

Electrical characterization of alkane monolayers using micro-transfer printing: tunneling and molecular transport

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Abstract. We present the characterization of a decanedithiol monolayer using a technique which is based on micro-transfer printing. This technique allows us to contact molecular monolayers on the scale of $100 \mu\text{m}^2$ without producing electrical shorts between the metallic contacts. This opens the possibility to characterize the behavior of metal–molecule contacts on a large ensemble. Electrical measurements of the decanes show that two main transport mechanisms dominate conduction through this monolayer, tunneling between the electrodes and transport through electric states of the molecules. In our setup, tunneling is temperature dependent, because a length change of the molecules causes changes of the effective tunneling width.

Contents

1. Introduction	2
2. Experimental techniques	2
3. Results	4
4. Discussion	5
5. Conclusion	10
Acknowledgment	10
References	10

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1. Introduction

Providing reliable test structures for the measurement of molecular conductivity is one of the main prerequisites for the foundation of molecular electronics [1, 2]. Although many successful experiments have demonstrated electrical contacts to single molecules [3]–[9] or molecular ensembles [10]–[14], the molecule–metal bond is still rather poorly characterized electrically. This uncertainty arises from the fact that all processing and characterization techniques are not well defined on the molecular scale. It is therefore important to rely on statistical information in such a contact formation [7, 15], i.e. to either repeat the experiments a large number of times and compare the results or to contact a large number of molecules in parallel. The first approach has been demonstrated successfully in a number of techniques, e.g. mechanical break junctions [16, 17], scanning probe microscopy [8], [18]–[21] and electro-migrated junctions [7]. In order to contact many molecules in parallel, special precautions have to be taken in order not to damage the molecular layers and thus create metallic shorts between the electrodes [12, 13]. On the other hand, it is also important to note that transport through molecular monolayers can in principle be different from transport through single molecules, since interactions between the molecules and interactions of the monolayer with the contacting metal can alter the energy landscape between the contacts [11, 22].

The most successful technique to date providing reliable contacts to a large number of molecules has been demonstrated in [13]. In this technique one contact to the molecules is provided by a conductive polymer. For understanding the contact properties to metal electrodes, which is important for fabrication of contacts on the scale of single molecules, this additional interface causes additional difficulties. Fabrication of metal–molecule–metal junctions via a combination of etching techniques in a silicon-nitride structure was demonstrated in [12, 23, 24], but with inconclusive results. In this work, we demonstrate an alternative approach based on the nano-transfer printing technique, which was developed by Loo *et al* [14]. This technique allows us to produce reliable metal–molecule–metal junctions on the micron-scale with decanedithiol molecules as active molecules. We characterize the electrical behavior of these junctions at several temperatures ranging from 5 K to room temperature. The results deviate clearly from curves expected for tunneling through an insulating layer, which was reported in [12] and would be anticipated for a molecule with a large HOMO–LUMO gap. Similar results were found on alkane monolayers created by Langmuir Blodgett techniques [24]. We explain our data with conformational changes of the molecules, which were discussed in [25] and lead to a change of the electrode distance in our devices.

2. Experimental techniques

The micro-transfer printing (μ TP) technique is based on the weak adhesion of metals to (polydimethylsiloxane PDMS, Sylgard 451). This enables transfer of the metal from a PDMS stamp to a molecular monolayer, if the monolayer provides a chemical functionality which binds stronger to the metal than PDMS. This monolayer is formed on an insulating substrate and a bottom electrode. The overlap between the stamped top electrode and the bottom electrode defines the junction area. A sketch of the experimental scenario is shown in figure 1. The contact between the top electrode and the substrate depends on the substrate chosen. In first experiments, we used a GaAs substrate, because dense molecular monolayers can be formed on this substrate using standard thiol chemistry and the electrical metal–molecules semiconductor

