Ph.D. THESIS booklet

Investigation of atomic and molecular nanojunctions beyond conductance histograms

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Introduction

Integrated circuits have undergone a tremendous miniaturization. To sustain the exponential growth of microelectronics governed by Moore's law already requires significant efforts, moreover miniaturization can not be continued for long with the current technologies. At these extremely small sizes, already quantum mechanical effects must be taken into account, and completely new effects, not seen in the macroworld arise. This completely different behavior of matter can be exploited, so new alternatives to the current technologies from spintronics to *molecular electronics* appeared.

The idea that a single atom or molecule can function as the active part of an electrical unit is more than 35 years old [Aviram74], however, experiments have only turned this vision into a promising alternative during the last decade. Several interesting results, such as the conductance switching of molecular junctions by light irradiation have been reported [vanderMolen09] and even single molecule transistors, where large currents can be switched by putting a single electron charge on a molecule have already been realized [Park02]. Although these results hold the promise for various future applications (from nanosensors to molecular memories), the reliability and reproducibility of these devices are not yet resolved. Therefore, the main goal of my PhD work was to develop reliable methods for contacting single molecules and construct proper characterization tools for these devices.

Investigation methods

Atomic and molecular junctions can be created by the Mechanical Controllable Break Junction (MCBJ) technique [Cuevas10, Agraït03]. The method relies on the controlled rupture of a metallic wire: during the rupture the wire gets thinner, and atomic-sized contacts can be created by stopping the process before the complete rupture of the wire. After the wire is broken the small distance between the electrodes enables the contacting of molecules.

The measurements were carried out at low temperature, which guarantees high stability of the system. Also, for metallic samples freshly broken at low temperature, the cleanness of contact surfaces can be guaranteed for a long time, and a big variety of materials, including strongly reactive metals can be applied as electrodes. After the breaking of the junction, the electrodes can be reconnected again thousands of times, thus a statistical analysis is possible.

However, at low temperatures the introduction of molecules to the junction is quite challenging, because most of the molecules freeze at 4 K. The setup used for dosing of the molecules was a main development of my PhD and is described in the Thesis in detail.

Goals

Our long term goal of building functional single-molecule electronic devices necessitates the development of reliable characterization techniques. Usually, single molecule devices cannot be observed directly due to their extremely small sizes, and all the information about the device is obtained from indirect electronic measurements. In many cases, even the most fundamental question, i.e. whether or not a single piece of a chosen molecule is contacted is difficult to answer, and obtaining more detailed information about the conformation of the molecular arrangement is almost impossible. Although, a wide of range of possibilities in the nanoscale chemical design of molecular structures is already available in the literature [Venkataraman06], the reproducibility and the stability of these devices are yet unsolved, critical issues.

The conduction properties of such contacts can be characterized by the so-called mesoscopic PIN-code, i.e. a set of transmission eigenvalues of the junction [Ihn10]. The transmission values can not be determined from simple conductance measurements, but by placing the junction between superconducting electrodes, and measuring the nonlinear sub-gap features in the current-voltage characteristic, principally all the transmission eigenvalues can be determined. One of my goals was to study several superconducting electrodes and their interaction with small molecules.

However, most measurements in the literature are conducted at room temperature, where the subgap method can not be used. (Also for conductance fluctuations or for vibration mode measurements the required energy resolution is not available). Mostly conductance histograms are measured, which display the conductance of frequently occurring atomic and molecular configurations [Cuevas10]. Still, as shown in this Thesis, one can go beyond conductance histograms and can study the correlation of these atomic configurations. The method can reveal details of contact formation hidden in the conductance histogram, and can identify correlating and anticorrelating configurations.

List of Publications

Publications related to the thesis points

[1] A. Halbritter, Sz. Csonka, P. Makk and Gy. Mihály: *Interaction of hydrogen with metallic nanojunctions*,
Journal of physics-conference series **61** 214-218. (2007).

[2] P. Makk, Sz. Csonka and A. Halbritter: *Effect of hydrogen molecules on the electronic transport through atomic-sized metallic junctions in the superconducting state*,
Physical Review B **78**, 045414 (2008).

[3] A. Halbritter, P. Makk, Sz. Csonka and G. Mihály: *Huge negative differential conductance in Au-H_2 molecular nanojunctions*,
Physical Review B **77**, 075402 (2008).

