Instruction for the Experiment Mechanically Controllable Break Junctions

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1. Introduction

The intention of this experiment is to investigate the charge transfer characteristic of metal/molecule/metal junctions. Recently, charge transfer investigations became feasible even on the level of individual molecules by the realization of a variety of nanoelectrode configurations where the electrodes are separated by a gap of molecular dimensions. Mechanically controllable break junction setups with tunable distance between the nanoelectrodes give control over the number of molecules electrically connected in the junction.

This experiment has three main goals:

1. Determine the value of quantum conductance G_0

2. Determine the single molecular conductance.

3. Determine the I-V characteristics of the single molecule junction.

2. Principle of the Mechanically Controllable Break Junction

In the scope of this experiment two different samples will be investigated. The first sample will be prepared by the students and mainly consists of a thin gold wire, which will be glued onto the substrate. The second sample will be provided by PGI-8 scientists, and consists of a nanowire fabricated by ebeam lithography. Both, macro- and nanowire possess a freely suspended constriction, made by cutting and lithography, respectively. In the MCBJ set-up, the as prepared chip is mounted into a home made three-point bending apparatus, see **Figure 1**.

The two outer posts of the three-point bending apparatus are fixed while the third one works as push rod in Z direction. When the push rod exerts a bending force on the substrate, the movement in Z direction will cause an elongation of the constriction until the bridge breaks, resulting in two separated nanoelectrodes, see **Figure 2**. Flexible spring steel substrates are used for the fabrication of the MCBJ chips to facilitate the bending of the substrate.

The distance between the electrodes for both the opened and the closed directions is controlled by bending or relaxing the substrate, respectively. An attenuation factor of the employed setup is $a = \Delta x / \Delta z \approx 6ut / L^2$ of $5*10^{-6}$ where Δx is the gap distance change, and Δz is the push rod displacement, which implies that we are, in principle able to control the distance between the electrodes with sub Angstrom accuracy. a is the attenuation factor; u is the length of the suspend bridge; t is the thick of the steel substrate; L is the length between the two out support point.

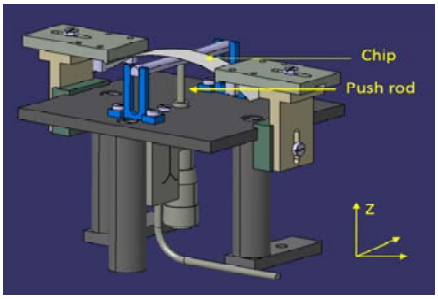

Figure 1. The set up of MCBJ

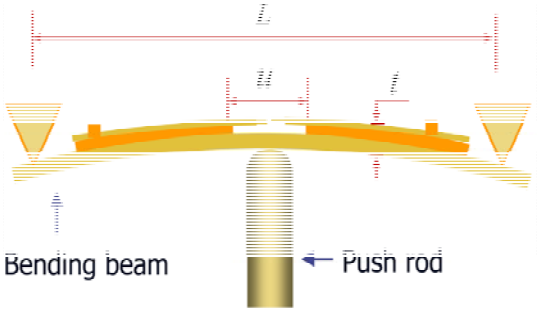

Figure 2. Principle of the MCBJ

3. Experiment

3.1 Prearrangements

Before the electrical measurement can be performed, you should get familiar to three basic techniques:

1) Fabrication of a model break junction containing a macrowire: for this purpose you will prepare a constriction in a gold wire and fix the gold wire on a string steel substrate, see Figure 3. The wire will be connected to the electrical interface via probe needles of a probe station PM5 Süss, See Figure 4.

