Molecular electronics: connection across nano-sized electrode gaps†

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Prefabricated nano-scale structures in which gold electrodes are separated by an insulating core permit self-assembly of a single string "molecular necklace" around its circumference; these devices require no further invasive metal deposition following molecular insertion and exhibit symmetrical current–voltage (*I*–*V*) curves that mimic those of self-assembled films on planar substrates.

Interest in molecular electronics arises from reports that molecules can act as diodes[1] and wires.[2–4] It also provides the means to overcome the miniaturisation threshold of silicon-based devices but experimental difficulty increases as studies progress from ultra-thin films to small clusters and ultimately single molecules. Innovative electrical contacting[5–9] is necessary and, to achieve this, we now report a novel bottom-up technique for self-assembly of molecules between gold electrodes with a predefined nano-scale gap. Optical lithography has been used to mass produce skeleton structures in which the top and bottom contacts are separated by an insulating core with about a 3.5 nm electrode gap around its circumference to locate a "molecular necklace" (Fig. 1 and 2). These structures are robust and require no further invasive metal deposition following molecular self-assembly.

Fabrication involves the following steps: deposition of gold contacts on epi-ready Si/SiO_2 substrates; MOCVD deposition of *ca.* 6 μm diameter Si_3N_4 layers on top of the gold as well as Si_3N_4 pads on either side; deposition of SiO_2 mushroom-shaped domes on Au|Si_3N_4 by exploiting the conformal deposition properties of low-energy RF plasma sputtering and the large aspect ratio bilayer resist process; deposition of thin gold contacts by sputtering followed by electroplating of thick gold bridges between the central structure and separate bond pads to form the top contact region; and finally, wet etching with buffered hydrofluoric acid to wash out the thin Si_3N_4 dielectric layer to an extent that it only just undercuts the electrodes to create an ultra-narrow gold rim around the periphery of the SiO_2 dome and a nano-scale gap between the top and bottom gold electrodes.† Improved stability is achieved by forming a top electrode structure with two bridges (rather than a single bridge) symmetrically located on either side of the central insulating core. It alleviates stresses on the contact and maximises yield in terms of mechanical failure due to the electrode lifting.

Crucial to this technology is the insulating SiO_2/Si_3N_4 core: it permits small contact gap areas to be achieved for relatively modest lithographic resolution and reduces the active region of the upper electrode to only its circumference for self-assembly of molecules across the gap. In the dark and under ambient environmental conditions, the empty skeleton device exhibits asymmetric *I*–*V* characteristics, as shown in Fig. 3, these being obtained using a Keithley Instruments model 6430 sub-femtoamp source meter. The device properties are desirable in terms of leakage and provide a useful comparison when sufficient molecules bridge the electrodes to dominate the current relative to leakage through the Si_3N_4/SiO_2 core.

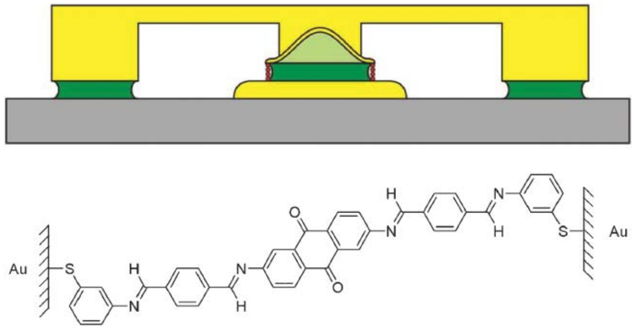

Fig. 1 Schematic side-view of the device and structure of molecule that bridges the nano-scale electrode gap: dark green corresponds to Si_3N_4, light green to a SiO_2 mushroom-shaped dome and yellow to gold contacts. The connecting red beads between the top and bottom electrodes indicate an annular region where molecular wires self-assemble as a necklace-like structure around the central core.

