

# Development of a Nanowire-Based Test Bed Device for Molecular Electronics Applications

Catherine E. Gardner,<sup>†</sup> Mohamed A. Ghanem,<sup>†</sup> James W. Wilson, and David C. Smith\*

School of Physics and Astronomy, University of Southampton, Highfield, Southampton, SO17 1BJ, U.K.

In this paper, we present a novel test bed system which we believe addresses several key challenges in molecular electronics, i.e., the need to fabricate metal–molecule–metal junctions that have the potential to facilitate single-molecule measurements, are easily characterized, and are reproducible. The system is based upon template-electrodeposited metal nanowires incorporating a self-assembled monolayer spacer that are fabricated into electrical devices using direct-write photolithography. Removal of the spacer leaves a nanometer-sized, characterizable gap to which nanoparticles or a test molecule of interest can be attached postfabrication. Here we report the fabrication procedure together with results showing the application of these devices to the study of the *i/V* characteristics of Au nanoparticles at cryogenic temperatures. These data demonstrate that the performance of these easily produced, inexpensive, novel devices compares favorably to that of devices made using preexisting methods.

The field of molecular electronics<sup>1,2</sup> has led to many important scientific and technological advances.<sup>3–5</sup> It has been asserted that the nature of the contact between the device and the molecule is of key importance;<sup>3</sup> thus, a number of different systems for electrically contacting molecules have been developed. As yet, however, none has proved entirely successful.

One class of methods, including the nanopore system,<sup>6,7</sup> Hg drop,<sup>8,9</sup> and crossed-wire self-assembled monolayer (SAM) junction,<sup>10,11</sup> has been used to contact large numbers of molecules in parallel, as many as  $\sim 10^{11}$  in the case of the Hg drop junction. It is frequently desirable, however, to have the capacity to make

measurements of the properties of low numbers of, or even single, molecules.

Single-molecule measurements can be made by employing scan probe microscopy (SPM) techniques such as scanning tunneling microscopy<sup>12–14</sup> and conducting atomic force microscopy (C-AFM).<sup>15–17</sup> In these experiments, single molecules of interest, adsorbed at defect sites in an insulating SAM, are identified topographically, using the SPM, and their electrical properties measured. These methods, however, require relatively complex equipment and are the hardest to relate to a practical electronic device.

A further important strategy is based on the fabrication of nanometer-scale gaps between two metal electrodes where, ideally, only a small number of molecules and preferably a single molecule will be attached to bridge the gap. One method of forming such gaps is electromigration.<sup>18–21</sup> Here, a high current passed through a metal nanowire causes electromigration of the metal ions and thus breakage of the wire, creating gaps that are  $\sim 1$ – $2$  nm in size to which the molecular wire under investigation can then be added.

Nanogaps can also be created by mechanically breaking a substrate onto which a metal wire has been evaporated, using piezoelectric actuators.<sup>22,23</sup> The molecule of interest is then deposited from solution onto either side of the break, and the two halves of the device are brought together until a single

\* To whom correspondence should be addressed. E-mail: dcsmith@phys.soton.ac.uk.

<sup>†</sup> These authors contributed equally to this work.

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molecule bridges the gap. The main concerns with these types of junctions are that their production requires expensive infrastructure, the exact structure of the junction is unknown, and device reproducibility can be problematic to attain.

Highly intricate methods, such as “sculpting” a Au film, using a focused transmission electron microscopy (TEM) beam, to produce two electrodes with a 2-nm gap between them,<sup>24</sup> can also be adopted for the formation of nanoscopic gaps. A further approach has been to sequentially define two, differently spaced, arrays of metal nanowires on a Si<sub>3</sub>N<sub>4</sub> surface using electron beam lithography<sup>25</sup> and to identify, by electron microscopic inspection, pairs of wires at nanometer-scale separations. These are then lithographically contacted to produce devices containing two wire electrodes separated by a 1-nm gap. No method for attaching molecules across these gaps has, as yet, been described.

