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Nanoscale electrode gaps to study single molecule conduction

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ABSTRACT

The fabrication of electrode pairs with a small electrode gap separation using a focussed-ion-beam is reported. Using a previously developed technique, the gap between the electrodes was bridged using several benzenedimethanethiol molecules and a single gold nanoparticle. The electrical properties of this whole ensemble were measured and the results interpreted with regards to the amount of molecules connecting the electrodes to the nanoparticle. It is shown that the resistance of the single molecule is low compared to some of the values quoted in literature.

1. Introduction

In the quest to further miniaturise electronic networks one of the possibilities that are currently being investigated are molecular networks. This research is mainly focussed on the understanding of the electronic properties of single molecules [1–4]. Recent discoveries in this area have yielded surprising results in that a molecule has several fundamentally different conduction groups with the current consensus being that this is caused by the connection of the molecule to the electrodes [5,6]. However, if the molecular conduction is critically dependent on the electrical contact of the molecule to surrounding electronics, this will severely limit the applicability of molecular electronics.

The experimental techniques employed thus far have in common that they consist of moveable contacts, e.g. AFM/STM tip. Hence, during the experiment to determine the electrical properties, stresses are applied to the molecule and its contact to the electrodes. As a result the contact of the molecule with the electrodes can change during the experiment [5]. However, when the molecules get integrated into a complete molecular network and subsequently into a large semiconductor based environment, the contacts will become static. Therefore no additional stress is applied to the contact during electrical operation and the contact resistance will remain constant. Moreover, the embedding of these molecules in semiconductor technology generated structures, ensures the manufacturability and reproducibility of such switches for future applications. The main question with regards to the contact resistance that remains, is whether these static contacts all have the same resistance or different resistances from contact to contact.

Here, a technique is employed that has previously been used to study the properties of nanoparticles [7]. A set of gold electrodes with a gap separation varying between 20 nm and 50 nm, has been functionalised with a self-assembled-monolayer of 1,4-benzenedimethanethiol (BDMT). On this layer, gold nanoparticles are deposited in order to bridge the gap between the two electrodes. The size of the nanoparticles will determine the number of BDMT molecules that are able to connect the electrodes with the nanoparticle thus determining the resistance of the whole ensemble.

2. Experimental details

The electrodes were fabricated on a 4-in. silicon wafer. In the first step, a 50 nm thick insulating layer of silicon oxide was thermally grown on the wafer. On this layer, a pair of electrodes, both with a current feed- and a voltage measurement-contact point and connected by a narrow line (‘four point measurement’ pattern), was deposited using a lift-off technique, i.e. exposure and development of the electrode pattern in a 1.5 μm thick HPR504 resist layer using an i-line contact aligner, static evaporation of the metal layers (2 nm chromium attachment layer followed by a 10 nm gold

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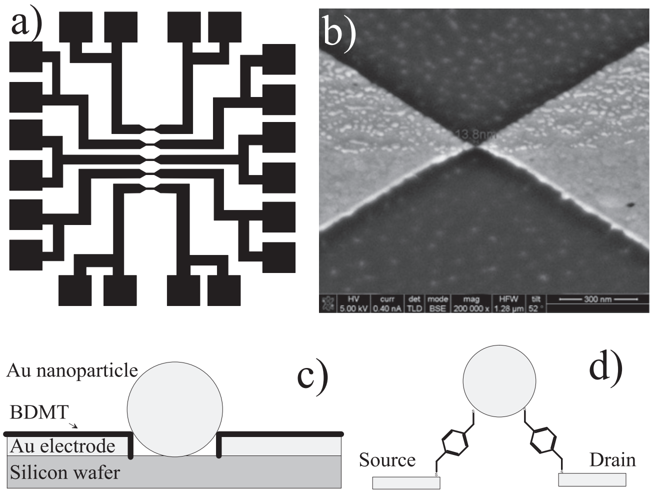

Fig. 1. (a) depicts the layout of the electrodes, (b) shows a SEM image of an electrode gap that measures 13 nm before functionalisation, (c) shows a schematic representation of the functionalised electrodes and the location of the nanoparticle, and (d) schematically depicts the path for the charge carrier to travel from source to drain; note that several BDMT molecules can be present parallel to each other.

layer) and lifting of the resist (with metal on top) in hot acetone. Subsequently, 200 nm thick gold electrode pads (for thickening the four feed and measurement-contact points) were deposited using this same lift-off technique. By means of a focussed-ion-beam (FIB) system (FEI Nova Nanolab200 with a Ga Liquid Metal Ion Source), gaps of varying dimensions ranging from 9 nm to 100 nm were fabricated in the electrode pattern; in the narrowest part of the electrode pattern (2 µm wide), two opposing triangles were etched out, resulting in an 'hour glass' shaped junction. The FIB parameters used were as follows: A 10 nm wide Gaussian beam at 30 kV and 9.7 pA was stepped in a serpentine raster scan at 6.5 nm pitch in x and y with a dwell time of 1 µs per spot. In this way, the triangles were exposed with 207 passes and a 40 ms loop time resulting in a total 8 s exposure time per triangle pair. In Fig. 1, the layout of the electrodes and an example of the electrode gap before functionalisation is presented in (a) and (b) respectively.