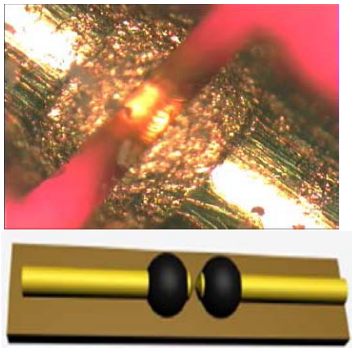

Figure 3. Prepare a sample by mechanical cutting

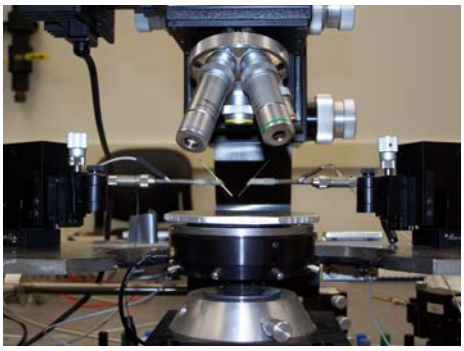

Figure 4.Probe station

2) You have to get familiar to the software of the Keithley Multichannel Parameter Analyzer. This device is operated as voltage source and measures the current of the break junction as function of time and bias voltage. You will get an instruction and record IV responses of model devices.

Figure 5. Soft ware interface and the hard ware of Keithley for electric measurement. From above to bottom is Keithley interface test environment, Keithley 595 Quasistatic CV meter, Keithley 590 CV analyzer respectively.

3) You will learn how to operate the piezo actuator, see figure 6 and figure 7. The piezo actuator PIE-755 is responsible for the movement of the push rod in z direction and is controlled via a

computer interface. You can set defined starting and end positions for the movement of the push rod. Furthermore, the moving velocity can be adjusted.

Figure 6. Piezo actuator PI E-755

Figure7. Interface of PI Mikromove for PIE-755

3.2 Observe the quantized conductance

At the beginning of the experiments you will bend a gold wire (macroscopic or nanoscopic wire) and thus elongate the suspended constriction until it breaks. During the breaking process, two nanoelectrodes are formed which are bridged by only few gold atoms right before the final breaking occurs, Figure 8. At this point, corresponding conductance values of one or multiples of $G_0 (G_0 = 2e^2 / h)$ can be obtained due to quantization of the electron transport through the junction. After breaking the junction, the electron transport is controlled by tunneling processes. The distance between the electrodes for both opening and closing directions can be controlled by bending or relaxing the substrate, respectively. The gap between the electrodes can be adjusted with Ångstrom accuracy.

Your task will be to break and close repeatedly a gold wire junction and to record several tens of breaking curves. From these individual breaking traces you should calculate a conductance histogram and determine the value of G_0 for a defined bias.

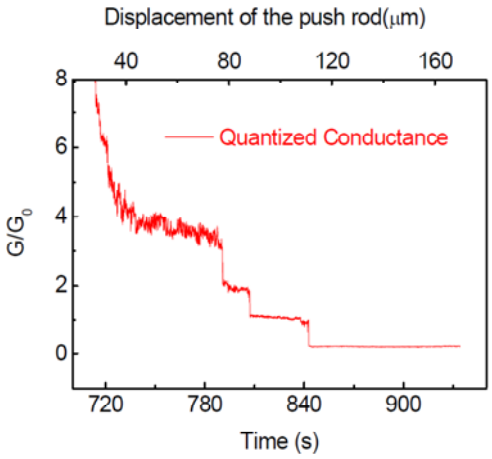

Figure 8. Single breaking curve showing quantized conductance of gold.

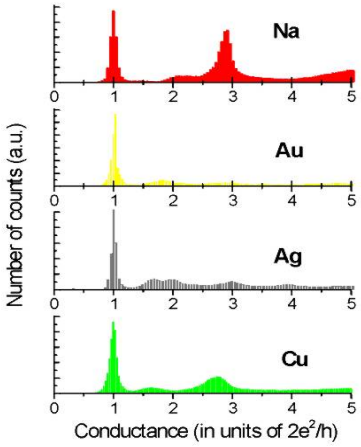

Figure 9. Conductance histogram of different metals.

3.3 Measure the single molecular conductance

After determining G_0, target molecules will be applied to the nanoelectrodes by a solution phase self assembly process to generate a metal/molecules/metal junction. For this purpose, 1 mM ethanolic solution of a model molecule (for instance 1,8-octanedithiol ODT), which contains two thiol termini as binding groups, will be prepared. A droplet of this solution will be placed on the junction area. After a self-assembly period of at least 30 minutes, the sample will be thoroughly rinsed with ethanol and dried in a nitrogen stream.

