Ph.D. thesis booklet

Interaction of atomic junctions with carbon-monoxide molecules

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Introduction

In the last few decades the electronic equipements have undergone very fast developement and miniaturisation. The rate of this trend is well demonstrated with the so-called Moore's law, which describes the experience that the number of the transistors per one chip is doubled in every 18 months.

But nowadays it is clear, that the current fabrication techniques reach their size-limits. Thus if we want to continue the advanced miniaturization, we have to change the principle of the manufacturing technique of electronic devices. For this an opportunity is the so-called molecular electronics, which aims at electronic devices, in which the active region is constructed from a single or a few molecules. The main goal of this research field is the investigation of the transport phenomena at atomic or molecular scale. At this scale, the self-assembling processes of the materials are also very important, so their deatiled knowledge is also essential if we would like to make molecular scale elctronic devices. My Ph.D. work is related to this research field [1–5], and more deatiled introduction of this topic can be read in the book: *Molecular Electronics: An introduction to Theory and Experiment* [6]. The main advantage of the molecules is the very small size, but beside this we can make use of other properties, as well for example different organic molecules can be designed by chemical methods, and different side groups can be attached to them, so molecular switches, memories and sensors can be built [7–12].

Methods

In my research I have applied the so-called Mechanically Controllable Break Junction Technique (MCBJ) [13]. In this method an atomic-sized junction and afterwards a nanogap for the molecules is created during the controlled rupture of a wire. One of the main advantages of the MCBJ technique is that, it is appropriate for statistical investigation, because with the repeated opening and closing of the wire a lot of independent molecular junctions can be investigated.

In my Ph.D. work I have measured conductance traces of molecular junctions, which were created with the MCBJ technique. I have investigated the experimental data with various statistical methods, like conductance histograms [13], 2D correlational analysis [14], plateau length histograms and 2D conductance-electrode displacement histograms [12, 13, 15].

My measurements were carried out usually at low temperature (4.2 K), but I have also developed measurement systems, which can be used at room

temperature as well.

Goals

At the beginning of my research work our research group already had a low temperature (4.2 K) measurement system for the investigation of atomic junctions [16], but the molecular measurements were carried out only with hydrogen [17–20], because this molecule could be dosed easily due to the finite vapour pressure at 4.2 K. The investigation of other molecules requires a more complex measurement system, based on a well-controlled and reproducible dosing process. I have started my work with the developement of a new molecular dosing system based on a heated tube and an electromagnetic dosing valve. I have carried out test measurements with CO molecule, because this molecules was investigated by other groups at low temperature before [21–25].

However, in these works usually only the conductance histogram of the junctions were shown, which is actually just an *average*, so with this a lot of useful information is lost. This motivated me to introduce and apply different statistical methods, which are appropriate for the deatiled investigation of molecular junctions, and with which we can obtain information beyond the conductance histograms. Our research group has already developed a new method, the so-called correlational analysis technique [1, 14]. I joined this developement and I aimed at the introduction of new statistical methods and their application on molecular junctions. In my work I have combined former methods from the literature (conductance, plateau length and conductance-electrode displacement histograms [13, 15, 26]) and novel methods introduced by me (opening-closing correlational analysis, different selection techniques). Beyond my specific results on CO single molecule junctions it was my general goal to develop novel data analysis methods that could be applied in any single molecule conductance measurement.

With the molecular dosing system which was mentioned above we can dose other moleculers (like O_2, CO_2, etc.), and it can be used for smaller organic molecules (like benzene) as well [27, 28]. But for the investigation of more complex organic molecules we need new molecular measurement systems, based on other dosing processes. One of my goals was the developement of new measurement systems. At first I have built a measurement system with a liquid cell to make room temperature measurements and gain experience with the usage of organic molecules and the cleaning process. In addition, because the low temperature measurements were always in the focus of our research group [29–34], and in this temperature regime a lot

of further measurement methods can be applied, it was my further goal to build another measurment system, which could be used for low temperature conductance measurment on single organic molecules.

