Device for conductance measurements of molecular systems

Michael Lambacher*, Christian J.-F. Dupraz*, Udo Beierlein*, Jörg P. Kotthaus*,
Ulrich S. Schubert†, Philip R. Andres†

*Center for NanoScience and Sektion Physik,
Ludwig-Maximilians-Universität-München, Geschwister-Scholl-Platz 1,
80539 München (Germany),
†Laboratory of Macromolecular Chemistry and Nanoscience,
Eindhoven University of Technology and Dutch Polymer Institute,
P. O. Box 513, 5600 MB Eindhoven (The Netherlands)
Email: udo.beierlein@physik.uni-muenchen.de

***Abstract*— A device for conductance measurements of small molecular systems was fabricated. The device consists of two overlapping electrodes, separated by a thin layer of aluminium oxide. The oxide was partly etch away giving rise to a slit in which molecules can be inserted. Measurements were carried out on terpyridine based molecular chains.**

***Index Terms*— molecular electronics, conductance measurements**

I. Introduction

In the past few years, significant progress has been made in the fabrication and demonstration of molecular wires [1]-[3], molecular diodes [4] and switches [5]. Many of these advances have been made possible by using the self-assembly of molecules on nanofabricated semiconductor and/or metallic structures. The most studied molecular system for electronic transport is the Au-SR system, where a self-assembled monolayer (SAM) of an oligomer (R) binds to a gold surface via a thiol-group. In order to measure the electrical current through such a molecular layer, a second electrode is needed. This counterelectrode can be provided by an STM-tip [6]-[9], by another gold wire that can be approached using a mechanical break-junction [1], [10] or by evaporation of a gold layer on top of the SAM [4]. Other techniques employ electromigration of Au [11] or Au particles to achieve small interelectrode distances [12]. In spite of a growing number of publications dealing with electronic transport through molecules, even the conductance and transport mechanisms of relatively simple molecules are not well understood. The reasons lie in the difficulty of providing stable, well-defined metallic contacts at the two ends of a molecule, allowing reproducible transport measurements. It is the purpose of this paper to present a novel sample design for conductance measurements which were applied to SAMs of terpyridine based molecular chains.

II. Experimental

Our samples were prepared on highly p-doped Si with a top layer of 150 nm of SiO_2 as a substrate. Metal electrodes were fabricated by a combination of photolithography for the bonding pads and electron beam lithography for the patterning of the fine structures. A first (source) electrode of typically 2 μm length and 100 nm width was patterned by electron beam lithography, followed by the evaporation of 3 nm of NiCr and 50 nm of Au. This is followed by sputtering of a thin layer of Al_2O_3 with

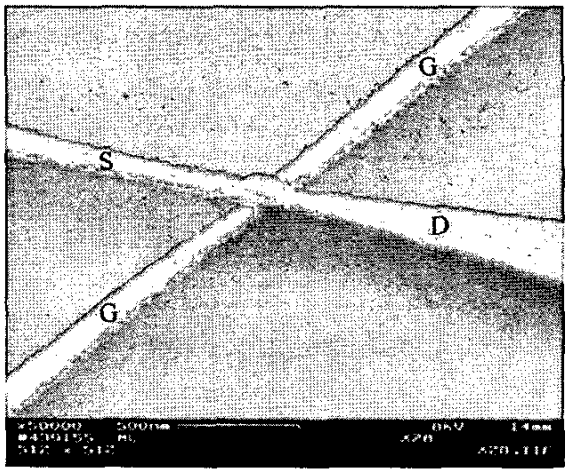

Fig. 1. SEM image of the contact structures showing source (S), drain (D) and gate (G) electrodes.

a variable thickness of 3 to 10 nm. The thickness and surface roughness were characterized by X-ray reflectivity measurements. Typical values for the surface roughness range between 1.1 and 1.2 nm. The oxide layer defines the electrode distance between source and drain contact of the device. After liftoff in acetone, the second (drain) electrode is defined by electron beam lithography and evaporation

0-7803-8536-5/04/$20.00 ©2004 IEEE

of 50 nm of gold such that it overlaps the source electrode over an area of about 50 x 100 nm^2. In the same step, gate electrodes can be patterned which approach the source and drain overlap area perpendicularly. The smallest distance of these gate electrodes to the source and drain electrodes is about 50 nm (Fig. 1).

Alternatively, similar overlapping electrode pairs with Al_2O_3 oxide spacer can be defined only by optical lithography. In this case, the overlap area of source and drain electrodes is of the order of several μm^2.

In order to insert molecules between the source and the drain electrode, some nm of the Al_2O_3 layer is removed by wet etching in H_3PO_4. Phosphoric acid selectively etches Al_2O_3 and leaves the underlying SiO_2 substrate intact. A cut through the device is shown schematically in Fig. 2 a).