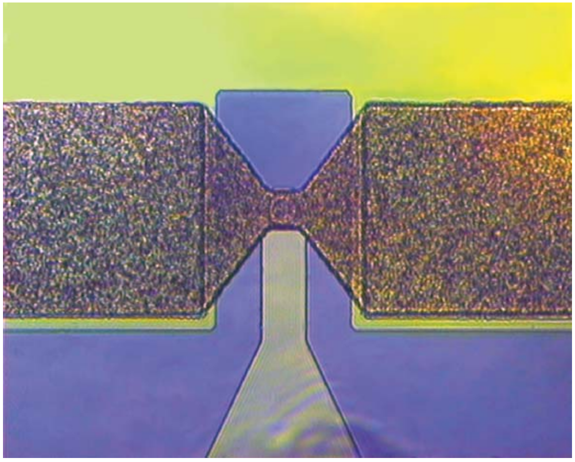

Fig. 2 Magnified top-view image showing the rough surface structure of the two electrochemically formed wings of the top contact connected to a horizontal gold lead with the bottom contact extending forwards from the device. A 6 μm diameter SiO_2/Si_3N_4 core separates the top and bottom contacts and its circular outline can be seen in the middle of the image.

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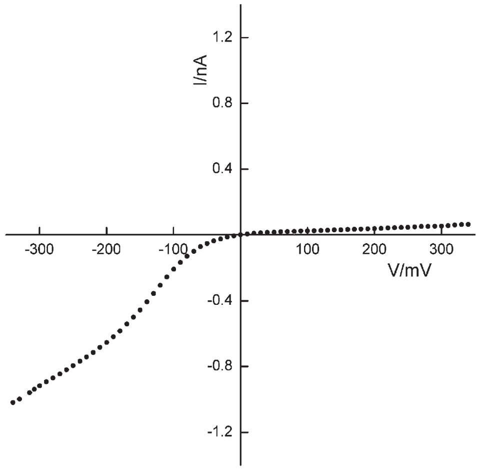

Fig. 3 *I–V* characteristics of the empty mushroom device where electrical asymmetry arises from the Au|Si_3N_4|SiO_2|Au core. Control experiments in which the device was immersed in solvent without the chemisorbing molecules present, and then dried in nitrogen, provided similar curves.

In this work, molecules were deposited in two steps by using a previously reported modular chemistry approach.[10,11] Firstly, 4-[(3-mercaptophenylimino)-methyl]-benzaldehyde was chemisorbed on the upper and lower electrodes by immersion of the device in an ultra-pure chloroform solution of this component (0.1 mg cm^{-3}), following which the device was rinsed with pure solvent and dried in a nitrogen stream. The self-assembled monolayers (SAMs) are isolated on opposite sides of the gap and the *I–V* curves following this step mimic those of the empty device. Secondly, the coated device was immersed in an acetone solution of 2,6-diaminoanthra-9,10-quinone (0.1 mg cm^{-3}) to which acetic acid (0.05 cm^3) was added to assist reaction. The device structure was rinsed and dried. Condensation of the surface aldehydes and the amino substituents of the solution based reactant results in molecular wire formation across the electrode gap when the contacting geometry and distance are appropriate. This is demonstrated by huge current increases and altered *I–V* curves that are stable when the voltage is cycled between +0.3 and −0.3 V (Fig. 4), the range under investigation. Significantly, the properties revert to those of the empty structure when molecules are removed by prolonged rinsing with acidified acetone, which disconnects the molecular wires by breaking the gold–thiolate links.

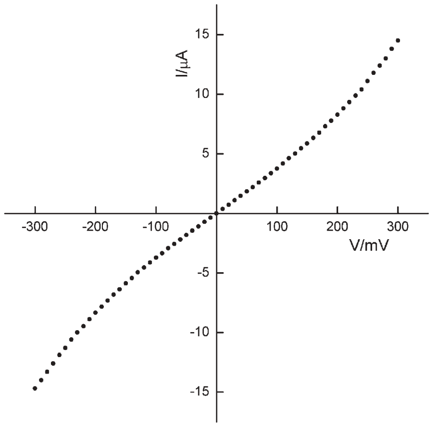

Fig. 4 *I–V* characteristics of the molecule-inserted mushroom device obtained for 48 h immersion periods for each of the deposition steps.