New scientific results

The main results of my work are summarized in the following thesis points:

1. Investigation of individual molecules with atomic-sized metal junctions

I have developed a new measurement system which is appropriate for dosing the molecules through a heated tube to the low temprerature atomic junctions. For the well-controlled and reprodulcible dosing I have built a vacuum-system which is based on an electromagnetic valve, and I have installed a sorption pump and a electromagnetic shutter in the low temperature head of the sample-holder. I have standardized the preparation of the measurements and the dosing of the molecules. I have applied the new setup in Pt-CO-Pt, Ag-CO-Ag and Au-CO-Au molecular measurements, and recorded the conductance histograms of these single-molecule junctions [1–5].

Furthermore I have built a new sample holder with a liquid cell, and another one which is based on the so-called in-situ dosing. These setups are appropriate for the investigation of organic molecules. For these measurements I have developed the cleaning and measurment protocol and I have carried out conductance histogram measurements on 4,4'-bipyridine single-molecule junction [5]. In addition I have shown that the in-situ dosing method can be used for the investigation of organic molecules at low temperature.

2. Interaction of carbon-monoxide molecules with platinum nanojunctions

I have investigated Pt-CO-Pt molecular junctions at low temperature, and determined the different molecular configurations during the breaking of the wire, and the post-rupture evolution [1, 2, 5].

I have applied the final-configuration analysis and identified the breaking proceses with different final-configurations, and I have also determined the ratio of the different breaking scenarios. I have investigated the typical length of the configurations with the help of the plateau length histograms of the selected traces. I have observed the binding of CO molecule to the Pt

electrodes, and its turning from perpendicular to parallel orientation. These results agreed with the simulations, and verified that the peak with higher conductance ($1.1\,G_0$) corresponds to the perpendicular, the peak with lower conductance ($0.5\,G_0$) corresponds the parallel molecular configuration [2].

I have investigated the post-rupture evolution of the junction with opening-closing correlation analysis and conditional histograms. I have shown that in case of short plateaus (witout atomic chains) a strong memory effect can be observed, which means that similar configurations are formed during the closing as during the opening. However, in case of chain formation this effect dissapears because of the random relaxation of the chain atoms after the rupture [5].

3. Investigation of the precursor configuraton and post-rupture evolution of Ag-CO-Ag molecular junctions

I have investigated the opening and closing process of silver–carbon-monoxide molecular junctions at low temperature, and compared the results to density functional theory simulations [3].

In the Ag-CO-Ag measurements a new peak appeared in the conductance histogram, but the final configuration histogram technique showed that this is rather the result of two neighbouring subpeaks, which cannot be resolved with the regular conductance histogram. I have applied the correlational analysis and investigated the relation of different conductance regions. Clear anti-correlation between the molecular peak and the Ag single-atomic region, and positive correlation between the molecular region and the region above the single atomic peak were observed. It means that the shift of the single-atomic plateau from $1\,G_0$ to $1.3\,G_0$ forecasts the formation of molecular junctions, so I have named this region as a precursor configuration. In addition I have applied the opening-closing correlation analysis, and demonstrated that the CO molecule stays in the junction after the rupture.

These results were compared to theoretical simulations, which verified the above observations. Both the precursor configuration and the two molecular configurations (perpendicular and parallel molecular oriantations) were observed in the simulations, and similarly the molecule stayed in the junction after the rupture.

4. Alternative configurations of carbon-monoxide in gold break junction measurement

I have investigated the breaking of gold nanojunctions in the presence of CO molecules at low temperature [4].

In the Au-CO-Au molecular measurement two molecular configurations were observed, and the investigation of the breaking lengths has shown, that atomic chains can be formed throught both configurations. I have investigated the correlations between the different conductance regions, and observed that the two molecular configurations exclude each other. This means that the behaviour of the Au-CO-Au junctions is completly different from the behaviour of Pt-CO-Pt junctions, where the two molecular configurations correspond to the different stages of the same atomic chain formation process: the molecule turns form perpendicular to parallel orientation. Contrarily, in case of Au-CO-Au, the two chain formation processes are completly different and exclude eachother. According the simulations one chain formation process was interpreted as a perpendicular CO molecule inside a gold chain, whereas in the other case the molecule binds to the side of a chain atom in the so-called atop configuration.