Then the chip will be mounted to the probe station and electrically connected to the Keithley parameter analyzer. Afterwards, a bending force will be exerted also on this substrate by the push rod. The whole breaking process of the junction can be monitored by the conductance measurement of the junction, see for example Figure 8 and 9. Due to the ability of the molecule to form covalent bonds to the gold electrodes, a metal-molecule-metal junction will form automatically after the constriction breaks. The two tips will be bridged by only few molecules since the two tips are atomically sharp. Further elongation of the junction will consecutively result in a rupture of all molecule-electrode bonds until a single molecule junction remains, see Figure 10 and 11.

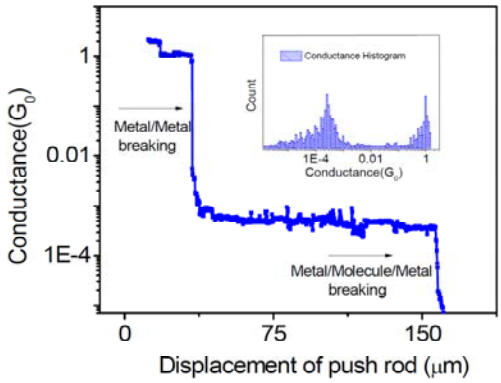

Figure 10. Conductance change in the break process

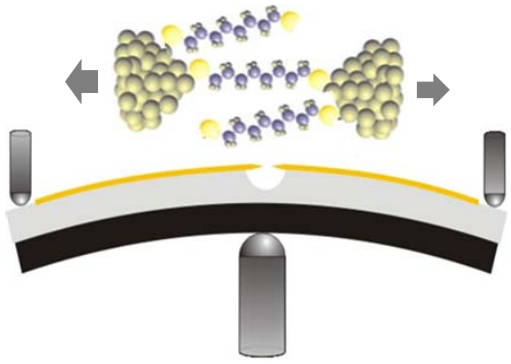

Figure 11. Metal/molecules/metal junction

The single molecule conductance can be determined from the last plateau. Nevertheless, your task will be to break and close repeatedly the metal-molecule-metal junction and to determine the single molecule conductance for a defined bias by generating and analyzing a conductance histogram. You will investigate one of the following three model molecules: octanedithiol $(CH_2)_8(SH)_2$, decanedithiol $(CH_2)_{10}(SH)_2$, dodecanedithiol $(CH_2)_{12}$ $(SH)_2$. You should try to estimate single molecule conductance of your molecule from the last plateau already during the experiment and compare this value with the conductance that you have determined from the conductance histogram.

3.4 Measure I-V curves of single molecular junction

The single molecule conductance that you have determined from the last plateau can be used as benchmark to establish a single molecule junction. Therefore, you should elongate a closed junction until you are close to conductance values of $1G_0$. At this point you should interrupt the bending process and wait unit a stable conductance has established. Afterwards you continue the breaking process stepwise until you observe the value of the single molecule conductance you have determined before. After you have established a single molecule junction, you will start recording I-V curves. Therefore you should start at zero bias and increase the bias until you

reach maximum bias (V_{max}) values of 0.4V. Afterwards, V_{max} should be enlarged to max. 1.1V. Please record at least 5 I-V curves for each V_{max} value. After the I-V response was recorded, you should try to further reduced the gap size in 0.2 nm / steps (according to the attenuation factor, this corresponds to a displacement of the push rod by 40 μm / step) and measure the I-V characteristic again. By doing so, you will be able to investigate the influence of gap size on the I-V characteristic and correspondingly on the tunneling mechanism. To reveal the underlying tunnel mechanism, you should convert the data from I-V to $\ln(I/V^2)$ versus $1/V$ presentation and determine the transition voltage.

