An electrostatic gate for mechanically controlled single-molecule junctions

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Abstract. We present a fabrication scheme for a tunable single-molecule transistor that allows for controlling the electrode separation and provides an electrostatic gate. The experimental approach is based on the mechanically controlled break junction technique but integrates an additional bottom gate electrode and an uninterrupted high-$\kappa$ gate dielectric. The device performance is demonstrated for a single-molecule junction showing Coulomb blockade characteristics.

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1. Introduction

For single-molecule junction experiments at low temperatures, there are typically two classes of device architectures. Firstly, there are two-terminal experiments, which reliably form stable metal–molecule–metal contacts [1–3]. Secondly, there are three-terminal experiments with a gate potential as a controllable parameter [4, 5], which suffer, however, from uncontrolled contact formation. Although three-terminal experiments with controlled contact formation are highly desirable, very few experiments have been reported in the literature. In [6], C60 has been introduced in a gated mechanically controlled break junction (MCBJ), which was built on an ultra-thin (200 µm) silicon substrate. A small gate effect was observed, which may originate from the desired electrostatic gating, but also from the undesired mechanical instability of the device. In [7] sandwich-type MCBJs have been reported using plasma-oxidized aluminum gates, which are mechanically stable but the nature of the island inside the source–drain electrode pair is fairly unclear. However, it became evident that the most problematic issue in single-molecule three-terminal devices is the screening of the gate potential by the source and drain electrodes, which often leads to vanishing gate efficiency [8]. As an intrinsic effect in single-molecule scale junctions, the reproducibility is limited since the metal–molecule–metal junction is very sensitive to atomic scale details. This is equally true in three-terminal devices. Note also that there is a further class of experiments in the electrochemical environment that have shown gating effects at room temperature [3, 9]. However, room temperature data and low-temperature data cannot be easily compared due to the predominant influence of vibrations [10, 11]. We focus here on experiments in vacuum and at low temperatures, which are more sensitive to the fundamental mechanisms of charge transport in nano-junctions.

Our approach is based on a device architecture similar to [7], which is made free-standing on phosphorus bronze substrates coated with polyimide (PI). Like the well-established two-terminal MCBJ devices, the samples allow for the creation of mechanically stable, atomically sharp electrode tips to immobilize single molecules. In contrast to [7], we employ a high-κ insulator in order to support improved gate coupling systematically.

2. Sample processing and the experimental method

The sample preparation includes many process steps that are necessary for the fabrication of conventional MCBJ devices (coating of wafers with PI, patterning of a resist mask by electron beam lithography, evaporation of contact metal, lift-off in acetone, and partial removal of PI by reactive ion etching) [12]. In order to implement a gate electrode as well as a dielectric/oxide, additional fabrication steps are necessary, which require in particular exact alignment (a few nanometers) with respect to predefined markers. On the highly insulating PI substrate this is only possible when conducting (aluminum) sacrificial layers are introduced at any stage prior to e-beam patterning. We now describe the fabrication step by step: firstly, markers (5 nm Ti and 100 nm Au) are deposited on the substrates. Secondly, contact pads (3 nm Ti and 25 nm Au) for electrical access to the gate electrode are structured, followed by connecting the gate structure (45 nm Al) to the pads. The gate is patterned with a nearest constriction of 300 nm and aligned with respect to the markers. The next step comprises the patterning of a mask for the dielectric (10 nm Ta2O5) as well as a thin gold bridge (15 nm Au), which later serves as the source and the drain contact. The oxide is deposited under small variation of the evaporation angle in order to ensure good electrical insulation between the aluminum and the gold bridge. The next step
Figure 1. (a), (b) Scanning electron micrographs (colored for clarity) of the samples. A stacked structure of (i) an aluminum gate (blue), (ii) a high-$\kappa$ insulator ($\text{Ta}_2\text{O}_5$, white, nearly congruent with the gold layer) and (iii) a gold source and drain electrode pair (yellow) was built and finally underetched such that the bridge is entirely free-standing. The gold leads were reinforced by an additional gold layer (orange) to ensure electrical continuity over the stepped profile. (c) Schematic representation of the three-point bending mechanism employed in MCBJ experiments. (d) Leakage current at room temperature for a device with 10 nm $\text{Ta}_2\text{O}_5$ as the gate dielectric.

includes the patterning of large-area leads and contact pads (3 nm Ti and 130 nm Au) for a sufficient electrical connection to the gold bridge. In the last step, the total structure is made free-standing by reactive ion etching (96% $\text{O}_2$ and 4% $\text{SF}_6$). Scanning electron micrographs (colored for clarity) of the resulting samples are shown in figures 1(a) and (b). The highly precise alignment allows for an overlap of the gate and the source–drain bridge which is as small as 1 $\mu$m$^2$, leading to a significant reduction of leakage current paths through the oxide. For further characterization, the samples are mounted on a three-point bending mechanism and contacted electrically (see figure 1(c)).