The molecules used in this study are depicted in Fig. 2

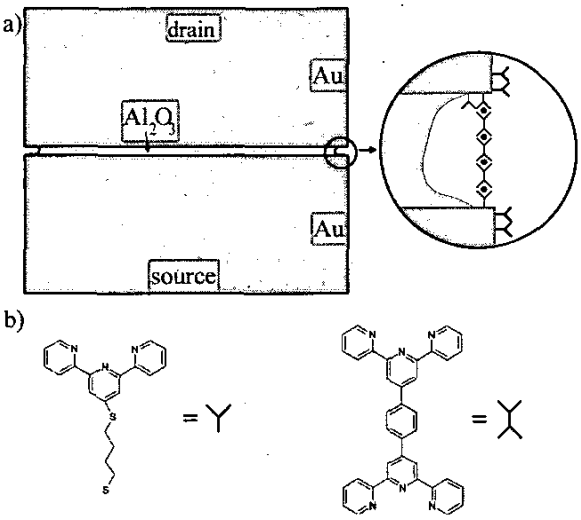

Fig. 2. a) Schematic view of the device. The encircled area shows a molecular chain between source and drain electrodes. b) Molecules $C_{19}H_{19}N_3S_2$ and $C_{36}H_{24}N_6$ used in this study. The symbols correspond to the drawing in a).

b). Molecule 1 ($C_{19}H_{19}N_3S_2$, 4-(2,2':6',2"-terpyridin-4'-ylsulfanyl)-butane-1-thiol) consists of a terpyridine and a thiol endgroup, connected by a short alkyl chain. Linker-molecule 2 ($C_{36}H_{24}N_6$, 1,4-bis(terpyrid-4-yl)benzene) has terpyridine endgroups on both sides, with a phenylene ring in between. These molecules were chosen because of their ability to build stable coordination complexes in which a transition element atom, e.g. Cobalt, is bonded to two terpyridine groups. Using molecule 2, it is possible to create molecular chains which can bridge the gap between the source and drain electrode of our device. Park et al. [11] have observed Coulomb blockade and the Kondo effect using similar molecules to molecule 1. These authors also showed that the charge state of Co atom in the coordination complex can be changed from 2+ to 3+ by applying a gate voltage.

The preparation of molecular chains in our device was carried out in the following way: First, the samples were immersed into a 1 mM solution of molecule 1 in ethanol for a day or more in order to form a self-assembled monolayer on the gold electrodes. Then, the samples were rinsed in pure ethanol. The sample was then transfered into a 1 mM solution of the linker-molecule 2 in chloroform which was mixed with an equal amount of ethanol. A 1 mM solution of $CoCl_2$ in chloroform/ethanol was added in order to initiate polymerization of the molecules. After several hours, the samples were removed from this solution and carefully rinsed in ethanol.

Before insertion of the molecular chains, the samples were electrically tested. Only samples with low leakage currents of a few tens of pA at V_{SD} = 1 V were used for the experiments. Typical breakthrough voltages of the oxide, e.g. for an oxide thickness of 10 nm, range between 1.8 and 2.4 V.

After build-up of the molecular chains, most samples show a significant increase of the source-drain current. Fig. 3 shows an example of such a current measurement as a function of source-drain voltage at different temperatures. All curves, at T = 290, 77 and 4.2 K are almost linear, the current decreases as the temperature is lowered. Also shown is a curve before insertion of the molecules, with current values of 30 pA at V_{SD} = 0.5 V. The inset in Fig.

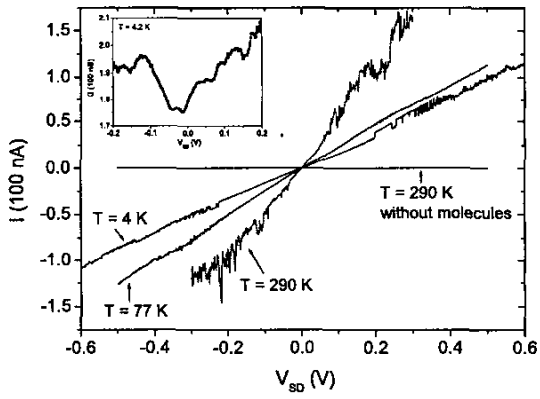

Fig. 3. Current versus source-drain voltage of the device with and without molecular chains at different temperatures. Inset: Conductance as a function of V_{SD} at T = 4.2 K.

3 depicts a conductance versus V_{SD} curve at 4.2 K where peak structures are clearly seen. Note that other samples showed similar features, although the peak positions and the peak distances vary from sample to sample. Similar features were observed in other measurements using different molecules and different measurement techniques [13],

[14]. The molecules were removed afterwards by a piranha etch solution. In current measurements after removal of the molecules currents of a few tens of pA where observed, similar to the measurements before insertion of the molecules.

