The Art of Catching and Probing Single Molecules

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Abstract: Probing the electronic properties of an individual molecule is a far from trivial task. In order to measure, for instance, the conductance of a single molecule, the molecule must be contacted by two nanoscopic electrodes. Here we will give two examples of how a single molecule can be caught between two metallic electrodes. In the first example the conductance of a single octanethiol molecule is measured by trapping the molecule between an atomic Pt chain on a semiconductor surface and the apex of a scanning tunneling microscope tip. In the second example a Cu-phthalocyanine molecule is caught between two adjacent nanowires on a semiconductor surface. In this 'bridge' adsorption configuration the core of the CuPc molecule, *i.e. the* Cu atom, is fully decoupled from the underlying substrate. The electronic properties of the core of Cu-phthalocyanine molecule are probed with scanning tunneling spectroscopy.

Keywords: Molecular electronics · Scanning tunneling microscopy · Scanning tunneling spectroscopy

1. Introduction

The current electronic industry relies heavily on silicon (Si) based technology and so far this approach has proven to be extremely successful. However, below a length scale of about 10–20 nm the inevitable random variations in *e.g.* the number of dopant atoms in the active region of the device will lead to an unacceptably wide spread of the device characteristics. A way out would be to use single electron-based devices, though the critical dimensions for *e.g.* single electron transistors to operate properly at room temperature would be about 1 nm and this size is not compatible with the current and even forthcoming lithographic techniques, which rely on extreme ultraviolet radiation and electron beams. The most logical way to proceed is to hybridize the technologies, *i.e.* to combine the advantages of molecular electronics, where single molecules are used as elementary building blocks for electronic devices,[1–8] with the powerful and well-established Si technology. The use of single molecules for tasks currently managed by larger scale Si-based electronics will require understanding of electron transport on the molecular scale.[9–12] Although recent measurements of molecular transport properties have revealed several interesting aspects, a coherent understanding of the electronic transport has never materialized. The main reason for this deficiency is the inherent problem to contact a single molecule. In order to measure the resistance of a single molecule one has to connect a macroscopic current source and voltmeter to each end of the molecule. Contacting a single molecule with electrical leads to the outside macroscopic world is a delicate and challenging process. The electrical contacts must also be ohmic, so that any non-linearity in the conductivity can be correctly attributed and studied. Moreover the contact resistances should be much smaller than the resistance of the molecule itself. And finally the medium supporting and surrounding the molecule should be much more insulating than the molecule. The ability to understand, control, and exploit the flow of electronic charge through a single molecule is not only very interesting from an academic point of view, but is also essential for further progress and expansion of molecular electronics.

In this article we will propose two routes to contact and measure the properties of a single molecule. In the first series of experiments the conductance of a single octanethiol molecule is measured by capturing the molecule between a platinum (Pt) nanowire and the apex of the scanning tunneling microscope tip. In the second series experiments a Cu-phthalocyanine (CuPc) molecule is caught between two adjacent nanowires. Subsequently, scanning tunneling spectroscopy measurements are performed on the core of the CuPc molecule.

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2. Experimental

In order to capture a single molecule between two electrodes we make use of a smart template that consists of a germanium (Ge) (001) surface coated with perfectly straight and nearly defect-free Pt or Au induced nanowire arrays. These nanowires will act as nanoscopic alligator clips, *i.e.* electrodes. The Ge(001) samples are cleaned by prolonged 800 eV Ar^+ ion sputtering and annealing *via* resistive heating at 1100±25 K. The temperature is measured with a pyrometer. After several cleaning cycles the Ge(001) samples were atomically clean and exhibited a well-ordered (2×1)/c(4×2) domain pattern.[13–15] Subsequently, we deposited a monolayer of Pt or Au on the Ge(001) substrate at room temperature. After the Pt (Au) deposition the sample was annealed for a few minutes at 1100 K in the case of Pt and 650 K in the case of Au. The Pt- or Au-modified Ge(001) sample was then inserted in the scanning tunneling microscope (STM) for imaging. This procedure results in densely packed and well-ordered nano wire arrays, as have been described and discussed elsewhere in great detail.[16–22]

After the formation of the Pt nanowire arrays on Ge(001), the Pt-modified Ge(001) surface was exposed to octanethiol (Sigma-Aldrich). A small amount of octanethiol was introduced in the preparation chamber of our UHV system *via* a leak valve. This valve allows us to controllably adjust the pressure of the octanethiol in the preparation chamber. We have exposed the samples to doses of 10–100 L of octanethiol. After exposure and pumping down of the preparation chamber, the sample is transferred to the LT-STM chamber for cooling down and imaging.