3. Device characterization

We tested three different oxides as the gate dielectric: plasma-enhanced $\text{AlO}_x$ (4 nm), $\text{SiO}_2$ (10 nm) and $\text{Ta}_2\text{O}_5$ (10 nm). The latter turned out to be an excellent choice as it allows for gate
Figure 2. (a) Conductance trace and (b) SEM micrograph for the breaking of the electrode pair by mechanical bending at which the entire gate stack breaks. Nevertheless, opening and closing the contact is repeatedly possible and leads to conductance quantization (see the inset in (a), showing three subsequent opening curves). With some statistical and systematic uncertainties, 1500 motor steps translate to 1 Å variation of electrode spacing [14].

voltages up to ±5 V at room temperature (leakage current well below ±1 pA, see figure 1(d)). It has been verified by a large-area plate capacitor measurement that its dielectric permittivity $\kappa \approx 24–28$ is in agreement with [13].

In order to analyze the mechanical properties of the junction, we bend the substrate at $V_{SD} = V_G = 1$ mV in ultra-high vacuum at room temperature. The conductance $G$ of the gold bridge (in units of the conductance quantum $G_0$) as well as the leakage current $I_G$ are measured as a function of the bending, which is defined by the position of the driving linear motor. At this point, we were interested in knowing whether the source–drain gold bridge and the intimately connected gate bridge break simultaneously or successively. It turns out that an abrupt breaking of the gold bridge is observed in the conductance measurements upon bending, which is always accompanied by an irreversible breaking of the gate bridge, as seen in subsequent electron microscopy (see figure 2). This behavior is different from the findings in [7], where it was pointed out that gold might slide on plasma-enhanced aluminum oxides AlO$_x$, preventing the breaking of the gate. Interestingly, even the broken bridge could be opened and closed several hundred times mechanically (see the inset of figure 2(a)). At this point, we added molecules from solution following the usual procedure [2]. The resulting junctions are characterized at low temperatures and show current–voltage ($I$–$V$) characteristics that are very similar to previous two-terminal measurements. When applying gate voltages up to ±5 V, no effect on the $I$–$V$ characteristics is resolved. This becomes clear when considering the sketch in figure 2(b). The electric field in between the gate and the molecule goes through regions with $\kappa = 1$ (vacuum), instead of the more efficient high-κ dielectric material. For improved gate performance, a breaking of the dielectric layer should be prevented.

For this purpose, we reconsidered a different technique for the creation of a nanoscale gap in the gold layer, namely an initial electromigration step [15, 16]. We bend the substrate carefully but avoid the critical event of breaking the gate. Then the bending is stopped and
the source–drain voltage is ramped until an increase of resistance is observed. Then we reduce the bias immediately to 1 mV. This procedure is typically called electromigration. Thereby, the high current density results in a thermally assisted migration of gold atoms in the nearest constriction so that a successive reduction of the width of the bridge is obtained. Most frequently, the junction is left with resistances of a few k\(\Omega\). Up to this point we have a fabrication yield close to 100% for the overall process, applying strict criteria to the leakage current (<10 pA at \(V_G = \pm 5\) V). Next, we choose a strategy which has been successfully applied to aluminum oxide and predominantly led to small gaps [17]: when leaving the contact at low bias and at room temperature for minutes or even hours, the conductance drops to zero (self-breaking, see figure 3(b)). Microscopically, it is assumed that the thermally activated motion of gold atoms leads to a retraction of the electrode tips such that a small gap is created. Another advantage of this approach is that the probability for undesired formation of gold clusters within the gap is reduced significantly [18–20]. Note the appearance of the plateau at \(1G_0\), indicating a single-atom gold contact before the gap opens up (see the dashed red line in figure 3(b)). We now have disconnected source and drain electrodes, which reside on an intact gate stack. Surprisingly, upon variation of the bending, the contact can be opened and closed purely mechanically several hundred times (see blue and green curves in figure 3(a)) again without breaking the gate stack, for about 50% of the devices. Now, the electrode pair behaves very similarly to two-terminal devices: we observe conductance quantization at room temperature and conductance histograms with a pronounced peak at \(1G_0\) (see the inset of figure 3(c)). We verified by electrical measurements that the gate bridge remains electrically conducting, and the gate stack remains well insulating. A subsequent SEM imaging showed that the overall bridge is intact; only the gold wire on top has been converted into an electrode pair with a barely resolvable gap (see figure 3(d)). Now we have the prerequisite for a stable, electrically and mechanically tunable single-molecule transistor.