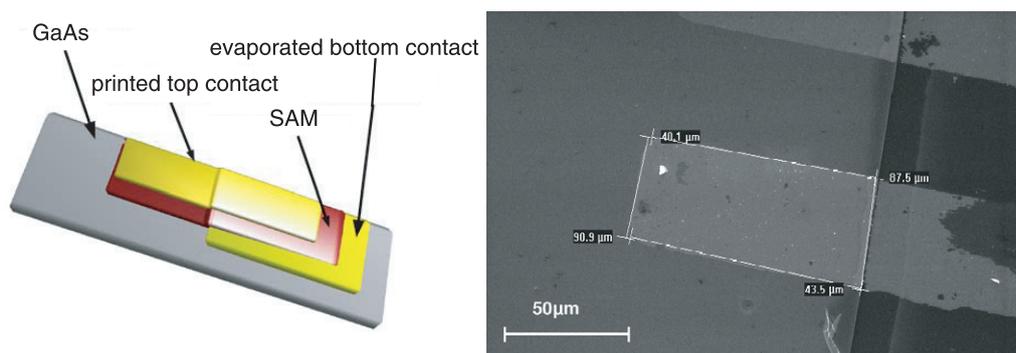


Figure 1. Left: sketch of the design of a junction created by μ TP. The top metal electrode is defined on top of the bare GaAs and on top of the lower, evaporated metal electrode. Both are covered with a monolayer of molecules. The lower electrode is additionally isolated from the substrate by an SiO₂ layer (15 nm). Right: scanning electron micrograph of the final structure. The junction area is highlighted by the white rectangle. The dark areas inside the printed structure indicate that the metal transfer is not complete. This will lead to a lower number of contacted molecules, but has no effect on the electrical properties of the junctions.

contact is well characterized and expected to be ohmic [14]. Therefore artifacts from this contact are not expected, additionally the bottom electrode is electrically isolated from the substrate by a layer of SiO₂ (15 nm). We use semi-insulating GaAs, which shows no measurable conductance at low temperatures in dark conditions. In order to avoid any light-induced effects, the whole sample space is covered with black cardboard to shield external light during the electrical measurements.

The shape of the PDMS stamp is defined by optical lithography. We define elevated stripes, which are in contact with the substrate during the printing process. The metal from these areas is transferred to the molecular monolayers, while the metal, which is situated on the receding parts, remains on the stamp. Hereby, we define metallic stripes on the substrate. A sketch of this scheme is shown in figure 2. In order to do this, an optical resist (Microchem SU8-2010) is structured on a silicon substrate. The PDMS is cast into this mold and cured at 60 °C for 24 h. Sticking of the PDMS to the silicon is prevented by deposition of a layer of trichlorosilane before casting. The stamp is then carefully removed from the mold, cut into suitable pieces and immediately transferred to the evaporation chamber. Evaporation is done from a thermal evaporation source at a pressure of 10⁻⁷ Pa and a rate of 1 Å s⁻¹ in order to avoid unwanted heating effects; the final thickness of the metal is 15 nm.

The bottom electrode is evaporated on the substrate through a shadow mask, which is situated about 1 mm above the surface. This ensures that the edges of the metal are smooth; therefore, the printed top electrode can cover the transition from the substrate to the metal without disruption. Subsequently the samples are cleaned in NH₄OH (25% for 3 min) and rinsed with millipore H₂O to remove oxide layers on the GaAs. The monolayers of decanedithiols are deposited from a 50 mmol solution in ethanol during 24 h. After this deposition step, the samples are rinsed in ethanol in order to remove all molecules which are not chemisorbed on the surface. Immediately after this step, the PDMS stamp is aligned with the bottom electrode and pressed