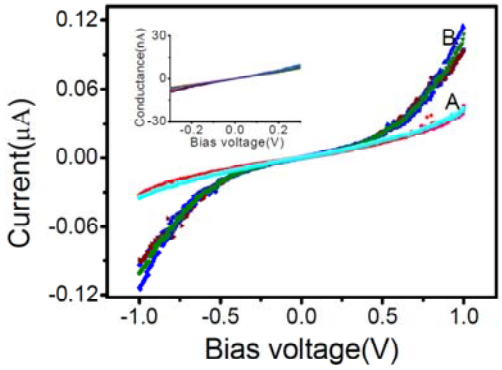

Figure 12. I-V curves of the single molecule junction with two different gap sizes. Curves A and B were recorded at different gap sizes. The inset shows the linearly regime of curves A and B within ± 0.3 V, which indicates that both sets of curves correspond to a single molecule junction.

Reference

[1] M. A. Reed, C. Zhou, C .J. Muller, T. P. Burgin, J. M. Tour, *Science*. **1997**, 278, 252.

[2] L.Grüter, M.T.Gonz ález, R.Huber, M.Calame, C.Schönenberger, *Small*. **2005**, 1, 1067-1070.

Supplementary information

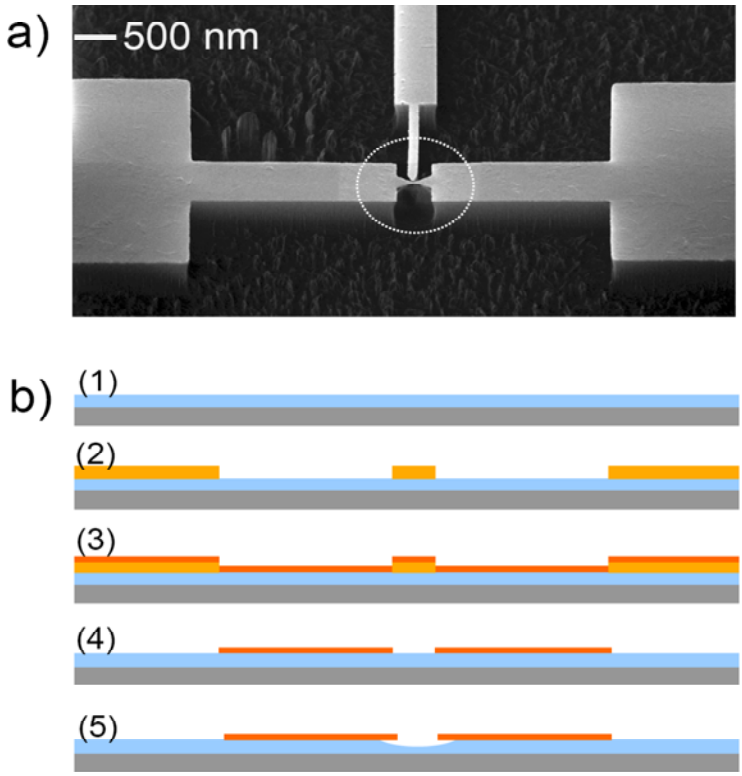

Figure S(a). Top view SEM picture of the chip. Figure S(b). Side view of the chips fabrication process which consists of five main steps 1-5. 1) A polyimide layer (HD-4100, HD Microsystem) about 3 μm thick, is spun on the string steel substrate. After baking it at 200^0C for 20 minutes the substrate was annealed for one hour at 300^0C and 10^{-3}mbar. The polyimide serves as an insulating layer between the gold electrodes and the steel substrate. 2) The E-beam lithography process consists of three sub-steps. First, 200 nm of a positive-tone resist (PMMA, Polymethylmetacylate 649.04 from ALLRESIST) was spin coated onto the substrate and baked at 180^0C for 2 minutes. Second, the electrode pattern was written into the resist by a electron beam lithography system (Leica Vistec EBPG-5000 plus). Finally, a standard development procedure is applied by inserting the substrate into development solution (ALLESIST AR 600-55) for about 50 seconds, then the substrate is transferred into isopropanol to stop the development. 3) After the development, 2 nm Ti and 40 nm Au are deposited on the substrate surface by electron beam evaporation. 4) After the metallization, the sample is immersed in acetone for lift off. 5) In the final step, the polyimide is isotropically dry etched to obtain a suspended metal bridge. This is done by Reactive Iron Etching (RIE) under the following conditions: 32 sccm of oxygen and 8 sccm of CHF_3 and a power of 100W.