4. A tunable single-molecule transistor

As a first system, we use the pyridine-endcapped molecular wire [11, 21] (Py–(C≡C)₄–Py; Py = 4-pyridyl, see figure 4(a)). The molecules are applied from a dilute solution (concentration \(c \approx 5 \times 10^{-4}\) mol l\(^{-1}\)) onto a junction, as prepared according to the last paragraph. Upon closing the contact again, a single molecule can bridge the gap between the source and the drain. Contact formation is indicated by highly nonlinear \(I–V\) characteristics at low temperatures \(T\). Measured stability diagrams \((V_G–V_{SD}–dI_{SD}/dV_{SD}\) plot\) at \(T = 100\) K are shown in figures 4(c) and (d). Regions of vanishing differential conductance (colored in purple) determine the non-resonant tunneling regime where charge transport is strongly suppressed. The edges of these regions mark the onset of current. They resemble a smaller section of a Coulomb diamond. At the edges, the chemical potentials \(\mu_S\) or \(\mu_D\) of the source and drain electrodes are in resonance with an electronic level, respectively. Although a degeneracy point of a Coulomb diamond is almost reached for \(V_G = -3\) V, a full Coulomb diamond is not accessible. Unfortunately, for this particular device, we have not recorded data beyond \(\pm 3\) V. Nevertheless, the measurement allows for an extraction of the capacitance ratios of \(S\), \(D\) and \(G\), but not for an absolute evaluation. A linear fit to the edges of the Coulomb diamonds determines the positive slope \(\beta = C_G/(C_G + C_D) \approx C_G/C_D\) and the negative slope \(\gamma = C_G/C_S\) for \(R_i \gg 1/G_0\) \((i = S, D\), see figure 4(b)). Correspondingly, we find that \(C_D/C_G \approx 63\) and \(C_S/C_G \approx 50\). Moreover, the slopes
allow for an evaluation of the gate coupling \([22]\)

\[
\alpha = \left(\frac{1}{\beta} + \frac{1}{\gamma}\right)^{-1} = \frac{C_G}{C_G + C_S + C_D} \approx \frac{C_G}{C_S + C_D} \approx 8.9 \times 10^{-3}.
\]

Upon increasing the distance of the electrodes by 9000 motor steps \((\Delta d \approx 5 \text{ Å})\), the width of the blockade is enlarged and the differential conductance is reduced (see figure 4(d)). Hence, distance variations change the slopes since \(C_S\) and \(C_D\) are altered, resulting in \(C'_S\) and \(C'_D\).
In the measurement we find that $\beta' < \beta$ and $\gamma' > \gamma$ ($C_D'/C_G' \approx 83$, $C_S'/C_G' \approx 36$, $\alpha' \approx 8.4 \times 10^{-3} \approx \alpha$). Here, we contacted well-defined molecules, whereas Martin et al measured an unspecified island. Not unexpectedly, the very similar geometries of both experiments led to very similar ratios of the capacitances [7].

Combining both the ability to shift the electronic levels with respect to the Fermi energy and the ability to vary the distance of the electrodes, one may qualitatively investigate the underlying coupling scenarios. Assuming that the position of the molecule is maintained within the contact, we consider the simplification $C_G' \approx C_G$. In this case, the increase of the electrode spacing results in an increase of $C_D$ and simultaneously a decrease of $C_S$. Hence the stretching does not act on both sides symmetrically but creates asymmetric contacts. Asymmetric contacts with symmetric molecules have been discussed before based on asymmetric $I-V$ characteristics [2]. Here, the analysis of the capacitive asymmetries gives additional information on this rather subtle effect.