In order to study the electrical properties of the target molecule, a simple chemical way of self-assembling nanostructured material was employed. It has been previously shown that alternating layers of a dithiol and gold nanoparticles can be self-assembled on a gold substrate, to build up a three-dimensional film in a 'layer-by-layer' fashion [8–10]. A similar procedure was used here in order to build a two-dimensional network connecting the two electrodes, allowing the electrical properties of the target molecule to be studied.

The gold electrodes were functionalised by immersing the electrodes in a 5 mM solution of BDMT (Sigma–Aldrich, used as received) in ethanol for at least 16 h. This resulted in a full self-assembled-monolayer on the surface of the gold electrodes. The sample was subsequently washed with ethanol in order to remove any unbound BDMT and blown dry with nitrogen. After this step, the sample was immersed for 16 h in an aqueous solution of gold nanoparticles (BBInternational used as received) with an average diameter of 40 nm, subsequently washed with MilliQ-water to remove excess nanoparticles, and blown dry with nitrogen. The gold nanoparticles will bind to the unbound thiol of the BDMT. At every step, the I–V characteristics of the device were measured using a source measure unit (Keithley 236) in combination with a home developed Labview program. A schematic representation of the junction is shown in Fig. 1c.

3. Results and discussion

The gap region in the device has been etched in the 10 nm thick Au layer using 207 passes of a serpentine raster scan in the FIB system; given the thin Au layer etched and the multi-pass writing strategy employed, the influence of re-deposition within the gap region will be negligible. Re-deposition or contamination outside this region will have no influence on the resistance measurements performed in this 4-terminal device.

The original 10 nm thick Au layer showed some granularity, which may be related to the limited Au thickness deposited and the chemical nature of the materials underneath. After FIB etching, this topography is transposed to material underneath. Hence, the bright spots in the dark area of the SEM graphs may originate from this topography being transposed in the oxide underneath, or from some Cr residues. These spots are, however, even if they were metallic in nature, too isolated to contribute to conduction through [BDMT-nanoparticle-BDMT] junctions. In a new set of experiments, thicker Au layers are being employed and the roughness and bright spots seem to be lacking.

The characterisation of the [BDMT-nanoparticle-BDMT] junction was performed using the I–V characteristics. In Fig. 2 the average I–V-curve of approximately 40 experiments is shown, both before the nanoparticle was present (circles) and after (squares). It can be seen that before any modification of the electrodes takes place, they display an infinite resistance. Once the electrodes have been functionalised with the BDMT, the electrodes also display an infinite resistance, indicating that the BDMT molecules do not form an electrical connection between the two electrodes. However, when a nanoparticle is inserted in the gap, the resistance drops to (1.89 ± 0.01) MΩ. This can be explained by the formation of a conductive pathway via the BDMT monolayer and the nanoparticle as schematically depicted in Fig. 1d.

Surprisingly, these results are very similar to those obtained using the same technique, but with smaller nanoparticles, therefore needing several alternating layers of BDMT and nanoparticles [10]. Although there are obvious similarities in the experiments, there is still a significant difference in the fact that the nanoparticles used have massively different sizes, and in the number of BDMT molecules that are needed in order to bridge the electrode gap. In order to further interpret the result obtained, the best comparison is with experiments that studied the single molecule resistance of BDMT. In recent experiments it has been shown that the conduction of a single molecule displays several fundamentally

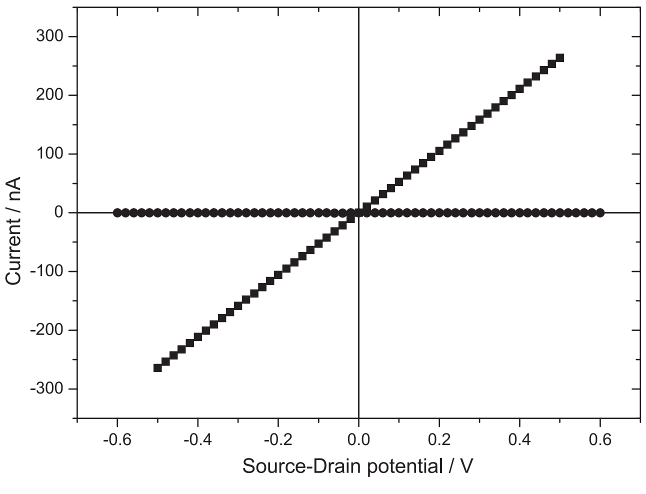

Fig. 2. I–V characteristic of a 'bare' electrode gap (circles) and bridged electrode gap (squares).