In a second series of experiments CuPc molecules were adsorbed on a Au-modified Ge(001) substrate. CuPc (>99% pure) was deposited using a Knudsen cell with a quartz crucible. The sample was directly facing the Knudsen cell's outlet at a distance of about 2 cm. During the deposition the temperature of the Knudsen cell was kept at 573±5 K and the sample was at room temperature. The deposited amount of CuPc varied from less than 1% to about 10% of a monolayer. After deposition the sample was annealed at a temperature of 600±25 K for two minutes. Subsequently, the sample was transferred to the STM chamber and cooled down to 77 K.

3. Results and Discussion

In Fig. 1 an STM image of an array of self-organizing Pt chains on a Ge(001) is shown. The atomic Pt chains consist of Pt dimers which have their dimer bonds aligned in the direction of the chains. The dimerized atomic Pt chains are virtually defect-free, perfectly straight and spaced 1.6 nm apart. In Fig. 2 an STM image of a Pt decorated Ge(001) surface recorded at 77 K after being exposed to 60 L of octanethiol at room temperature is shown. Clearly present in Fig. 2 are several white, circular-shaped spots located on top of the Pt chains. These spots were not present before exposure to octanethiol. The apparent size of these spherical features agrees well with the size of a single octanethiol molecule. Therefore, we attribute these features to octanethiol molecules adsorbed on the atomic Pt chains. In addition, the STM image reveals that the octanethiol molecules almost exclusively adsorb on-top of the Pt chains and only very rarely in the troughs between the chains. The density of these white spots increases with increasing exposure to octanethiol molecules.

Alkanethiols are thoroughly studied because they form nearly perfect self-assembled monolayers on several metal surfaces. The sulfur atom of the thiol head group binds to the surface and for a densely packed monolayer the alkane chains are pointing upright due to the intermolecular Van der Waals forces. At low thiol coverages the alkane chains are, however, lying flat down on the metal surface. Our STM measurements reveal that the sulfur atom of the octanethiol molecule binds on-top to one of the Pt atoms of the chain and that the tail of the octanethiol lies flat down on the Pt chain.

Subsequently, we positioned the STM tip on top of a pre-selected octanethiol molecule and measured the current as a function of time with the feedback loop of the STM electronics disabled. The time resolution in this open feedback mode (about
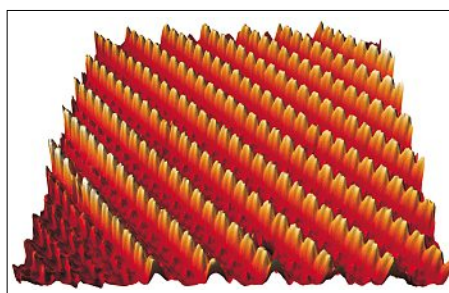

Fig. 1. Scanning tunneling microscopy image of a Ge(001) surface covered with an array of self-organizing atomic Pt chains (15 nm by 15 nm). The image is taken at room temperature (V = –1.45 V and I = 0.5 nA). The spacings between adjacent Pt dimers within a chain and neighboring Pt chains are 0.8 and 1.6 nm, respectively.
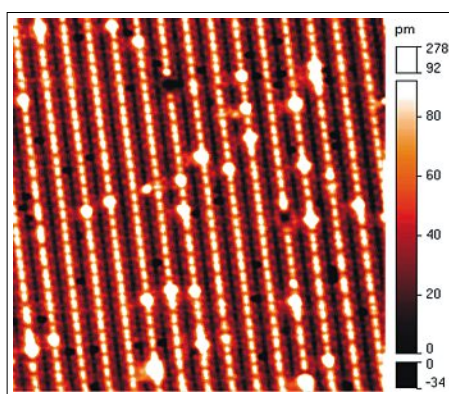

Fig. 2. Scanning tunneling microscopy image of a Pt-modified Ge(001) surface after exposing it to 60 L of octanethiol, recorded at 77 K. The octanethiol molecules (circular-shaped white spots) almost exclusively adsorb on the Pt atomic chains. Image size is 25 nm × 25 nm, sample bias is –0.90 V and the tunneling current is 0.5 nA.