By considering the different approaches set out above it becomes clear that a successful method for making single-molecule contacts has to compare favorably against a number of different criteria: (i) The gap size needs to be accurately controlled and known before the junction is used. (ii) The test bed should facilitate single-molecule measurements without the need for dilution. (iii) The ability to change the metal from which the contacts are made and fabricate asymmetric junctions with different metals on either side provide additional information about the molecule–metal interface.<sup>26</sup> (iv) The molecules under test should not be exposed to any potentially harmful environments, e.g., during metal evaporation, lithography, or electrodeposition. (v) The junction should function at cryogenic temperatures to allow the temperature-dependent measurement of electron transport. Clearly these criteria are not exhaustive and are open to discussion. For example, ease and cost of production and ease of use will affect the applicability of the technique. It is also clear that a number of different experimental approaches can be employed in order to separate effects arising due to a specific contacting technique from data arising due to the electronic properties of a molecular wire.

In this paper, we introduce a novel molecular electronics test bed system that we believe is competitive with the state of the art under most of the criteria described above. This system is based upon previous work on electrochemically grown molecular contacts.

Electrochemical deposition of a wide range of metals and semiconductors in porous templates, such as nanoporous alumina or track-etched polycarbonate membranes, has been widely explored.<sup>27,28</sup> By employing this strategy, it is possible to produce wires that are nanometers in diameter yet micrometers in length, making them appropriate for the subsequent fabrication of electronic devices.

The groups of Bao<sup>29</sup> and Mirkin<sup>30</sup> have demonstrated that, by careful control of the electrodeposition process, nanometer thick,

“sacrificial” layers of metals such as Ag<sup>29,30</sup> or Ni<sup>30</sup> can be introduced into Au nanowires. After release, the wires are supported either by device fabrication on a SiO<sub>2</sub>/Si substrate<sup>29</sup> or by the plasma-enhanced chemical vapor deposition of a layer of silica, which gives the wire a “backbone”.<sup>30</sup> The sacrificial metal layer is then removed by chemical etching or heating. This approach has produced gaps of between 5 and 200 nm.<sup>30</sup> Nanowire electrodes incorporating 100-nm gaps have been used to fabricate organic field-effect transistors with poly(3-hexylthiophene).<sup>29</sup> Moreover, the conductivity of wires containing 13-nm gaps has been tested in the absence and presence of deposits of conducting polymer.<sup>30</sup>

Recently, a method of growing nanowires that incorporate a SAM junction has been reported.<sup>26,31</sup> Au nanowires are grown to a length of ~3 μm in the pores of a templating membrane, and then a SAM is formed on top of the nanowires in the membrane pores. A layer of electroless Au,<sup>32</sup> deposited on top of the SAM, forms a seed layer for electrodeposition of the second half of the nanowires. The nanowires are released and devices are fabricated, using electrofluidic assembly, where single nanowires are contacted to metal electrodes.<sup>33</sup>

This technique has been used to characterize the conducting behavior of SAMs of 16-mercaptohexadecanoic acid,<sup>31</sup> dodecane, oligo(phenyleneethynylene), and oligo(phenylenevinylene).<sup>26</sup> A potential drawback of this technique is, however, that the mechanical stability of the wire depends on the SAM formation capability of the molecule of interest. Moreover, the molecules of the SAM are exposed to the environments associated with the device fabrication procedure.

In the test bed system introduced in this paper, metal nanowires incorporating a single or multilayer SAM junction are grown by electrodeposition into the nanopores of an alumina templating membrane. The second part of the nanowire is then deposited directly onto the SAM without the need of an electrolessly plated metal seeding layer.<sup>26,31</sup> This method allows a wide range of metals, and possibly conducting semiconductors, to be used as contacts in either symmetric or asymmetric arrangements. Direct-write photolithography<sup>34</sup> is employed to produce devices that contain a single, electrically contacted metal nanowire. No external alignment techniques are necessary,<sup>31</sup> and each wire is individually selected.