Table 1
Literature values of the single molecule resistance of BDMT, the number of BDMT molecules with this particular resistance needed to obtain the electrode resistance observed in this paper, and the area required to accommodate this number of BDMT molecules.

Molecular resistance/ MΩ	Reference	No. of molecules	Area required/ nm^2
150	[10]	167	37
66.7	[11]	74	16
21.7	[12]	24	5
3.2	[11]	4	1

different conduction groups, which are assumed to be associated with the way in which the thiol binding group attaches to the surface [5,6]. The different resistance groups that have thus far been observed for BDMT, are shown in Table 1, alongside with the number of BDMT molecules with this particular resistance needed to obtain the electrode resistance observed in this paper, and the area required to accommodate this number of BDMT molecules.

An alternative which might affect the resistance of the junction, as reported here, is a Coulomb blockading effect in the nanoparticle. This will, however, not be observed for the nanoparticles used here as they are too large to display such effects at room temperature. It is therefore reasonable to assume that the nanoparticle acts in these experiments as a conducting element that can accommodate as many charge carriers as required. The result of this is that the system as studied here can be interpreted as two decoupled resistors with the resistance of each determined by the number of BDMT molecules that connect the electrode to the gold. A final assumption is that the two electrodes are symmetric which means that the total resistance that is measured in the experiment is twice the resistance of a single electrode-nanoparticle connection.

Using the dimensions obtained from a SEM image of the actual electrode gap as used in this experiment, it is possible to estimate the area where a nanoparticle and BDMT molecules are able to connect the two electrodes. This is depicted in Fig. 3, where in black the electrodes are shown and in light grey the area where a nanoparticle can be in order to attach to an electrode. The dark gray area indicates the area in which a single nanoparticle can connect the two electrodes (centre Fig. 3b). These calculations have taken into account that the nanoparticle's radius is larger than the height of the electrodes resulting in a smaller 'contact area'. The example shown here is for a nanoparticle that has a diameter of 40 nm. It can be seen in Fig. 3b that the actual area where this size of nanoparticle will bridge the gap is relatively small (3.8 nm). The total area which can (for this particle) contribute to the conduction is therefore in the order of 4 nm^2.

The footprint of a single BDMT molecule is approximately 0.22 nm^2 [13]. This suggests that the maximum number of molecules that can contribute to the conduction is in the order of about 20. In order to create the observed resistance this requires the BDMT molecule to be in a low resistance state (as indicated in Table 1).

In order to be able to utilise molecules in an electronic network, eventually leading to a completely molecular network, it is essential that multiple resistance values are understood and prevented. The results shown here indicate that when a molecule is left to self assemble it is more likely to display one of the lower resistance groups although further experiments are required to ensure that the contact has a particular resistance.

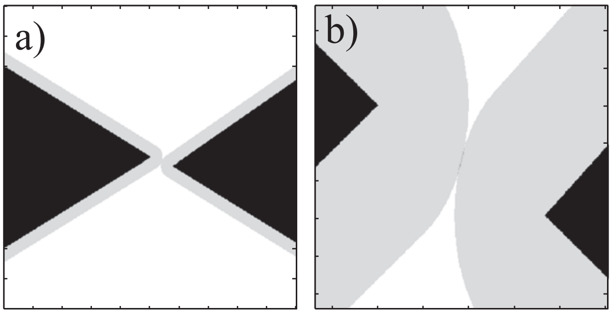

Fig. 3. (a) shows the location where the centre of a 40 nm nanoparticle has to be in order to contact an electrode, the dimensions are those as used in the current experiment. (b) shows a close-up of the electrode gap area. In light gray is indicated the location where a nanoparticle can connect to one electrode, in dark grey to two electrodes.

4. Conclusions

In conclusion we have succeeded in the fabrication of small gap electrodes. The gap between the two electrodes was shown to be successfully bridged with an ensemble of BDMT molecules and a single gold nanoparticle. Due to geometric reasons the amount of molecules estimated to bind the nanoparticle to the electrodes was found to be less than 20, this in sharp contrast to previous similar experiments where the results were explained using 200 parallel (conducting) channels bridging the two electrodes.

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