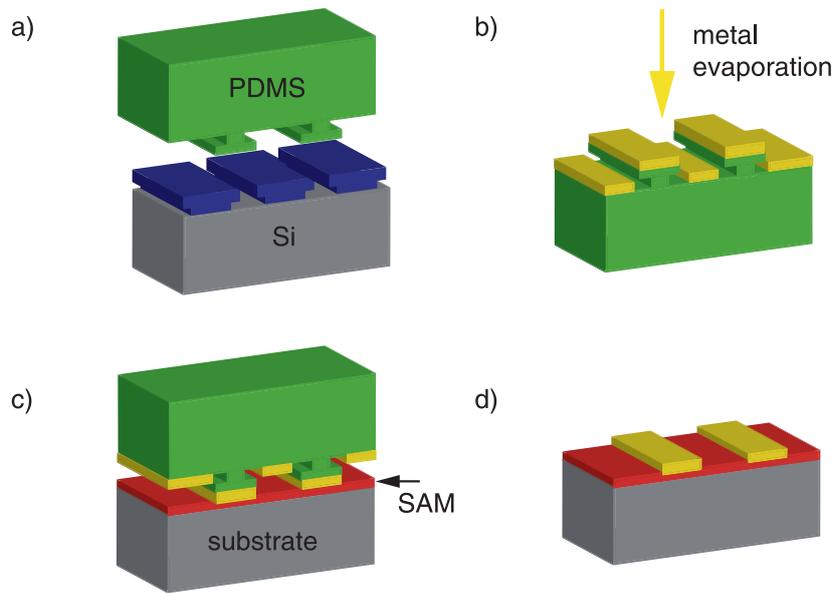


Figure 2. Sketch of the μ TP principle. (a) Definition of the pattern in the resist and transfer to the stamp. (b) Metal evaporation. (c) Transfer of the pattern to the molecular monolayer. (d) Final structure.

onto the surface. In order to allow the molecules to bind reliably to the printed gold only a very small pressing force should be applied. In most cases, the weight of the stamp is already enough. After a relaxation period of about 10 min the stamp is removed and the gold which was on the elevated structures on the stamp, remains on top of the molecular monolayer. An electron micrograph of the final structure, indicating the junction area, is shown in figure 1.

The samples are characterized in a low-temperature probe station (Desert Cryogenics) and electrically contacted with tungsten tips of radius $25 \mu\text{m}$. One of these tips is situated on the evaporated gold, the other one on top of the printed gold in an area where no overlap between the top and the bottom electrode is formed. The force which is applied to this latter tip can influence the overall measured resistance. In our discussion of the results, we only take junctions into account where repeated contacting (also during taking temperature sweeps) lead to consistent resistance values. The source–drain voltage is provided by a Yokogawa 7651 device, the current measured by a Femto DLPCA 200 current–voltage converter and read out by an Agilent 34401a multimeter without any filtering.

3. Results

The sample from which we report data in this study consisted of 67 junctions, which were characterized during a timespan of 4.5 months before showing degradation effects. Thirty-three of these junctions show metallic shorts, 21 conduction under light irradiation but no conduction in complete darkness and the remaining 13 measurable currents in darkness at low temperatures. Similar results were obtained for two further samples. The yield strongly depends on the area of overlap which is created between the top and the bottom electrode. Samples showing overlap areas larger than about $50 \times 50 \mu\text{m}^2$ generally show metallic shorts, i.e. the resistance between

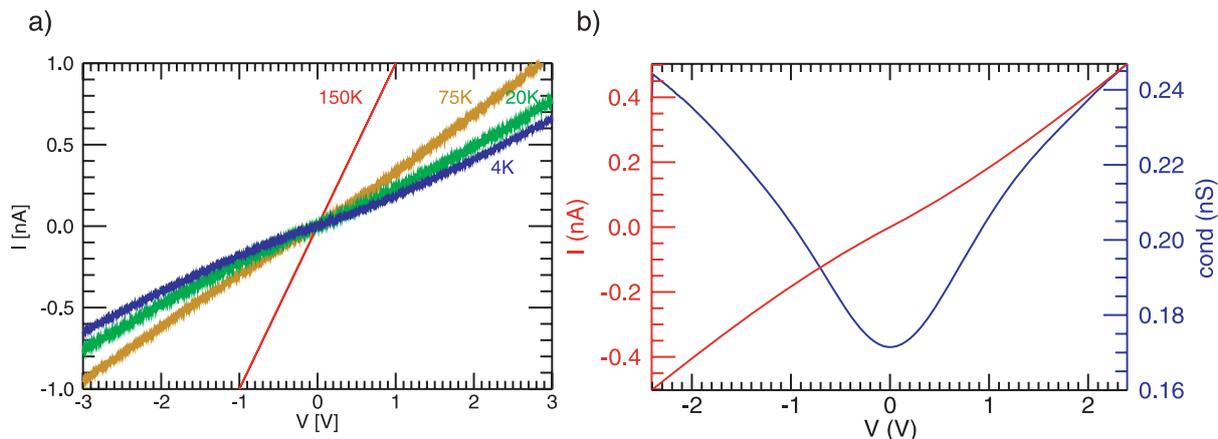


Figure 3. (a) I - V curves of a device with an area of $360 \mu\text{m}^2$ taken at various temperatures without light irradiation. (b) I - V curve and dI/dV curve of a typical junction. The current values have been smoothed digitally over 30 points, in order to be able to take the numerical derivative (shown as dI/dV curve).