I have applied the opening-closing correlation technique for the Au-CO-Au junctions, and determined similar behaviour to the Pt-CO-Pt junctions: in case of short plateaus (without atomic chain) the memory effect was observed, but in case of chain formation the opening-closing correlation dissapeared.

Publications related to the thesis points

[1] P. Makk, D. Tomaszewski, J. Martinek, Z. Balogh, S. Csonka, M. Wawrzyniak, M. Frei, L. Venkataraman, and A. Halbritter, *Correlation Analysis of Atomic and Single-Molecule Junction Conductance;* ACS Nano, **6**, 3411–3423 (2012)

[2] P. Makk, Z. Balogh, S. Csonka, and A. Halbritter, *Pulling platinum atomic chains by carbon monoxide molecules;* Nanoscale, **4**, 4739–4745 (2012)

[3] Z. Balogh, D. Visontai, P. Makk, K. Gillemot, L. Oroszlany, L. Posa, C. Lambert, and A. Halbritter, *Precursor configurations and post-rupture evolution of Ag-CO-Ag single-molecule junctions;* Nanoscale, **6**, 14784–14791 (2014)

[4] Z. Balogh, P. Makk, and A. Halbritter, *Alternative types of molecule-decorated atomic chains in Au–CO–Au single-molecule junctions;* Beilstein Journal of Nanotechnology, **6**, 1369–1376 (2015)

[5] A. Magyarkuti, K. P. Lauritzen, Z. Balogh, A. Nyáry, G. Mészáros, P. Makk, G. C. Solomon, and A. Halbritter, *Temporal correlations and structural memory effects in break junction measurements;* The Journal of Chemical Physics, **146**, 092319 (2017)

References

[6] J. C. Cuevas and E. Scheer. *Molecular Electronics: An introduction to Theory and Experiment*. Ed. by M. Reed. Singapore: World Scientific, 2010.

[7] H. Park, J. Park, A. K. L. Kim, and P. L. M. E. H. Anderson A. P. Alivisatos, *Nanomechanical oscillations in a single C_{60} transistor;* Nature, **407**, 57 (2000)

[8] J. Park et al., *Coulomb blockade and the Kondo effect in single-atom transistors;* Nature, **417**, 722–725 (2002)

[9] S. J. van der Molen and P. Liljeroth, *Charge transport through molecular switches;* Journal of Physics: Condensed Matter, **22**, 133001 (2010)

[10] S. J. van der Molen, J. Liao, T. Kudernac, J. S. Agustsson, L. Bernard, M. Calame, B. J. van Wees, B. L. Feringa, and C. Schonenberger, *Light-Controlled Conductance Switching of Ordered Metala-Molecule-Metal Devices;* Nano Letters, **9**, 76–80 (2009)

[11] P. Liljeroth, J. Repp, and G. Meyer, *Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules;* Science, **317**, 1203–1206 (2007)

[12] S. Y. Quek, M. Kamenetska, M. L. Steigerwald, H. J. Choi, S. G. Louie, M. S. Hybertsen, N. B., and VenkataramanLatha, *Mechanically controlled binary conductance switching of a single-molecule junction;* Nat Nano, **4**, 230–234 (2009)

[13] N. Agraït, A. Levy Yeyati, and J. M. van Ruitenbeek, *Quantum properties of atomic-sized conductors;* Phys. Rep., **377**, 81–279 (2003)

[14] A. Halbritter, P. Makk, S. Mackowiak, S. Csonka, M. Wawrzyniak, and J. Martinek, *Regular Atomic Narrowing of Ni, Fe, and V Nanowires Resolved by Two-Dimensional Correlation Analysis;* Phys. Rev. Lett., **105**, 266805 (2010)

[15] S. H. Choi, B. Kim, and C. D. Frisbie, *Electrical Resistance of Long Conjugated Molecular Wires;* Science, **320**, 1482 (2008)

[16] A. Halbritter, *Investigation of atomic-sized conductors with the mechanically controllable break junction technique* (PhD thesis) (2003)

[17] S. Csonka, A. Halbritter, and G. Mihály, *Pulling gold nanowires with a hydrogen clamp: Strong interactions of hydrogen molecules with gold nanojunctions;* Phys. Rev. B, **73**, 075405 (2006)