Once device fabrication is complete, the original SAM spacer is removed to leave a clean, nanometer-sized gap in the wire across which the molecules/particles to be electronically tested can be attached. This has two key advantages: First, the choice of molecules to be studied is not limited by the need to mechanically stabilize the wire. Second, the molecules of interest are attached postfabrication under optimized environmental conditions. Furthermore, the gap size can be tailored through the use of multilayer SAM junctions, allowing a larger range of molecular species to be accommodated. In this paper, the fabrication and characterization processes for these devices are described, together with the results of initial cryogenic temperature charge

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transport studies on colloidal Au nanoparticles, which are a frequently employed test sample for characterizing single-molecule test beds.<sup>19,24,35</sup>

## EXPERIMENTAL SECTION

**Templated Electrodeposition of Metal Nanowires.** Alumina membranes 60  $\mu\text{m}$  thick, 13 mm in diameter, and with a pore diameter of 100 nm (Anopore 13, Whatman International, nominal porosity 20–50%) were used as templates for metal nanowire electrodeposition.

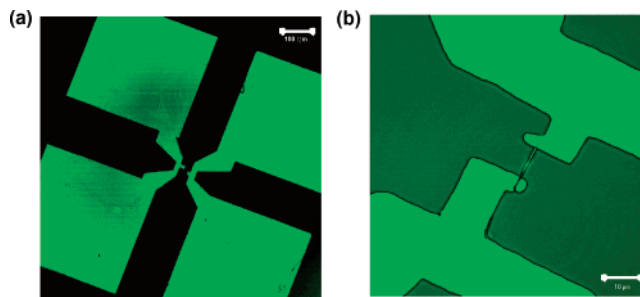
An anchor layer of Cr ( $\sim 10$  nm) was thermally evaporated onto one side of the membrane followed by  $\sim 200$ -nm Au (99.99%, Agar Scientific). The metallized face of the membrane was mounted onto a glass slide support using double-sided adhesive Cu tape (Agar). The completed substrate was then insulated with nail varnish such that only the unmetallized side of the membrane was exposed to the plating solution. This was used as the working electrode in conjunction with a homemade saturated calomel reference electrode and Pt gauze counter in a three-electrode plating cell. Au wires were deposited from a fully bright cyanide-free commercial Au plating solution (Au concentration 10 g L<sup>-1</sup>), (ECF60 and E3, Metalor, Cinderford, U.K.). Ag wires were deposited from a commercial Ag plating solution (Silver 150, Metalor) and Pt wires from a 50 mmol dm<sup>-3</sup> hydrogen hexachloroplatinate(IV) (Aldrich)/10 mmol dm<sup>-3</sup> sodium dodecyl sulfate solution.

Electrochemical measurements were made using a computer-controlled workstation (Autolab PGSTAT30, EcoChemie, Utrecht, The Netherlands). The optimum deposition potential, typically between  $-0.7$  and  $-0.8$  V for Au (charge density during growth  $\sim 1.0$  C cm<sup>-2</sup>  $\mu\text{m}^{-1}$ ),  $-0.8$  V for Ag (charge density during growth  $\sim 1.0$  C cm<sup>-2</sup>  $\mu\text{m}^{-1}$ ), and 0 V for Pt (charge density during growth  $\sim 3.0$  C cm<sup>-2</sup>  $\mu\text{m}^{-1}$ ), was determined pre-experiment by cyclic voltammetry. Initially, nanowires were grown to a length of  $\sim 5$   $\mu\text{m}$ .