the two electrodes is less than $1 \text{ k}\Omega$, I - V curves are completely linear and do not change when the temperature is changed.

Samples with smaller areas of overlap show a different behavior. A typical I - V curve and dI/dV curve taken from such a device at a temperature of 5 K are shown in figure 3(b). The following discussion of the results will concentrate on measurements performed on this device. The I - V curves are slightly nonlinear with a decrease in slope around zero bias ($V = 0$). Such characteristic curves are well known from transport measurements through molecules with a HOMO-LUMO gap, for example transport measurements through DNA molecules studied with STM [26] or mechanically controlled breakjunction [27] techniques. Since the physical origin for such a behavior can be manifold, such curves have been termed ‘s-shaped’-curves.

The behavior of all junctions with a similar area of overlap is comparable. The total conductance of a single junction increases with the area of overlap but the overall shape of the curves remain the same. The suppression of conductance around zero source-drain bias is generally weak, the conductance drops only by about 30% even at the lowest temperatures of 5 K . Increasing the temperature leads to an overall increase of the conductance and a decrease of the nonlinearity of the I - V curve. This behavior is demonstrated in figure 3(b).

4. Discussion

The HOMO-LUMO gap of alkane molecules is large (of the order of 8 eV) due to the σ -bonds constituting the molecules [22]. Therefore an alignment of the HOMO or the LUMO with respect to the Fermi energy E_F of contacting metals cannot be expected. The generally anticipated conduction mechanism is thus pure tunneling, the role of the molecules being that of an effective tunneling barrier with the length of the molecule d (1 nm in the case of the decanedithiols measured here). Our experimental results do not agree at all with this expectation, the temperature dependence and the low-bias conductance both indicate deviations from the tunneling at much lower energies than expected from the HOMO-LUMO gap. In order to

understand the origin for these deviations we tried to apply several models to our data, which arise from different, already known, transport mechanisms.

It is apparent from the temperature dependence that pure tunneling cannot explain our data. Tunneling is a purely stochastic process and therefore independent of temperature. Tunneling can be either linear in source–drain voltage V for small applied voltages across the tunnel barrier or, if the bias voltage starts to affect the barrier height, obey the Fowler–Nordheim approximation:

$$I \propto V^2 \exp\left(-\frac{4d\sqrt{2m}\Phi^{3/2}}{3e\hbar V}\right), \quad (1)$$

with Φ being the work function of the metallic electrodes, m the effective mass of the electrons ($1.1m_e$ for bulk gold can be assumed here). We verified that none of these functional dependences alone describe the measured data well, the results of these fits are shown in figure 4(a). If the tunnel height of the tunnel barrier is of the order of the thermal energy, thermal excitations can lead to transport across the barrier. In this regime, the thermionic emission, the current through the junction should be described by the following law:

$$I \propto T^2 \exp\left(-\frac{\Phi - e\sqrt{eV/4\pi\epsilon d}}{k_B T}\right). \quad (2)$$

This dependence can be tested by plotting $\ln(I/T^2)$ versus $1/T$ and $\ln(I)$ versus \sqrt{V} . The results of these tests are summarized in the insets of figures 4(b) and (c).

These two models, which would be expected from the molecular properties of the alkane molecules, do not describe our data well either. A similar situation was found in [24] (on C_{20} molecules, which were deposited using a Langmuir–Blodgett technique) and in [25] (on alkanes with various chain lengths) as well as in [28] on self-assembled monolayers of alkanedithiols contacted through small openings in a silicon nitride membrane. While Stewart *et al* point out the discrepancy from simple models and suggest a heuristic model (see below), this fact is not discussed by Wang *et al*, although the deviations are clearly seen in the I – V curves, which display a pronounced change in slope around 0.2 V as in our data.

