Analysis of Break Junction Measurements with Single Organic Molecules using Advanced Statistical Methods

Ph.D. thesis booklet

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Introduction

During the last half-century, we have witnessed tremendous progress in the applications, the computational power, and the complexity of microelectronic devices. A series of scientific discoveries contributed to the exponential development of silicon-based technology, often referred to as Moore's law. In recent years, this growth is coming to an end, as the size of the building blocks for these devices is approaching to the technological and physical limits around 10 nm. Quantum mechanical effects already have to be considered during the design of today's state of the art devices, the continued advancement of micro- or possibly nanoelectronics, demands new technologies and scientific discoveries.

The idea for using single molecules as components in electronic circuits dates back to the 1950s. Although, even today, it is infeasible to build up entire circuits using this approach, molecular electronics is a good candidate for providing progress by complementing silicon-based technology. Besides the reduction in size, such devices could also be used for implementing new functionalities, like ultra-sensitive molecular sensors or computational memory elements.

Break junction experiments provide a testbed for studying electronic transport at the single-molecule level. When elongating a macroscopic sized wire, the conductance changes continuously. Once the narrowest cross-section of the wire is defined by only a handful of atoms, the junction conductance is affected by both the quantum nature of the conductance and the discrete atomic changes in the size of the contact's cross-section. Upon elongating a stable junction configuration, the contact is elastically deformed by stretching the bonds between the atoms. During this process, the junction conductance does not change significantly, therefore a plateau is observed in the measured conductance. After a certain elongation, the atoms rearrange into an energetically more favorable configuration, which results in a sharp drop in the junction conductance. Then this process is repeated until finally the wire is completely ruptured. The last observed conductance plateau corresponds to a junction, with a singe-atom in the narrowest cross-section. When such a junction breaks away, two atomically sharp apexes form, that can be used as electrodes for contacting single molecules. When this experiment is carried out in an environment with molecules that are capable of forming a chemical bond with the atoms of the electrodes, additional conductance plateaus can be observed after the rupture of the metallic contact. These plateaus correspond to a single molecule bridging the gap between two metallic electrodes.

It is often a challenging task to analyze and properly interpret these measurements, as it is not possible to directly inspect single-molecule junctions. Thus, the junction geometry and the molecular binding configuration has to be inferred from the measured physical quantities. During my Ph.D. work, I analyzed break junction measurements with single organic molecules to determine the junction structure, molecular binding configuration, and the various junction trajectories that are realized during the elongation and rupture of a metallic/molecular contact [1–5].

Research objectives

In order to investigate the current-voltage and noise characteristics of molecular junctions, the elongation has to be stopped and the junction needs to be held steadily once

a molecular contact is established. In the literature, there are two different approaches used for controlling the electrode displacement. The first one is to elongate the junction very slowly [10]. In this case, the measurement control program, running on a PC, is fast enough to stop the elongation when the set conductance level is reached with only minor overshoots. However, due to the long measurement times, fewer traces can be recorded this way, which leads to less reliable statistics. The other solution is to simply pause the elongation at a fixed displacement position [11–13]. In this case, there is no direct control over the conductance of the junction during the period, when the junction is held steady. However, when a large number of traces are recorded this way, there will be a portion where the elongation was paused at the correct position, with a molecule bridging the gap between the electrodes. These traces are then selected for the analysis, while the others are filtered out. My goal was to develop a measurement control program that enables us to perform large speed break junction measurements in a fully automated way, with precise control over the rupture process.

Aromatic molecules, forming π-stacked dimers in break junction measurements were first reported by Wu et al. [14] when investigating the conductance of molecular junctions formed by oligo-phenylene ethynylene (OPE) molecules. Other studies, involving conductance [15–19] and also force [20] measurements showed similar results for different compounds of OPE type molecules. Break junction measurements on these molecules indicate the formation of two distinct molecular junction configurations with approximately an order of magnitude difference in the measured junction conductance. The higher conductance junction can be associated with a monomer junction, where a single molecule bridges the gap between the two electrodes. It is assumed that the lower conductance configuration corresponds to a dimer junction where one molecule is bound to each electrode and the two molecules are coupled through a molecule-molecule interaction. Since it is not possible to directly inspect single-molecule junctions, it is difficult to provide definitive evidence for this assumption, based solely on conductance measurements. My goal was to investigate the formation and study the properties of dimer junctions formed by aromatic molecules with amine linkers, through measuring various physical quantities.