**Formation of Molecular Junctions.** SAMs were formed by immersing the partially grown nanowire substrates, in a 10 mmol dm<sup>-3</sup> ethanolic solution of 16-mercaptohexadecanoic acid (C-16) (Aldrich) for 24 h. Multilayer junctions were formed using the method described by Evans et al.<sup>36</sup> with a 30-min immersion in a 10 mmol dm<sup>-3</sup> methanolic CuClO<sub>4</sub><sup>-</sup> (Aldrich) solution used to facilitate bonding between SAM layers. The second part of the nanowire was then electrochemically deposited directly onto the SAM junction. Wires were grown to a total length of  $\sim 10$ – $15$   $\mu\text{m}$ .

**Nanowire Release.** The membrane was separated from the Cu tape by acetone immersion. The evaporated Au/Cr film was then removed using 2–3 drops of KI/I<sub>2</sub> solution. Etching was stopped at the point where the observed apparent color of the membrane changed from gold to dark brown. This was achieved with little etching of the electrodeposited wire. Nanowires were released by dissolving the alumina membrane in 2 mol dm<sup>-3</sup> NaOH and suspended in 2-propanol by brief sonication (2–3 s) at low power before being rinsed and resuspended several times.

It should be noted that, due to heterogeneity of pore diameter throughout the thickness of the membrane, the nanowire diameter



**Figure 1.** Laser scanning confocal microscopy images showing (a) a completed nanowire molecular electronics test bed device and (b) a closeup image showing the electrically contacted molecular junction nanowire. Scale bars: (a) 100 and (b) 10  $\mu\text{m}$ .

may exceed the quoted membrane pore diameter and thus should be measured postrelease.

**Device Fabrication.** Nanowires were deposited from 2  $\mu\text{L}$  of suspension onto the surface of pieces of cleaned Si, oxidized to a depth of 0.3–1  $\mu\text{m}$ . A layer of S-1813 photoresist (Rohm & Haas Electronic Materials, Coventry, U.K.) was then spun onto the Si surface, covering the nanowires, and the samples were soft-baked at 115  $^{\circ}\text{C}$  for 60 s.

Direct-write photolithography was undertaken to pattern the resist using a Zeiss model LSM510 Axioplan 2 laser scanning confocal microscope (CLSM). Illumination at 543 nm (HeNe) was used for device imaging and illumination at 458 nm (Ar) for bleaching. Initially, the confocal was used to locate a single target nanowire. The first bleaching step, using a Plan-Neofluar 10 $\times$ /0.3 objective, defined bond pads. In the second step, using a Plan-Neofluar 40 $\times$ /0.75 objective, the pattern of the nanowire contacts was defined. The two-step exposure allowed fine structures, e.g., lines of width  $\sim 5$   $\mu\text{m}$  to be combined with large structures, e.g., the  $\sim 0.16$  mm<sup>2</sup> bond pads, and allowed the contact pattern to be adjusted to the length of the wire if necessary. The overall size of the completed device pattern was  $\sim 1$  mm<sup>2</sup>.

Following bleaching, the device was immersed in chlorobenzene for 2 min 30 s and the photoresist removed from the bleached areas of the device using MF-319 developing solution (Rohm & Haas). Next, an anchor layer of  $\sim 5$  nm of Cr followed by  $\sim 25$  nm of Au was thermally evaporated onto the device. Complete removal of the remaining photoresist was achieved by acetone immersion and verified using optical and confocal microscopy. CLSM images showing (a) the complete device and (b) a closeup image of the nanowire contacts is shown in Figure 1.

**Device Testing.** The  $i/V$  characteristics of the molecular junction were recorded using an Agilent model 4155C parameter analyzer in conjunction with a manual probe station. The SAM junction was then removed by heating the device to 200  $^{\circ}\text{C}$  for 1 h. The  $i/V$  behavior of the devices was subsequently recorded in order to (a) verify removal of the SAM and (b) determine the size of the gap in the wire.