The experiments which were presented in [25] were performed on isolated molecules. Experiments by Stewart *et al*, which were done on monolayers, could not be explained by any consistent model [24].

Therefore for these experiments a heuristic fit was attempted. The authors could fit the data with the following expression for the I – V curves

$$I \propto \exp\left(f(V) \left(T_1 \coth\left(\frac{T}{T_1} - T^*\right)\right)\right) \quad (3)$$

with

$$f(V) = 2.3\alpha \left(\sqrt{V} - \sqrt{V^*}\right). \quad (4)$$

Figure 4(d) shows the temperature dependence of the current in our sample at various source–drain voltages in a semi-log representation. A fit to equation (3) is shown as well. It is apparent that especially the low-temperature behavior of our samples deviates strongly from the behavior found in [24]. Fits to equation (4) also describe the dependence of the current on the source–drain bias only poorly, as shown in figure 4(e).

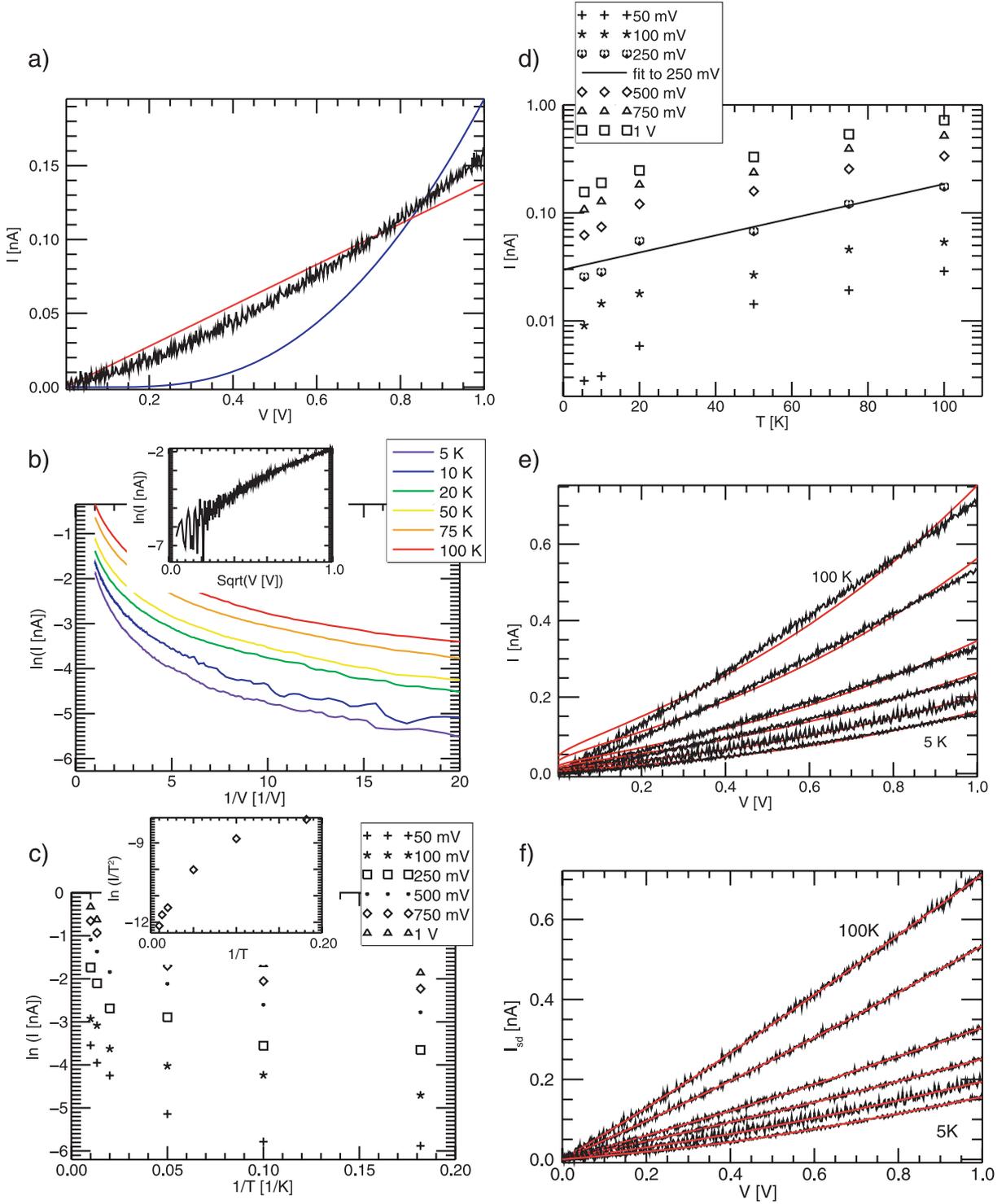


Figure 4. (a) Linear and Fowler–Nordheim fits to an I – V curve measured at 5 K. (b) $\ln(I)$ versus $1/V$ and (c) $\ln(I)$ versus $1/T$. Insets show $\ln(I)$ versus \sqrt{V} and $\ln(I/T^2)$ versus $1/T$. (d) Temperature dependence and (e) I – V curves plotted with fits according to equations (3) and (4). (f) I – V curves and fits to equation (7).

Experiments on isolated molecules could be explained by configurational changes of a single molecule contacted by STM [25]. The energy barrier for changes between different molecular configurations can be thermally overcome, thus leading to a dependence of the current on the temperature as:

$$I(T) \propto \exp(-E_{gT}/k_B T). \quad (5)$$

The energy which activates the system to a more conductive state, could in principle be provided by the source–drain voltage V , as well. The mechanism then leads to a similar dependence of the current on the voltage

$$I(V) \propto \exp(-E_{gV}/eV). \quad (6)$$

If the coupling of the thermal energy E_{gT} and the electrical energy E_{gV} to the molecular states are similar, both energies should be comparable. Figures 4(b) and (c) show Arrhenius plots of I versus $1/T$ and $1/V$, both indicating that a pure activation assumed by expressions (5) and (6) does not describe the experimental data well.