[4] A. Halbritter, P. Makk, Sz. Mackowiak, Sz. Csonka, M. Wawrzyniak and J. Martinek: *Regular Atomic Narrowing of Ni, Fe, and V Nanowires Resolved by Two-Dimensional Correlation Analysis*,
Physical Review Letters **105**, 266805 (2010).

[5] P. Makk, D. Visontai, L. Oroszlány, D.Zs. Manrique, Sz. Csonka, J. Cserti, C. Lambert and A. Halbritter: *Advanced simulation of conductance histograms validated through channel-sensitive experiments on indium nanojunctions*,
Accepted for publications in Physical Review Letters.

[6] P. Makk, J. Martinek, Z. Balogh, Sz. Csonka and A. Halbritter: *Correlation analyisis of atomic and molecular junctions*,
Manuscript in preparation.

Further Publications

[7] A. Geresdi, A. Gyenis, P. Makk, A. Halbritter and G. Mihály, *From stochastic single atomic switch to reproducible nanoscale memory device*,
Nanoscale **3**, 1504 (2011).

Summary

The major achievements of my PhD work are summarized in the following thesis points:

1. I have participated in the development of a measurement system capable of resolving the superconducting subgap features of atomic junctions. I have shown that the opening of conductance channels can be statistically traced as the conductance is changed, and that this evolution is different for different materials. I managed to verify a new methodology for the simulation of conductance histograms on indium nanojunctions by direct comparison of the experimentally measured and theoretically calculated channel evolutions and conductance histograms. With the help of the calculations I could identify the configurations formed during the rupture of an indium wire, and resolve the orbitals important for the conduction. The analysis has also pointed out that simulations on selected ideal geometries may show strong deviations from the experimental observations, therefore, a statistical analysis is desirable in theoretical simulations as well. [5]

2. I have investigated the interaction of hydrogen molecules with atomic-sized superconducting nanojunctions. I have demonstrated by conductance histogram measurements that the superconductors Nb, Ta, and Al show a strong interaction with hydrogen, whereas for Pb , Sn, In no significant interaction is detectable. I have applied the subgap method for Nb and Ta and determined the transmission eigenvalues of the nanojunctions in hydrogen environment. The analysis of data have shown that although the mechanical behavior of Nb and Ta nanojunctions is strongly modified in the presence of hydrogen molecules, as reflected by the pronounced changes in the histogram and by the appearance of extremely long conductance traces, the measured transmission eigenvalues are similar to those of pure junctions. The results imply that the interaction in Nb and Ta with hydrogen causes a plastic, ductile behavior and the formation of long nanoscale necks without well-defined single-molecule contacts being formed, and transport properties are still dominated by Nb and Ta. [1,2]

3. I have studied the excitations of hydrogen molecules contacted between platinum and gold electrodes. I found that differential conductance curves frequently exhibit peak-like structures instead of step-like vibration signals and even huge negative differential conductance phenomena can be observed. I have analyzed the results in terms of a two-level system (TLS) model, and showed that a simple TLS model cannot produce the peak-like structures, whereas an asymmetrically coupled TLS model gives perfect fit to the data.

The model implies that the excitation of a bound molecule to a large number of energetically similar loosely bound states is responsible for the peak-like structures. I have shown how recent experimental results in the literature can be explained with my model. [3]

4. I have participated in the development of a novel correlation analysis method applicable for atomic and molecular junctions. The method can detect correlating and anticorrelating configurations, and resolve features hidden in conductance histograms. I have constructed simulations for model traces demonstrating various features that can be resolved by the correlation diagrams. I have provided several experimental examples: I have resolved the presence and absence of adhesive instability for Ta junctions, and identified two ways of typical rupture for Al contacts. I have demonstrated the application of the correlation analysis supplemented with conditional 2D trace histogram method on Pt-CO molecular nanojunctions. This analysis resolved the incorporation of CO molecules in platinum atomic chains. [6]

5. I have studied the behavior of transition metal nanojunctions with the help of correlation analysis. The typical evolutions of conductance staircase could be resolved in Ni, Fe, V nanocontacts up to high conductance values. In have demonstrated a very well ordered atomic narrowing of the nanowire, indicating a very regular, stepwise decrease of the number of atoms in the minimal cross section of the junction, in contrast to the behavior of the majority of the metals. All these features are hidden in traditional conductance histograms. [4]

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