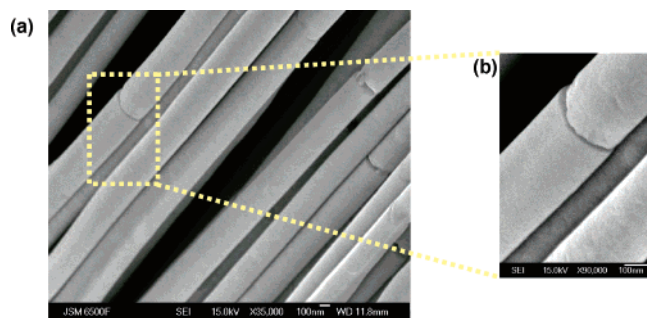
**Nanoparticle Experiments.** Au nanoparticles were trapped in the gap in a Au nanowire device from which a two-layer C-16 SAM junction had been removed using a procedure similar to that reported by Bezryadin et al.<sup>33,37</sup> A 10- $\mu\text{L}$  droplet of 5-nm Au colloid solution (BB International) was deposited onto the device. An alternating electric field of 1.0 V, 50 kHz was applied for 30 s

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**Figure 2.** (a) Scanning electron micrograph of Au nanowires containing a six-layer 16-mercaptohexadecanoic acid junction, electrodeposited in a 100-nm pore diameter alumina template membrane. A higher magnification image (b) of one of the nanowire junctions shows a uniform deposition of Au at the junction. Scale bars: (a) and (b) 100 nm.

to align nanoparticles into the gap in the wire. The nanoparticle devices were attached to a 16-pin header using Ag paint (R.S. Components, Corby, U.K.). Electrical connection between the header pins and device contact pads was achieved by attaching 50- $\mu\text{m}$ -diameter Au wire (Agar) between the two using Ag paint. For cryogenic charge transport measurements, samples were mounted into a cryostat (Microstat, Oxford Instruments) in conjunction with a temperature controller and  $i/V$  measurements made using the parameter analyzer as described previously.

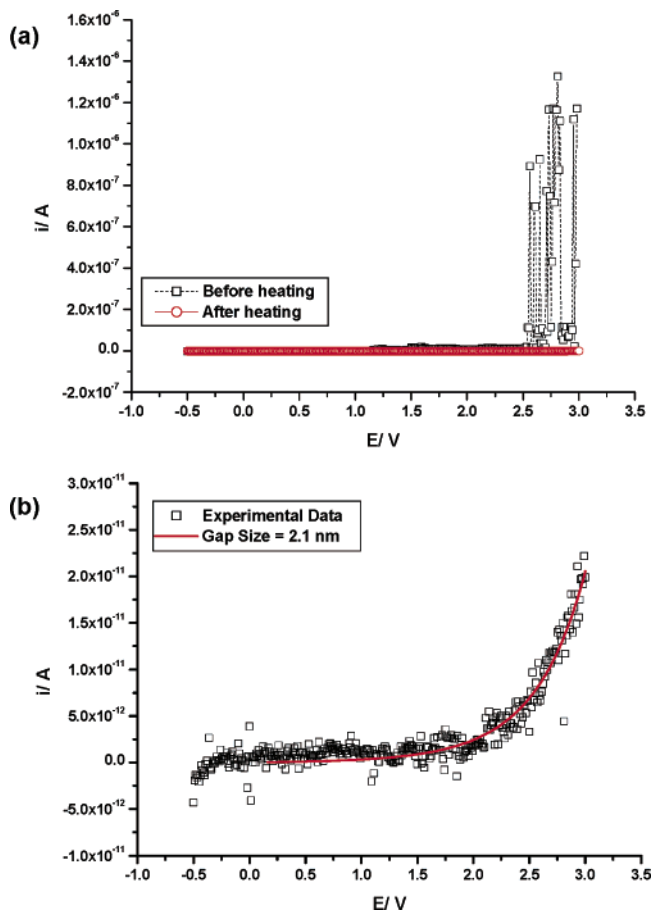
## RESULTS AND DISCUSSION

Figure 2 shows scanning electron microscopy (SEM) images of Au nanowires grown in a 100-nm-pore diameter alumina membrane template. The six-layer C-16 SAM junction can be identified in some of the wires imaged (see Figure 2b). It has been found that, for a range of junction sizes, the nanowires produced are monodisperse and mechanically stable with only  $\sim 10$ – $15\%$  breaking during the release process.