On the other hand, the molecules are not long enough (1 nm) to completely suppress tunneling. It can therefore be expected that at low temperatures a large contribution of the overall current originates from pure tunneling between the metallic electrodes. At elevated temperatures activated processes can add a second current contribution thus leading to a strong temperature dependence of the current. The I – V curves resulting from such a behavior will exhibit two contributions as well. An appropriate model would therefore be:

$$I(V) = \frac{1}{R_0} V + I_1 \exp(E_{gV}/eV). \quad (7)$$

Fits of the I – V curves to this function are shown in figure 4(f). Although the agreement is quite good, it has to be noted that the energy scale resulting from these fits (of order 1 eV) is much larger than the energy scale which is inferred from the temperature data (a few meV).

It is clear from the discussion above that no standard model alone can fit our data well. The reason for discrepancies to the data presented in [25] is certainly given by the fact that an ensemble of molecules is measured instead of single molecules. This also leads to a much larger overlap between the top and bottom electrode. Therefore contributions of tunneling currents, either through the molecules or through vacuum states, will be much more important in our contacting technique. On the other hand the distance between the bottom and the top electrode is only determined by the length of the molecules and not controlled, as it is in a STM setup. Therefore changes of the molecular length will also lead to changes in the tunneling distance. This can lead to an increase of the current with increasing temperature. The main difference to measurements shown in [24] is given by the length of the contacted molecules. Molecules in our measurements are about half as long as those characterized by Stewart *et al.* This also leads to an increased influence of the tunneling contribution to the overall current.

Therefore the following scenario seems to be appropriate to describe our data: the main contribution to the current stems from tunneling between the two electrodes. Since the energy scale for this process is given by the work function of bulk gold (5.1 eV) we can assume that the I – V curves are linear. In addition to this we see transport through the molecules; the energy scale for this process is given by the offset of the HOMO of the alkane molecules with respect to E_F . I – V curves measured in this regime will be described by relation (6).

