mono and dithiol, C10, C12, and C16 alkanethiol molecules.

Molecule	Average $\Phi$ (eV)	Average $\alpha$
C16	$2.1 \pm 0.1$	$0.56 \pm 0.02$
C12	$2.1 \pm 0.1$	$0.55 \pm 0.05$
C10	$2.0 \pm 0.1$	$0.75 \pm 0.02$
C8 (monothiol)	$2.1 \pm 0.1$	$0.77 \pm 0.05$
C8 (dithiol)	$2.05 \pm 0.15$	$0.72 \pm 0.04$
Literature values	$1.42$ eV <sup>a</sup>	$0.66$ for C12 <sup>a</sup>
	$2.2$ eV <sup>b</sup>	$0.68$ for C16 <sup>a</sup>

<sup>a</sup>Reference 15.

<sup>b</sup>Reference 9.

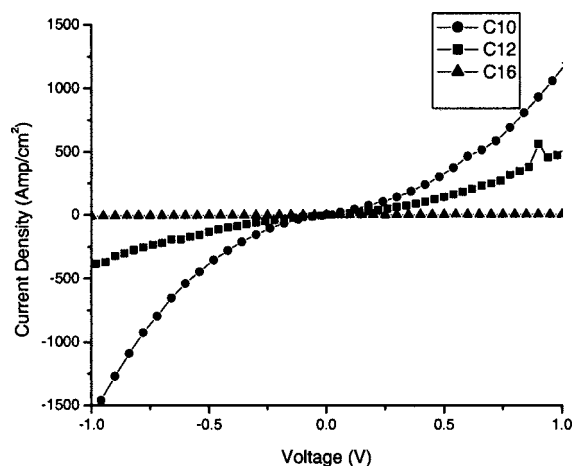


FIG. 5. Plot of current density versus voltage for C10, C12, and C16 alkanethiol molecules tested in the nanowell device. The current density is found to decrease with the increase in chain length.

less than unity.<sup>15</sup> As Table I shows, all of the alkanethiol  $\alpha$  values measured with the nanowell were less than 0.77. These lower  $\alpha$  values confirm that the potential barrier shape was not rectangular and that the tunneling did not occur exclusively through silicon dioxide or air.

The average  $\alpha$  value was found to be 0.55–0.56 for longer chain molecules (C12 and C16), which compares well with  $\alpha$  values of 0.66 for C12 and 0.68 for C16.<sup>15</sup> The average potential barrier height was found to be 2.1 V, which also compares well with the literature value of 2.2 V.<sup>9</sup> The observation of predicted  $\alpha$  and  $\phi_b$  values showed that the current flow was consistent with molecular tunneling.

Additionally, we were able to obtain some insight into the relationship between potential barrier shape and molecule chain length. We found  $\alpha$  values of 0.75 and 0.77 for C10 and C8 molecules, respectively. These values were higher than the average  $\alpha$  values for the longer chained molecules of 0.55–0.56. This difference in  $\alpha$  values indicated that the alkanethiol potential barrier shape is chain-length dependent.

## B. Current density of alkanethiol molecules

Molecular tunneling was also confirmed by establishing the relationship between current density and molecular chain length. The electron transfer rate through a molecular bridge can be described by Eq. (2), where  $J$  is the current density through the metal–molecule–metal junction at a particular voltage,  $J_0$  is a constant current density,  $d$  is the length of the bridge or molecule, and  $\beta$  is a structure dependent attenuation factor that describes the decay of the current through a metal–molecule–metal junction as the separation distance between the electrodes increases.<sup>8,9,15</sup> The value of this decay factor  $\beta$  depends on the molecular structure,

$$J = J_0 \exp(-\beta d). \quad (2)$$

In order to determine the  $\beta$  values for the alkanethiols used in our system, we used the nanowell device and the Simmons equation to find the current densities for three alkanethiols of different lengths (C10, C12, and C16) (Fig. 5).

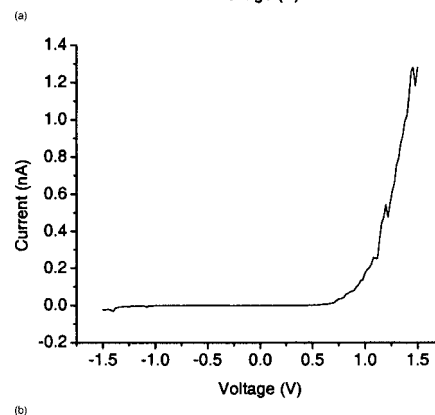
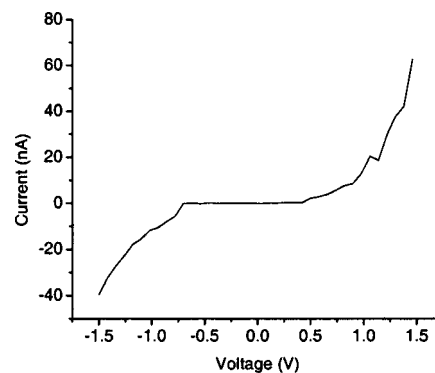


FIG. 6.  $I$ – $V$  characteristics of a conjugated (biphenyldithiol) molecule tested in the nanowell device. The current observed is more than 100 times greater than the current observed for alkanethiol molecules tested. (b) The rectification behavior observed from molecule 4 when tested in the nanowell device.