The skeleton device requires molecules with self-assembling groups at opposite ends and the length, allowing for tilt, should be equivalent to the size of the gap but it need not be an exact match as surface roughness probably permits some flexibility. We have used a modular chemistry approach to bridge the electrode gap and the *in situ* reactions on planar substrates have been investigated by X-ray photoelectron spectroscopy (XPS). Monolayers formed from 4-[3-mercaptophenylimino)-methyl]-benzaldehyde exhibit a doublet at 162.0 eV (S $2p_{3/2}$) and 163.7 eV (S $2p_{1/2}$), distinctive of the binding energy of the gold–thiolate link, and a symmetrical peak at 398.9 eV (N 1s) that corresponds to the imino nitrogen. Quantitative analysis of the areas under the peaks, fitted using a Gaussian–Lorentzian function, subtracting a linear background and correcting for atomic sensitivity factors, yields a sulfur to nitrogen ratio of *ca.* 1 : 1. The second step was accomplished by immersion of coated substrates in an acetone solution of 2,6-diaminoanthra-9,10-quinone to which a drop of acetic acid was added. XPS studies reveal the characteristic sulfur doublet but, this time, an asymmetric nitrogen peak that resolves into separate peaks with binding energies of 398.8 eV and 400.1 eV that correspond to imino (–N=CH–) and amino (–NH_2) nitrogens respectively. Their areas provide a ratio of 2 : 1 as well as a sulfur to nitrogen ratio of *ca.* 1 : 3 (*cf.* 1 : 1 after the first step) which is consistent with the expected molecular structure and confirms condensation between surface-based aldehydes and solution-based amino groups. Condensation is also indicated from the frequency change, following deposition on the gold electrodes of 10 MHz quartz crystals, a Sauerbrey analysis[12] of the data yielding a limiting area of *ca.* 0.35 nm^2 $molecule^{-1}$ which is consistent with the area anticipated from molecular modelling and that obtained for the initially assembled monolayer. The thiol-terminated component was then reacted and, on quartz crystals, the concentration of molecular wires (Fig. 5) may be controlled from the immersion time.

Films assembled on planar substrates were investigated using a Nanoscope IV MultiMode scanning tunnelling spectroscope, STM (Veeco Instruments, Cambridge). *I–V* characteristics were

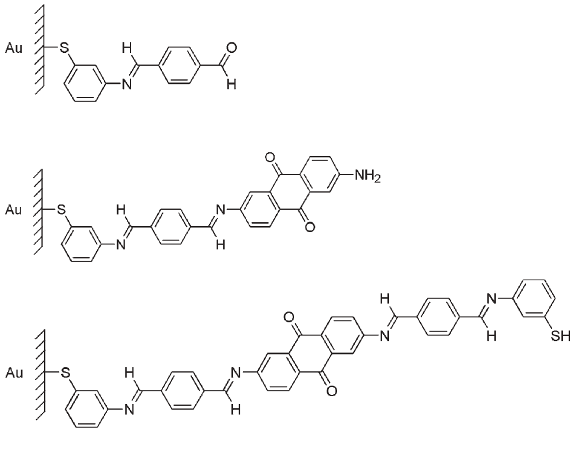

Fig. 5 Molecular structures of components obtained from the three-step process on planar gold-coated substrates.

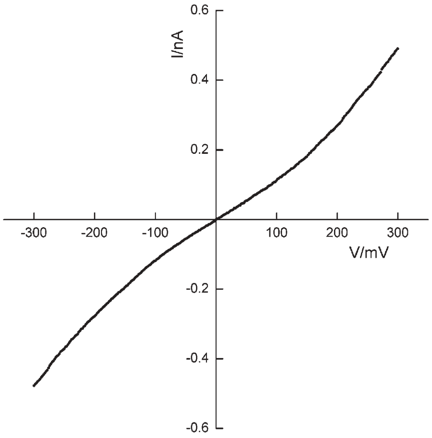

Fig. 6 *I–V* characteristics from a SAM of the symmetrical molecular wire on gold-coated highly oriented pyrolytic graphite contacted by a gold probe and obtained for a set point current of 0.5 nA at 10 mV.