The origin of the peaks is not very well understood. Coulomb blockade could cause such features if a conducting island is coupled by tunneling barriers to the source and drain contacts. Such islands could be created by the coordination complexes of the molecules, as proposed by Park et al. [11]. But we could not observe any gate voltage dependence which could support this explanation. The observed conductance peaks could also be understood in terms of the vibrational modes of the molecule. Vibration of molecules would change the coupling between the orbitals of the molecules and the coupling of the molecules to the contacts. If the energy of the incident electron exceeds the vibrational energy, this could lead to variations in the current through the molecules due to energy transfer from the electrons to the molecule. Another explanation for the peaks is that these features may reflect coherent transport through the molecular orbitals. In this picture, the Fermi energy at zero bias would be located somewhere between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). As the source-drain voltage is increased, the current will increase due to resonant tunnelling when the potential of one of the electrodes is equal to the nearest molecular level. By further increasing the potential difference between source and drain, more and more conductance channels will be opened giving rise to a conductance peak for every new molecular level.

III. Conclusion

We have developed a device for conductance measurements of molecules which allows to reduce the electrode distance down to 3 nm. With this technique, it is possible to test the device before insertion and after removal of the molecules giving more certainty that the obtained results really reflect the properties of the molecules. As an example, current and conductance measurements of molecular chains bound to the electrodes by thiol groups were presented.

Acknowledgment

We would like to thank G. Abstreiter and M. Tornow for stimulating discussions. Financial support by the Sonderforschungsbereich 486 is gratefully acknowledged.

References

[1] M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, J.M. Tour, "Conductance of a molecular junction", *Science*, vol. 278, pp. 252-254, october 1997.

[2] M.A. Reed, "Molecular-scale electronics", *Proc. IEEE*, vol. 87, pp. 652-658, april 1999.

[3] S.J. Tans, M.H. Devoret, H.J. Dai, A. Thess, R.E. Smalley, L.J. Geerligs, C. Dekker, "Individual single-wall carbon nanotubes as quantum wires", *Nature*, vol. 386, pp. 474-477, april 1997.

[4] C. Zhou, M.R. Deshpande, M.A. Reed, L. Jones, J.M. Tour,"Nanoscale metal self-assembled monolayer metal heterostructures", *Appl. Phys. Lett.*, vol. 71, pp. 611-613, august 1997.

[5] J. Chen, M.A. Reed, A.M. Rawlett, J.M. Tour, "Large on-off ratios and negative differential resistance in a molecular electronic device", *Science*, vol. 286, pp. 1550-1552, november 1999. 1550.

[6] L.A. Bumm, J.J. Arnold, M.T. Cygan, T.D. Dunbar, T.P. Burgin, L. Jones II, D.L. Allara, J.M. Tour, P.S. Weiss, "Are single molecular wires conducting?", *Science*, vol. 271, pp. 1705-1707, march 1996.

[7] R. P. Andres, T. Bein, M. Dorogi, S. Feng, J. I. Henderson, C.P. Kubiak, W. Mahoney, R.G. Osifchin, R. Reifenberger, ""Coulomb staircase" at room temperature in a self-assembled molecular nanostructure", *Science*, vol. 272, pp. 1323-1325, may 1996.

[8] X.D. Cui, A. Primak, X. Zarate, J. Tomfohr, O.F. Sankey, A.L. Moore, T.A. Moore, D. Gust, G. Harris, S.M. Lindsay, "Reproducible measurement of single-molecule conductivity", *Science* vol. 294, pp. 571-574, october 2001.

[9] S. Hong, R. Reifenberger, W. Tian, S. Datta, J. Henderson, C.P. Kubiak, "Molecular conductance spectroscopy of conjugated, phenyl-based molecules on Au(111): the effect of end groups on molecular conduction", *Superlattices Microstruct.*, vol. 28, 289-303, october 2000.

[10] J. Reichert, R. Ochs, D. Beckmann, H.B. Weber, M. Mayor, H.v. Löhneysen, "Driving current through single organic molecules", *Phys. Rev. Lett.*, vol. 88, pp. 176804, april 2002.

[11] J. Park, A.N. Pasupathy, J.I. Goldsmith, C. Chang, Y. Yaish, J.R. Petta, M. Rinkoski, J.P. Sethna, H.D. Abruña, P.L. McEuen, D.C. Ralph, "Coulomb blockade and the Kondo effect in single-atom transistors", *Nature*, vol. 417, pp. 722-725, june 2002.

[12] I. Amlani, A.M. Rawlett, L.A. Nagahara, R.K. Tsui, "An approach to transport measurements of electronic molecules", *Appl. Phys. Lett.*, vol. 80, pp. 2761-2763, april 1997.

[13] C. J.-F. Dupraz, U. Beierlein, J.P. Kotthaus, "Low temperature conductance measurements of self-assembled monolayers of 1,4-phenylene diisocyanide", *ChemPhysChem*, vol. 4, pp. 1247-1252, november 2003.

[14] J.-O. Lee, G. Lientschnig, F. Wiertz, M. Struijk, R.A.J. Jansen, R. Egberink, D.N. Reinhoudt, P. Hadley, C. Dekker, "Absence of strong gate effects in electrical measurements on phenylene-based conjugated molecules", *Nano Lett.*, vol. 3, pp. 113-117, february 2003.