In break junction measurements, a metallic contact is repeatedly formed and ruptured, oftentimes thousands of opening and closing conductance versus displacement traces are recorded using the same metallic wire. This raises the question: to what extent are these subsequently measured conductance traces independent? During our experiments, we have found that under certain conditions both deterministic and stochastic behavior can be observed. For the characterization of junction structure and molecular binding configurations, ideally, the measured conductance traces should be independent and representative of the attainable junction geometries. On the other hand, one can take advantage of the fully reproducible motion of several atoms upon the investigation of atomic-scale memories [21, 22]. Furthermore, repeating traces suggest that some level of structural memory can be preserved, even after the rupture of the contact. Similar structural memory effects can also be observed in conductance traces that are not entirely deterministic: for example, the final part of an opening trace can determine the beginning of the subsequently measured closing trace. My goal was to investigate structural memory effects in metallic and single-molecule junctions utilizing correlation analysis methods.

Single-molecule break junction measurements deliver a huge number of conductance vs. electrode separation traces. A portion of the measured traces may not exhibit molecular

signatures, these are referred to as tunneling traces, or the target molecules may attach to the electrodes in different binding geometries thus the evolution and rupture of the single-molecule junction can also follow distinct trajectories. The unraveling of the various typical trace classes is a prerequisite to the proper physical interpretation of the data. Traditionally, this is achieved using custom feature filtering methods that rely on the definition of various quantities which are able to identify targeted motifs of the traces [23–34]. Then appropriate thresholds need to be determined for these features in order to properly classify each measured trace. The design of these different features and the proper tuning of the thresholds can be a difficult task, that requires physical intuition about the trace classes, present in the dataset. Furthermore, care has to be taken to avoid introducing selection bias, which could lead to wrong conclusions. Manual classification is not only against objective data handling but in many cases, we also lack the a priori knowledge for judgment. Therefore we seek computer algorithms to automatically find the relevant trace classes in our data. In recent years, machine learning methods were also applied for the analysis of break junction measurements, to recognize relevant trace classes and provide an unbiased selection, without the need for proper intuition about the characteristics of the different junction trajectories [35–40]. The methods applied in the literature are often based on complex algorithms that are capable of classifying the measured conductance traces. However, they do not provide information about the features that are used to distinguish between the different types of traces. My goal was to introduce an unsupervised method for the classification of conductance traces, which also enables us to get insight into the decision-making mechanism, to determine the key features that identify the various trace classes.

New scientific results

I summarize the results of my work in the following thesis points:

1. Measurement system developments

I developed measurement control programs to perform break junction and point contact spectroscopy measurements. Through the utilization of hardware triggers, these programs enable the controlled investigation of metallic and molecular junctions by opening and closing the junction until a preset conductance value is reached. During point contact spectroscopy measurements, this can be used to automatically prepare a junction with a predefined conductance to perform current-voltage measurements. In break junction measurements, closing the junction until the same conductance is especially important when investigating temporal correlations and structural memory effects in metallic and single-molecule junctions [1].

I developed an FPGA based measurement control program, which can be used to perform automated measurements with a wide variety of measurement schemes, defined by a sequence of commands [2]. These commands include custom conditions for stopping the elongation/compression of the junction. Then a customized voltage signal can be applied on the junction, or the electrode separation can be further adjusted using the piezo positioner. I demonstrated the application of this measurement control system by

performing automated I(V) measurements on gold–4,4' bipyridine–gold junctions, at low temperature.