[18] P. Makk, S. Csonka, and A. Halbritter, *Effect of hydrogen molecules on the electronic transport through atomic-sized metallic junctions in the superconducting state;* Phys. Rev. B, **78**, 045414 (2008)

[19] A. Halbritter, P. Makk, S. Csonka, and G. Mihály, *Huge negative differential conductance in $Au-H2$ molecular nanojunctions;* Phys. Rev. B, **77**, 075402 (2008)

[20] S. Csonka, A. Halbritter, G. Mihály, O. I. Shklyarevskii, S. Speller, and H. van Kempen, *Conductance of Pd-H Nanojunctions;* Phys. Rev. Lett., **93**, 016802 (2004)

[21] O. Tal, M. Kiguchi, W. H. A. Thijssen, D. Djukic, C. Untiedt, R. H. M. Smit, and J. M. van Ruitenbeek, *Molecular signature of highly conductive metal-molecule-metal junctions;* Phys. Rev. B, **80**, 085427 (2009)

[22] T. Kim, H. Vázquez, M. S. Hybertsen, and L. Venkataraman, *Conductance of Molecular Junctions Formed with Silver Electrodes;* Nano Letters, **13**, 3358–3364 (2013)

[23] B. Ludoph, M. H. Devoret, D. Esteve, C. Urbina, and J. M. van Ruitenbeek, *Evidence for saturation of channel transmission from conductance fluctuations in atomic-size point contacts;* Phys. Rev. Lett., **82**, 1530–1533 (1999)

[24] S. Kaneko, T. Nakazumi, and M. Kiguchi, *Fabrication of a Well-Defined Single Benzene Molecule Junction Using Ag Electrodes;* The Journal of Physical Chemistry Letters, **1**, 3520–3523 (2010)

[25] M. Kiguchi, D. Djukic, and J. M. van Ruitenbeek, *The effect of bonding of a CO molecule on the conductance of atomic metal wires;* Nanotechnology, **18**, 035205 (2007)

[26] A. I. Yanson, G. Rubio Bollinger, H. E. van den Brom, N. Agraït, and J. M. van Ruitenbeek, *Formation and manipulation of a metallic wire of single gold atoms;* Nature, **395**, 783–785 (1998)

[27] T. Yelin, R. Vardimon, N. Kuritz, R. Korytár, A. Bagrets, F. Evers, L. Kronik, and O. Tal, *Atomically Wired Molecular Junctions: Connecting a Single Organic Molecule by Chains of Metal Atoms;* Nano Letters, **13**, 1956–1961 (2013)

[28] D. Rakhmilevitch and O. Tal, *Vibration-mediated Kondo transport in molecular junctions: conductance evolution during mechanical stretching;* Beilstein Journal of Nanotechnology, **6**, 2417–2422 (2015)

[29] A. Halbritter, S. Csonka, G. Mihály, O. I. Shklyarevskii, S. Speller, and H. van Kempen, *Quantum interference structures in the conductance plateaus of gold nanojunctions;* Phys. Rev. B, **69**, 121411 (2004)

[30] A. Halbritter, L. Borda, and A. Zawadowski, *Slow two-level systems in point contacts;* Advances in Physics, **53**, 939–1010 (2004)

[31] R. Vardimon, M. Matt, P. Nielaba, J. C. Cuevas, and O. Tal, *Orbital origin of the electrical conduction in ferromagnetic atomic-size contacts: Insights from shot noise measurements and theoretical simulations;* Phys. Rev. B, **93**, 085439 (2016)

[32] R. Ben-Zvi, R.Vardimon, T.Yelin, and O.Tal, *Electron vibration interaction in multichannel single-molecule junctions;* ACS Nano, **7**, 11147 (2013)

[33] H. E. van den Brom and J. M. van Ruitenbeek, *Quantum suppression of shot noise in atom-size metallic contacts;* **82**, 1526–1529 (1999)

[34] B. Ludoph, N. van der Post, E. N. Bratus', E. V. Bezuglyi, V. S. Shumeiko, G. Wendin, and J. M. van Ruitenbeek, *Multiple Andreev reflection in single atom niobium junctions;* **61**, 8561–8569 (2000)