The SEM images also show a uniform deposition of Au in the region of the SAM junction, in contrast to the rougher appearance, as shown by TEM images, of molecular junction wires where electroless deposition was employed.<sup>31</sup> This could have consequences for the quality of the junction between the metal nanowire and the SAM.

The properties of nanowire devices containing 1, 2, 4, and C-16 SAM layer junctions were investigated using  $i/V$  measurements. The results were typical of those recorded for molecular electronics junctions in that the  $i/V$  response was sigmoidal in shape with a linear portion in the region of 0 V. As the potential was increased beyond the linear region, the “breakdown voltage” was reached and the current increased exponentially. It was found that the breakdown voltage increased monotonically with increasing numbers of C-16 layers. Measurements of 10 one-layer C-16 SAM junctions gave an average breakdown voltage of  $2.2 \pm 0.2$  V, which is in good agreement with measurements made at Hg drop junctions.<sup>8</sup>

Assuming a 2-nm gap,<sup>36</sup> this corresponds to a breakdown field strength of  $\sim 1.1 \times 10^7$  V  $\text{cm}^{-1}$ , which is, again, within the range described by Hg drop<sup>8</sup> and C-AFM measurements.<sup>16</sup> Furthermore, calculating the junction resistance in the linear region of the  $i/V$  data gives an average value, for a one-layer C-16 junction, of  $1.4 \pm 0.7 \times 10^{12} \Omega$ . This is in excellent agreement with data calculated



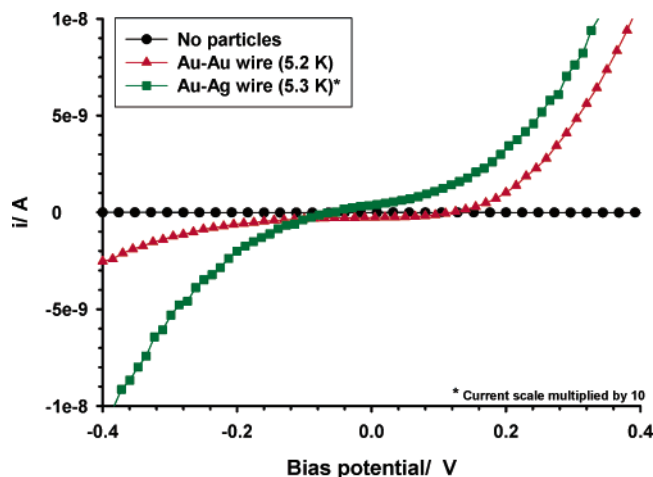
**Figure 3.** (a)  $i/V$  data for a1 layer C-16 SAM junction nanowire device before ( $\square$ ) and after ( $\circ$ ) removal of the SAM junction by oxidation. The current response is reduced by SAM removal from hundreds of picoamperes to a scale of  $\sim 10$  pA, which approaches the 5-pA leakage current of the device. (b)  $i/V$  data (—) for a gap from which a one-layer C-16 SAM junction has been removed. The theory fit line shows a gap size of 2.1 nm.

from the theory of Wold and Frisbie,<sup>16</sup> which predicts a resistance of  $2 \times 10^{12} \Omega$  for a C-16 junction and is 1 order of magnitude lower than that measured by Mallouk et al.<sup>31</sup> for a device based on C-16 molecular junction nanowires. While this lower resistance could be attributed to the formation of metallic contacts through the SAM, this is unlikely as the resistance is  $\sim 8$  orders of magnitude greater than the resistance quantum. Furthermore, in the  $\sim 10\%$  of wires where a significant metallic contact has been formed, devices fail at potentials of between  $\sim 0.5$  and  $1.0$  V.