10 μs) is several orders of magnitude better than in the standard STM imaging mode.[23] Recent experiments have revealed that this spectroscopic mode is extremely powerful to study the dynamics of single molecules on surfaces.[24–27]

In Fig. 3 (A) a typical current-time trace recorded at 77 K is depicted. The setpoint current before disabling the feedback loop was 1 nA, but after a few seconds the tunneling current suddenly jumps up to value of about 11 nA. After being at this

high current value for more than 10 seconds the tunneling current suddenly jumps back to its original value of 1 nA. The fact that the current returns to its starting value excludes a permanent change in the geometry of the adsorbed molecule. The latter is confirmed by a comparison of STM images taken just before and just after recording the current-time traces.

As an explanation of this sudden increase/decrease in the current signal we propose the following simple scenario: during the open-loop experiment, the tail of the octanethiol molecule occasionally flips up and jumps into contact with the apex of the STM tip.[28] Interestingly, the length of the tail of the octanethiol molecule is about the same as the width of the tunnel gap, *i.e.* about 1 nm. Hence, the tail of the octanethiol molecule is just long enough to contact the STM tip. We have repeated these open feedback loop experiments many times and in most cases the octanethiol molecule jumps into contact for a few seconds. The high current level was always in the range from 10–15 nA, resulting in a single-molecule resistance of 100–150 MΩ (the sample bias was 1.5 V), which is in excellent agreement with values reported in literature.[29] Since the single molecule resistance that we measured falls in the range of the reported values for C6 and C8-thiols we do not know whether the current flows through a major part of the tail of the molecule or just through the whole tail of the molecule.

It should be noted that the high current level is rather noisy. We believe that this is due to the fact that the contact between the tail of the octanethiol molecule and the apex of the STM tip is rather weak. Therefore, we believe that the end of the tail of the octanethiol molecule frequently jumps (on a timescale faster than our time resolution of about 10 μs) between comparable adsorption sites at the apex of the STM tip.

In the second series of experiments we have deposited phthalocyanine molecules on Pt- and Au-modified Ge(001) surfaces. The phthalocyanine molecules have recently attracted a lot of attention because their electrical, physical and optical prop-
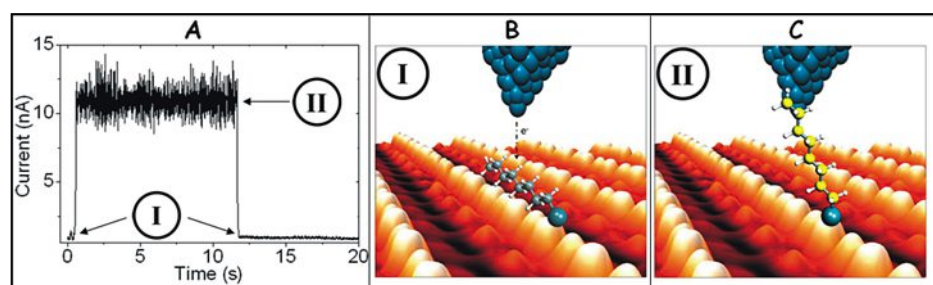