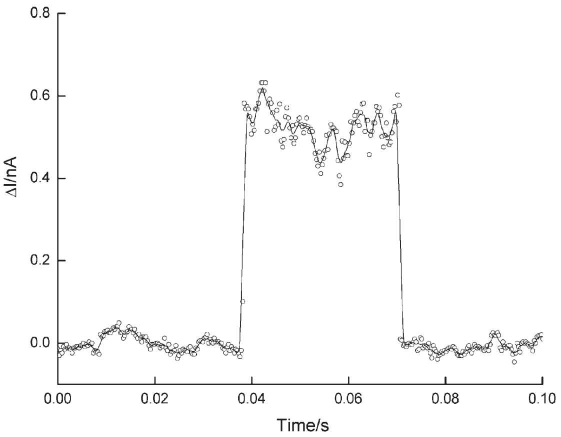

Fig. 7 Characteristic current jump at 300 mV with the gold probe located just above the surface, where open circles are original data and the line is generated from the average of five adjacent data points. The assumed single molecule current is 0.55 ± 0.05 nA at 300 mV.

obtained by landing the gold probe at different locations across each of the films and by averaging the data from multiple scans at each site to obtain relatively noise free plots. The self-assembled layer formed from the first step exhibits symmetrical *I–V* curves; the donor–acceptor assembly obtained by reaction with 2,6-diaminoanthra-9,10-quinone exhibits rectifying behaviour with a current ratio of *ca.* 8 at ±1 V and electron flow at forward bias from the cathode to anthraquinone acceptor; finally, following the third step, the thiol-terminated structure suppresses rectification as the molecule is now almost symmetrical.

We now focus upon the symmetrical molecular component as shown in Fig. 5: its *I–V* curves, which were obtained using a set point current of 0.5 nA at 10 mV, are shown in Fig. 6 and data from STM current jump studies at 300 mV are depicted in Fig. 7. The latter was performed using the method of Haiss *et al.*[13] by locating the gold probe at a fixed height above the surface and monitoring the current as a function of time. Abrupt changes in the current occur as the thiol-terminated molecules spontaneously adsorb and desorb, each event lasting from 10 to 150 ms with characteristic current increases of 0.55 ± 0.05 nA or multiples thereof at 300 mV. From these studies, *ca.* 30% of the observed changes correspond to this lower current and is attributed to single molecule adsorption; *ca.* 50% exhibit values of 1.2 ± 0.1 nA indicative of double molecule contact, and the remainder correspond to three to five molecules being adsorbed.

The *I–V* profile of the SAM on a planar substrate from these STM studies (Fig. 6) is almost identical with that of the mushroom device obtained using a source meter (*cf.* Fig. 4). The device current at 300 mV, however, is *ca.* 27 000 times larger than the single molecule value from the STM current jump investigation and, if this can be related to the number of contributory molecules, their mean spacing around the 6 μm diameter insulating core of the mushroom is *ca.* 0.7 nm (*cf.* 0.34 nm van der Waals distance). Without clustering, these data are consistent with a single string of loosely packed molecules, a "molecular necklace", but studies also confirm that the conditions may be varied to yield functionalised devices that are occupied by fewer molecules.

In conclusion, a mechanically stable structure with a nano-scale gap between gold electrodes has been fabricated for docking molecular wires and monitoring their electrical properties. It provides a stable platform for characterisation and may be likened to an insulating "mushroom" with a conducting "necklace" around its core. Its usefulness has been demonstrated by molecules whose length is *ca.* 3.5 nm and the fully functionalised structure exhibits at least a four order of magnitude increase in current compared with that of the empty device. We note that there is a report of a silicon nanogap structure for deposition of hybrid organic/nanoparticle arrays[14] but, as far as we are aware, the device reported here is the first prefabricated electrode structure for dithiol derivates that is robust and does not rely on the various forms of nanowire[6,7] and break junction[8,9] geometries.

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Notes and references

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