Figure 3a shows the  $i/V$  response of a two-layer C-16 SAM junction nanowire device before ( $\square$ ) and after ( $\circ$ ) removal of the SAM. There is a noticeable decrease in current between the two data sets with the current response of the nanowire on the scale of hundreds of picoamperes in the presence of the SAM being reduced to  $< 10$  pA, a value approaching the device leakage current of 5 pA, after SAM removal.

The transport behavior of the gap left after removal of a one-layer C-16 SAM junction (Figure 3b) can be characterized by a simple, rectangular barrier, tunneling model<sup>38</sup> using a standard data fitting program (OriginLab. Corp.). Using a wire diameter of 200 nm, as measured by SEM examination, it was determined

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**Figure 4.** Cryogenic  $i/V$  data for two-layer C-16 SAM junction nanowire Au-gap-Au (▲), and Ag-gap-Au (■) devices in the presence and absence (●) of 5-nm Au nanoparticles bridging the gap. These data demonstrate that (a) the presence of nanoparticles enhances the current response of the device and (b) this device fabrication strategy can be applied to produce deliberately asymmetric junctions. The asymmetry of the individual junction responses can be attributed to the colloid being closer to one side of the contact wire than the other.

that the gap size was  $2.07 \pm 0.02$  nm for a tunneling barrier height of 2.6 eV. The average gap width for nine one-layer C-16 wire devices was found to be  $1.95 \pm 0.16$  nm. This is in very good agreement with previous measurements.<sup>31</sup>

Figure 4 presents cryogenic measurements (5.2 K) of the  $i/V$  characteristics of Au nanoparticles bridging the  $\sim 4$ -nm gap left in a Au nanowire by the removal of a two-layer C-16 SAM junction. In the absence of nanoparticles (●), the current recorded was in the range of the leakage current of the device, 5–10 pA. In the presence of nanoparticles (▲), the current response of the device increased considerably. Coulomb blockade behavior was recorded over a potential range of 350 mV. The apparent asymmetry observed in the device junction can be explained if the colloid was closer to one contact lead than the other. These results are in good agreement with those previously observed when gaps in Au wires produced via electromigration were bridged with gold colloids.<sup>19</sup>

In addition to the Au-gap-Au wires, we have also produced Au-gap-Pt and Au-gap-Ag wires. These wires have been characterized before and after oxidation of the SAM and at

cryogenic temperatures in the presence of Au nanoparticles. Figure 4 also shows  $i/V$  data recorded for Au colloids trapped in the junction of a Au-Ag wire (■, current scale multiplied by 10). This shows that the data for the two different types of junction device were similar in character. In the case of the Au-gap-Ag wires, strong asymmetry was observed in some measurements. This is attributed to the oxidation of the Ag half of the wire under ambient conditions.

## CONCLUSIONS

We have presented a novel test bed for molecular electronic components that is competitive in many aspects with existing systems. The  $i/V$  characteristics of the empty nanowire gaps can be fitted to a standard electron tunneling model to give entirely reasonable values of the gap size and barrier height. Test experiments using 5-nm Au colloids demonstrate the suitability of these devices for measuring the electronic properties of molecular-scale objects, with the results of these tests consistent with those obtained using competing systems. Moreover, the measurements presented on the C-16 SAM used to produce the wires show that this new system is clearly compatible with conducting molecules.

The method of production is relatively simple and low cost; e.g., it does not require e-beam lithography. Once the wires have been produced, which takes roughly 10 h of work, a device takes on average 2 h to produce with a yield of  $\sim 80\%$ . Furthermore, we have shown that this method is not constrained to the production of symmetric wires but can also be used to produce asymmetric contacts, e.g., Au-gap-Ag and Au-gap-Pt.

Finally, in addition to the work presented on molecular electronics, we would like to draw the attention of the reader to the use of a standard scanning confocal microscope to undertake direct-write optical lithography. The large number of such microscopes available in biological science departments suggests that this extremely flexible approach to photolithography may find many applications.

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