Fig. 3. (A) Current-time trace recorded on-top of an octanethiol molecule at 77 K. The setpoint current is 1 nA and the sample bias is 1.5 V. (B) Octanethiol molecule lying flat down on the atomic chain (configuration I). (C) Octanethiol in the contact mode (configuration II).
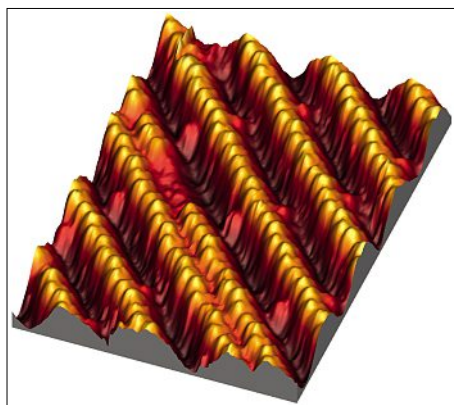
Fig. 4. Scanning tunneling microscopy image of a Ge(001) surface covered with an array of Au-induced nanowires. The image is recorded with a sample bias of –1.5 V and a tunnel current of 0.2 nA.

erties can be tuned by the large variety of substituents that can be attached to the basic Pc structure.[30,31] Additionally, it is possible to incorporate about 70 different atoms in the centre of the Pc molecule giving even more freedom to tailor its properties.[31] Understanding the interaction of phthalocyanine molecules with semiconductor surfaces is a prerequisite for finding their potential applications in electronics and nanotechnology.

The selected molecule here is Cu-phthalocyanine (CuPc). The Cu, with oxidation state of 2+, makes two coordinated covalent and two covalent bonds with the Pc ring which has an oxidation state of 2–. The Cu-ion is small enough to fit in the cavity of the Pc-molecule, making CuPc a planar, fourfold symmetric molecule. The size of CuPc molecule, *i.e.* about 1.4 nm by a 1.4 nm, is such that it would in principle nicely fit between two adjacent Pt chains. However, recent experiments[32] have revealed that the CuPc molecules prefer to adsorb on-top of the Pt chains. Moreover, the binding is relatively weak and during imaging with the STM the CuPc are shifted along the Pt chains.

As will be shown below the Au-modified Ge(001) substrate turns out to be a much more suitable template for CuPc molecules than the Pt-modified Ge(001) substrate. In Fig. 4 an STM image of an Au-modified Ge(001) surface is displayed. The image shows a regular array of Au-induced nanowires which are separated 1.6 nm apart.[18–22] It should be noted that the spacing between the third and fourth nanowire is only 0.8 nm. This phenomenon has already been reported by Wang *et al.*[18] and Schäfer *et al.*[19] The nanowires run along the [110] directions of the Ge(001) crystal. Their height is at least 0.6 nm, *i.e.* these structures are far too high to be explained by atomic chains on a substrate as in the case of Pt on Ge(001).[20,21] The ridges of the Au-induced nanowires con-

sist of dimers that have their dimer bonds aligned in a direction perpendicular to the nanowire. The zigzag appearance of the dimer rows is due to the fact that adjacent dimers prefer to buckle in opposite directions. In the trenches small protrusions are observed, which are regularly spaced on a distance of 3.2 nm. Van Houselt *et al.*[20] proposed that i) these trenches are comprised of small Ge(111) facets decorated with Au atoms and ii) the dimers located on top of the ridges are normal Ge dimers.

Fig. 5 shows an STM image after the deposition of a few percent of a monolayer of CuPc on a Au-modified Ge(001) substrate. The CuPc molecules have a clover-like appearance and are found to adsorb in six different configurations.[33] These adsorption configurations are labeled A–F, and are shown in the left column of Fig. 6. In the middle column the background corrected images of the configurations are depicted. The background correction is achieved with a 'flatten' filter. Schematic diagrams of the adsorption configurations are depicted in the right column. About 60% of the CuPc molecules are adsorbed in 'bridge' like configurations where all the four lobes of the CuPc bind to the Au-induced nanowires. Two lobes of the CuPc molecule bind to the dangling bonds of the Ge dimers on one nanowire, whereas the other two lobes bind to the dangling bonds of a neighboring nanowire. This results in CuPc molecules that form a 'bridge' between two adjacent nanowires. There are two types of these bridge configurations, which are displayed in Fig. 6A and Fig. 6B respectively. The bridge configuration shown in Fig. 6A is exactly perpendicular to the nanowire direction, whereas bridge configuration in Fig. 6B is slightly rotated with respect to configuration A.