2. Investigation of dimer molecular junctions

I investigated the formation of stacked dimers in break junction measurements with 4,4"-diamino-p-terphenyl, and 2,7-diaminofluorene molecules, and compared the electronic and mechanical characteristics of dimer and monomer junctions. I showed that the probability to form dimer junctions increases with increasing molecular concentration. A comparison of the conductance histograms for a series of molecules implies that the amine linkers play an important role in mechanically stabilizing the dimer junctions. I showed that the relation between the noise power and junction conductance can be used to distinguish between through-bond coupled monomer junctions and dimers with through-space intermolecular coupling. Then I performed noise measurements, confirming the hypothesis of dimer formation. I performed force measurements to demonstrate that a significantly smaller force is required to rupture dimer junctions, compared to monomer junctions. This result is consistent with a weak N–π interaction when compared with an Au-N donor-acceptor bond. Finally, I demonstrated, that for these dimer junctions, conductance and force decrease as the junction is elongated, which implies that the extent of the overlap between the two molecules dictates both the electronic and mechanical characteristics of dimers [3].

3. Temporal correlations in metallic junctions

I demonstrated that temporal histograms and shifted correlation plots can be utilized for visualizing and characterizing spontaneous or triggered temporal variations in break junction data, like the waving of conductance plateaus or the appearance of repeating traces as the contact is trained. I have shown, that any feature in the shifted correlation plot indicates statistically dependent conductance traces. The decay of these features, as the function of the shift number (s), characterizes the length of the temporal correlations. Using these techniques, I demonstrated that when atomic-sized gold contacts are ruptured at room temperature, the surface diffusion induced flattening of the electrodes helps to produce statistically independent conductance traces, whereas at low temperatures the rigid contacts are likely to show repeating traces and waving plateaus as long as the closing setpoint is not high enough. I showed that the closing setpoint, required to produce statistically independent conductance traces, can be determined using the opening/closing correlation analysis technique [1].

4. Structural memory effects in Au–4,4'-bipyridine–Au junctions

I analyzed gold–4,4' bipyridine–gold junctions measured at room temperature and at 4.2 K, using an MCBJ setup and an in-situ evaporation technique for the dosing of the molecules. I demonstrated, that at room temperature, almost all opening and closing conductance traces exhibit molecular plateaus after the successful dosing of molecules. Using the opening/closing cross-correlation, I showed that the junction trajectories, observed during the opening and subsequent closing of the junction, are mostly independent. This

result implies that after the rupture of the junction, the electrode structure flattens and the attached molecule relaxes on the surface, preventing contact memory effects. In contrast, at low temperature, a significant amount of tunneling traces are observed. Through using the combined classification method to recognize distinct junction trajectories, I demonstrated that the atomic chain formation, observed at cryogenic temperature, dictates the binding configuration of bipyridine molecule [5]. I further analyzed the conductance traces that exhibit molecular signatures during both the opening and the subsequent closing of the junction. The similarities and the correlations of the opening and closing junction trajectories imply, that after the rupture of the molecular junction, it is likely that the molecule stays protruding from one electrode, thus the same molecular junction can be reestablished upon closing the junction.

5. Unsupervised feature recognition in single-molecule break junction data

I used the classification task of tunneling versus molecular traces to compare the performance of different algorithms, using a manually labeled dataset. These include feature filtering algorithms based on the measured step length or linear regression, as well as neural networks with different architectures. I demonstrated, that a recurrent neural network employing LSTM units, capable of taking into account the temporal evolution of the conductance traces, or a simpler double-layer feed-forward network, using the one-dimensional single trace histograms as input, both perform well in this classification task [4, 5]. This also demonstrates, that due to the monotonic nature of the measured conductance traces, one-dimensional conductance histograms contain all the relevant information for this classification task. In comparison to the recurrent network, the simpler feed-forward layout provides a more robust solution, as the classification performance does not depend heavily on the network parameters. Furthermore, the simple layout enables us to investigate the decision making aspects of the network and determine the key features that identify the trace classes.

The training of these neural networks requires a set of labeled conductance traces. Manual classification is not only against objective data handling, but in many cases, we also lack the a priori knowledge for judgment, and therefore we seek computer algorithms to automatically find the relevant trace classes, which would help us to understand the various possible junction configurations. To this end, I have developed a combined method, which automatically generates training data according to the extreme values of the principal component projections, then the network captures the features of these characteristic traces and generalizes its inference to the entire dataset. The classification results obtained using this combined method are comparable to the results when using networks trained on manually labeled traces. Finally, I demonstrated that auxiliary measured quantities, like rupture force, can also be used for generating labels for the training of the neural network [5].

Publications related to the thesis points

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