The  $d$  values (chain lengths) for C10, C12, and C16 of 15.8, 18.2, and 23.2 Å, respectively were calculated by adding the length of an Au–S bond to the length of the particular alkane molecule.<sup>27</sup> We calculated  $\beta$  at bias points between 0.1 and 1 V and found values of 0.7 to 0.75/Å. These values agree with previously reported  $\beta$  results for alkanethiols of: 0.83 to 0.72/Å,<sup>15</sup> 0.8±0.2/Å,<sup>8</sup> and 0.94/Å.<sup>27</sup> Variation in calculated  $\beta$  values for the alkanethiol molecules has been observed among groups using different test devices.<sup>28</sup> The observation of chain-length current density dependence and  $\beta$  values similar to those in the literature reconfirms the effectiveness of the nanowell device.

## C. Conjugated molecules

We proved the nanowell device effective by testing alkanethiol molecules and comparing their characteristics to established results. In order to demonstrate the versatility of our device, we then tested different types of conjugated molecules. First was a simple dithiol conjugated molecule, molecule 3, tested in the nanowell device. The  $I$ – $V$  characteristics of molecule 3 are shown in Fig. 6(a). The  $I$ – $V$  characteristics for these molecules appear similar in shape to the  $I$ – $V$  curve for alkanethiols. However, for similarly sized devices, the conjugated molecules showed approximately 100 times greater current than the alkanethiol molecules. This current enhancement is explained by the fact that con-



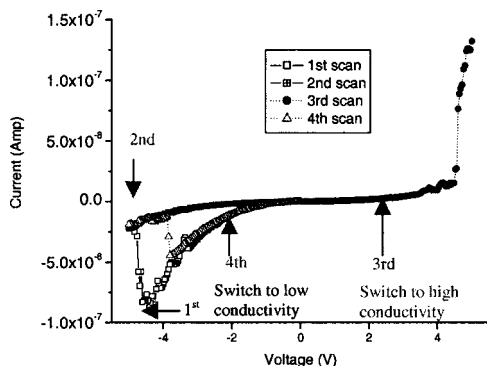


Fig. 7. Switching with memory observed from molecule 5 in the nanowell device. The first scan is from 0 to  $-5$  V and shows the change in conductivity from a high to a low state at a negative threshold voltage of  $-4.5$  V. The second scan is from 0 to  $-5$  V again and shows that the molecule holds the low conductivity state. The third scan is from 0 to  $+5$  V and shows the conductivity switch from a low to a high state at a positive threshold voltage of  $4.5$  V. The fourth scan is from 0 to  $-5$  V and shows the same change in conductivity seen with the first sweep, but at a lower threshold voltage.

jugation causes delocalization of electronic charge in the conjugated molecules enhancing the electron transmission.<sup>28</sup>

When tested in the nanowell device, molecule 4's  $I$ - $V$  curves showed current rectification that is evident in Fig. 6(b). As seen in Fig. 6(b), the current ratio between the current at  $1.5$  V and at  $-1.5$  V is approximately 100:1. Rectification may have resulted from an energetic asymmetry between the bonded and nonbonded end of the molecule.<sup>1,17</sup> Zhou *et al.*<sup>1</sup> and Kushmerick *et al.*<sup>17</sup> found similar rectification behavior in different conjugated monothiol molecules.

The nanowell test device was also used to characterize an oligo(phenylene-ethynylene) (OPE) (molecule 5) with a nitro side group. The  $I$ - $V$  characteristics of this molecule showed two distinct conductivity states, as can be seen in Fig. 7. In the first scan from 0 to  $-5$  V, current started in a high conductivity state and switched to a low conductivity state around  $-4.5$  V. Current continued in the low conductivity state during a repeated scan, which is shown in the second scan in Fig. 7. The current stayed in this low conductivity state until a high opposite voltage ( $+4.5$  V) was applied to switch it back to its initial high state, as observed in the third scan. Current was then switched back to the low state with the application of a high negative voltage ( $-3.7$  V), as seen in the fourth scan. This switching with memory behavior could be repeated several times before the device degraded. This behavior was not observed from an oligo(phenylene-ethynylene) (OPE) molecule without a nitro group and thus, can be attributed to the presence of the nitro group. The switching behavior was also repeatable, signifying a molecular phenomenon rather than an electrical short. Different groups have observed a variety of electrical results from this molecule. Some groups have observed switching as well as reversible negative differential resistance (NDR),<sup>2,4</sup> while others observed reversible NDR with no switching.<sup>18,19</sup> Others observed stochastic<sup>20</sup> or bias dependent switching<sup>21</sup> from the same molecule. As the  $I$ - $V$  plot in Fig. 7 shows, the only NDR-like peaks we observed were around  $-4.5$  V for the

first scan and around  $-3.7$  V for the fourth scan. These NDR peaks were nonreversible and they only occurred during the switch from a high conductivity state to a low conductivity state. Detailed analysis of this behavior will be presented in a future publication.<sup>25</sup>

#### IV. CONCLUSIONS

We built and tested a nanowell molecular test structure using simplified fabrication techniques. We confirmed the effectiveness of the nanowell device by testing the  $I$ - $V$  characteristics of alkanethiol and conjugated molecules. Calculated potential barrier heights ( $\phi$ ), barrier shapes ( $\alpha$ ), and exponential decay factors ( $\beta$ ) of the alkanethiol molecules matched the literature values.<sup>9,15</sup> Expected  $I$ - $V$  behavior, including rectification from the conjugated monothiol molecules and symmetric  $I$ - $V$  behavior from the conjugated dithiol molecules, was observed. Additionally, interesting electrical behavior, specifically switching with memory, was observed from the nitro molecules. The only NDR peaks observed were not reversible and resulted from a switch from a high to a low conductivity state, and thus, may not have device applications. However, the observed switching with memory may have potential applications in logic and memory devices.

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