By means of the gate coupling $\alpha$ and the typically accessible range in gate voltage $\Delta V_G = \pm 5 V$, we further give an estimation for the attainable shift of the electronic levels $\Delta \mu(|\Delta V_G|)$ with respect to the Fermi energy of the leads. Accordingly, the conceptualized device geometry allows for a shift which is as large as

$$\Delta \mu(|\Delta V_G|) = \pm \alpha e |\Delta V_G| \approx \pm 45 \text{ meV}.$$ 

This value underscores the potential of the devices for a characterization of spectral details like vibronic excitations but not for a scan through the whole electronic spectrum, which would require spectral shifts in the eV range. It should be stressed, however, that the gate does not act homogeneously on the molecule, in contrast to mesoscopic semiconductor quantum dots. Due
to the screening of the metallic source–drain electrodes, the electric gate field is strongest in the middle of the molecule and weak at the utmost ends [8]. This leads to charge reconfiguration inside the molecular wire when a gate field is changed. Due to the discrete nature of the molecule’s energy spectrum, a non-trivial response to changing the gate field is expected. As a consequence, the inverse problem, a clear assignment of features in the stability diagrams to microscopic details, is particularly difficult in single-molecule contacts due to the complicated electric field distribution on the nanoscale.

5. Conclusion

We have successfully implemented a bottom gate electrode and a high-κ insulator as the gate dielectric into conventional MCBJs. Due to a stacked architecture, rigid source–gate and drain–gate distances could be combined with a tunable source–drain distance that can be controlled mechanically in operando. The resulting three-terminal devices allow for the reliable formation of metal–molecule–metal junctions at low temperatures, and electrostatic gating. The performance of the devices has been demonstrated on a pyridine-endcapped molecular wire which exhibits Coulomb-blockade-like characteristics and allows for the extraction of the capacitance ratios as well as the gate coupling. This significant methodical improvement combines the advantages of two-terminal single-molecule junctions with mechanical control and three-terminal devices with electrostatic control.

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References

[1] Reed M A, Zhou C, Muller C J, Burgoin T P and Tour J M 1997 Science 278 252–4
[2] Reichert J, Ochs R, Beckmann D, Weber H B, Mayor M and Löhneysen H v 2002 Phys. Rev. Lett. 88 176804
[3] Tao N J 2006 Nature Nanotechnol. 1 173–81
[4] Osorio E A, Bjørnholm T, Lehn J-M, Ruben M and van der Zant H S J 2008 J. Phys.: Condens. Matter 20 374121
[5] Selzer Y and Allara D L 2006 Annu. Rev. Phys. Chem. 57 593–623
[6] Champagne A R, Pasupathy A N and Ralph D C 2005 Nano Lett. 5 305–8
[7] Martin C A, van Ruitenbeek J M and van der Zant H S J 2010 Nanotechnology 21 265201
[8] Datta S S, Strachan D R and Charlie Johnson A T 2009 Phys. Rev. B 79 205404
[9] Li C, Mishchenko A, Li Z, Pobelov I, Wandlowski Th, Li X Q, Würtzner F, Bagrets A and Evers F 2008 J. Phys.: Condens. Matter 20 374122
[10] Reichert J, Weber H B, Mayor M and Löhneysen H v 2003 Appl. Phys. Lett. 82 4137
[11] Ballmann S, Härtle R, Coto P B, Elbing M, Mayor M, Bryce M R, Thoss M and Weber H B 2012 Phys. Rev. Lett. 109 056801
[12] Martin C A, Ding D, van der Zant H S J and van Ruitenbeek J M 2008 New J. Phys. 10 065008
[13] Murarka S P, Eizenberg M and Sinha A K 2003 Interlayer Dielectrics for Semiconductor Technologies (New York: Academic)
[14] van Ruitenbeek J, Scheer E and Weber H B 2005 *Introducing Molecular Electronics (Lecture Notes in Physics* vol 680) ed G Cuniberti, K Richter and G Fagas (Berlin: Springer) pp 253–74
[15] van der Zant H S J, Osorio E A, Poot M and O’Neill K 2006 *Phys. Status Solidi b* 243 3408–12
[16] Ward D R, Scott G D, Keane Z K, Halas N J and Natelson D 2008 *J. Phys.: Condens. Matter* 20 374118
[17] van der Zant H S J et al 2006 *Faraday Discuss.* 131 347–56
[18] Tsutsui M, Shoji K, Taniguchi M and Kawai T 2008 *Nano Lett.* 8 345–9
[19] Tsutsui M, Ohshiro T, Matsubara K, Furuhashi M, Taniguchi M and Kawai T 2010 *J. Appl. Phys.* 108 064312
[20] O’Neill K, Osorio E A and van der Zant H S J 2007 *Appl. Phys. Lett.* 90 133109
[21] Wang C, Batsanov A S, Bryce M R, Martin S, Nichols R J, Higgins S J, García-Suárez V M and Lambert C J 2009 *J. Am. Chem. Soc.* 131 15647–54
[22] Thijssen J M and van der Zant H S J 2008 *Phys. Status Solidi b* 245 1455–70