The four lobes of the configurations depicted in Figs. 6A and 6B show up as bright dots, although they are not always equally bright. The core of the CuPc molecule, *i.e.* the Cu atom, however, always appears dark. Theoretical calculations of Lippel *et al.*[34] have revealed that contour plots of the charge densities of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of CuPc adsorbed on a Cu surface are very similar in appearance. In general, our results are in agreement with these theoretical calculations. For both molecular orbitals each lobe shows up as four bright spots in an almost square configuration, whereas the core is always dim. Scanning tunneling microscopy images recorded at variety of voltages revealed that the four aromatic rings of the molecule are visible at voltages above +0.8 V and below –0.8 V. The core of the CuPc molecule appears dark in the voltage range from –2.5 V to +2.5 V.
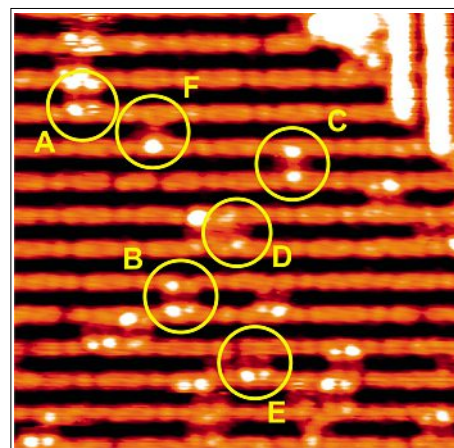

Fig. 5. An STM image of Au-induced nanowires with a few percent of a monolayer CuPc coverage showing six different CuPc adsorption configurations, labeled A–F. (outlined by circles) The image is recorded at a sample bias of +1.5 V and a tunnel current of 0.2 nA. The image size is 20 nm by 20 nm.

Fig. 6C and a rotated version D show a CuPc molecule adsorbed in another bridge-like configuration, where the bonding between the nanowires and CuPc only involves two lobes. The other two lobes are hanging freely in the 0.6 nm deep trough between the nanowires. In all cases the CuPc molecule has a clover-like appearance. One out of each four CuPc molecules is adsorbed in configuration C or D.

Finally, Fig. 6E and F show two configurations where no bridge is formed between adjacent nanowires. In Fig. 6E two lobes bind to a nanowire and the other two lobes lie in the trench between the nano wires. The configuration shown in Fig. 6F binds with just one lobe to a nanowire and the other lobes lies in the trench between the nanowires. In the configurations E and F the molecule adsorbs a little closer to one of the nanowires, where one or two lobes make a bond, whereas the remaining lobes are lying in the trench between the two nanowires. The lobes prefer to bind to the downward-buckled atom of the ridge dimer. Therefore, if the buckling of the dimers at two neighboring Au-induced nanowires is out of phase, it is harder for the CuPc molecule to adsorb in a bridge-like configuration.

I(V) measurements were recorded on the core as well as the lobes of CuPc molecule. In Fig. 7 the density of states ((dI/dV)/(I/V)) of the core of CuPc is shown. Most noticeable is a large gap at zero bias. If the core of the CuPc molecule is electronically decoupled from its four lobes and the underlying substrate this gap might be a Coulomb gap. However, it should be noted here that we did not observe any evidence for a Coulomb staircase in the I(V) traces and therefore the gap may also be explained by the HOMO-LUMO gap of lobes of the CuPc molecule.
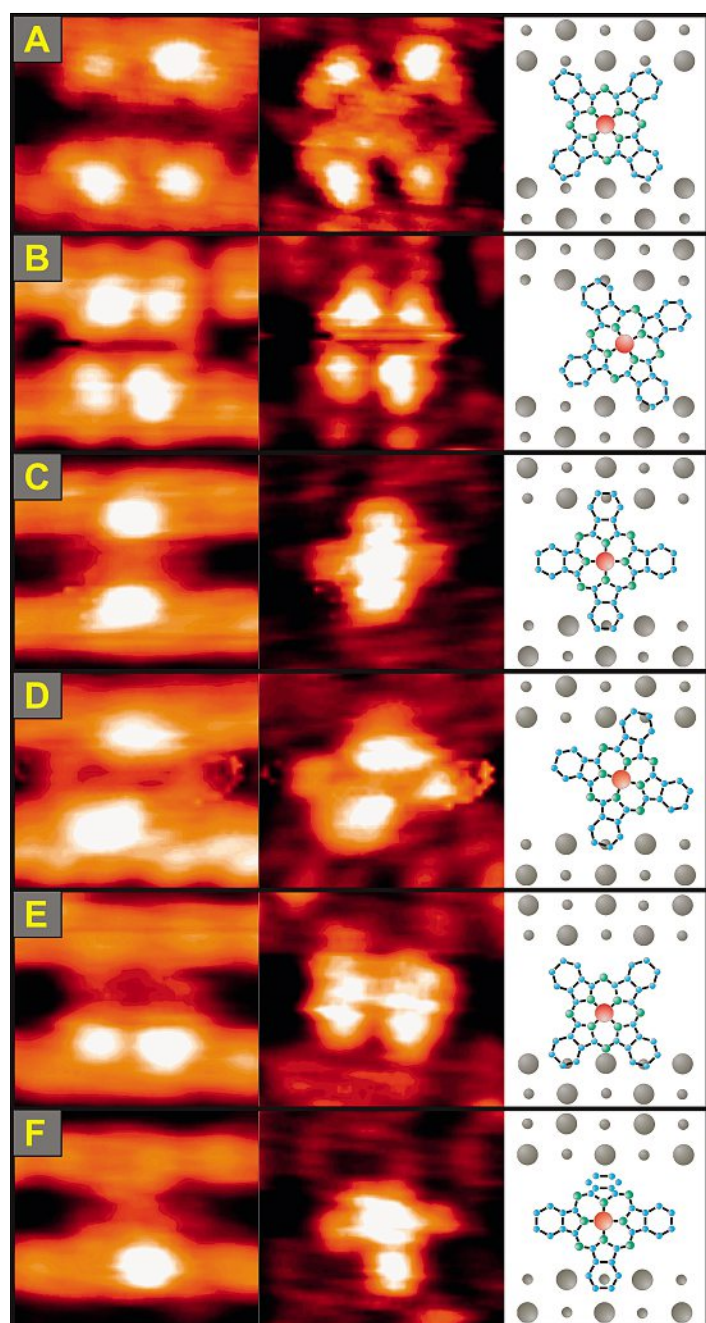
Fig. 6. In the first column of STM images, six different adsorption geometries of CuPc molecules on Au-induced nano wires are shown. The second column displays the background corrected images of the first column, revealing more detail of the molecule. The third column shows a schematic representation of the different adsorption geometries on top of the buckled Ge dimers. The large and small dots refer to the up- and downward buckled atoms of the Ge dimers, respectively. The STM images are recorded at a sample bias of +1.5 V and a tunnel current of 0.2 nA. The image size is 2.8 nm by 2.5 nm.

4. Summary

We have shown that there are several ways to catch a single molecule between two electrodes. Once the molecule is caught, it is rather straightforward to probe the electronic properties of the molecule. The methods we have put forward to catch single molecules are, however, not general applicable to other systems. The latter underlines that the true challenge in Molecular Electronics is how to contact single molecules in a proper and reproducible way.
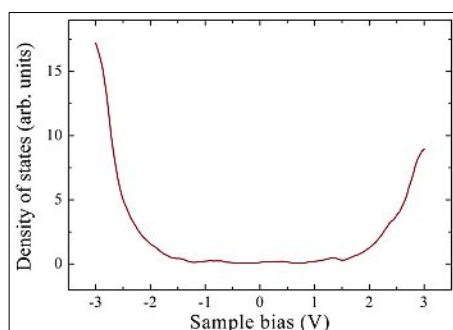
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Fig. 7. Density of states, (dI/dV)/(I/V), recorded on-top of the core of a CuPc molecule adsorbed in the bridge configuration A on an Au-modified Ge(001) surface at 77 K.

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