In order to test this hypothesis we subtracted the linear contribution of the I – V curves in a first step and analyzed the remaining nonlinear part. The linear part of the I – V curves

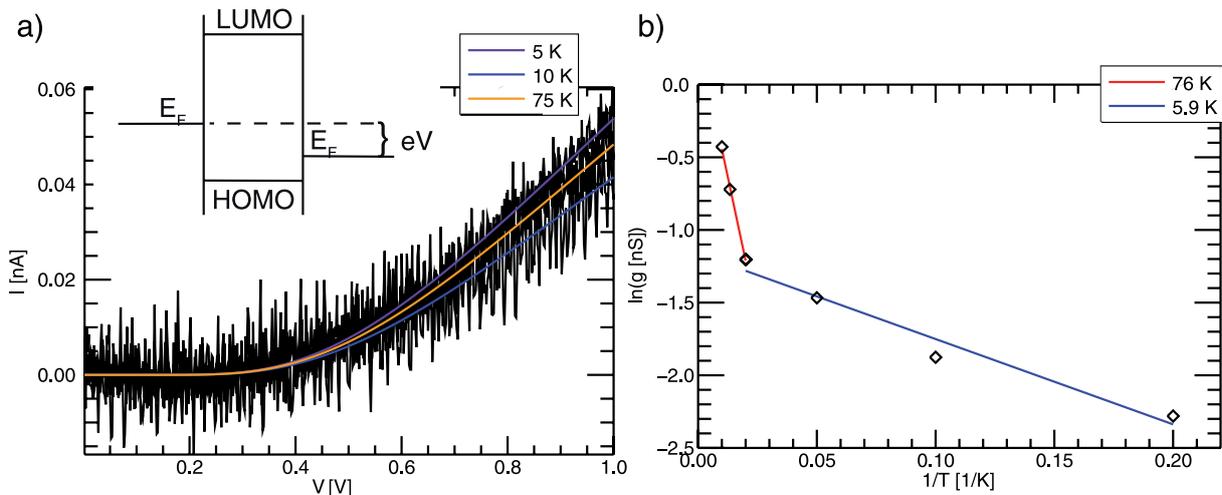


Figure 5. (a) A selection of I – V curves after subtraction of a linear background. The curves can be well fitted with the expression given in (7), the relevant energy scale is approximately 2 eV. It can also be seen that all curves are—within the error bars given by the electrical noise—collapsing to a single curve. (b) Arrhenius plot of the conductance calculated from the linear fit to the initial I – V curves. Two regimes can be identified, with slopes of 76 and 5.9 K, respectively.

was identified by fitting the low-voltage regime to a straight line. This fit was then subtracted from the whole curve. The result of this procedure is shown in figure 5(a). It is striking that all curves taken at various temperatures collapse onto a master curve, within the measurement accuracy. The remaining variations do not depend on the temperature in a systematic way, but seem to arise from the uncertainty in the determination of the linear part. Additionally shown are fits to expression (6), which show that after subtraction of the linear part, the data indeed follow an exponential behavior. The energy scale determining this behavior is 2 ± 0.2 eV, determined from the fit parameters. This gives an estimate for the offset of the HOMO of the alkane molecules from E_F of the contacting gold in our configuration. The large value of this energy also explains why no temperature dependence can be seen in this contribution to the current, since the change in thermal energy between 5 and 100 K corresponds to only a change of 10 meV in energy. Thus electrons cannot be thermally excited into the HOMO.

Measurements in [25] show that conformational changes of the alkane molecules can be thermally excited. In our configuration such a conformational change will always influence the distance between the metallic electrodes and therefore the tunneling distance. An estimation of this influence is deduced from the temperature dependence of the linear contribution to the current. This is obtained by plotting the slope of the linear fit to the current logarithmically as a function of the inverse temperature (figure 5(b)). Two regimes can be identified by the slope of this curve, one with a slope of 76 K and another (at lower temperatures) with a slope of 5.6 K. This is in agreement with Hartree–Fock calculations of the tunneling probability along alkane molecules presented in [25], which also show a decrease of this slope with decreasing temperature. We therefore conclude that our data indeed indicate transport through alkane molecules, which is determined by two mechanisms, temperature-independent transport through

molecular states and temperature-dependent tunneling between the electrodes. The absence of a prominent temperature dependence of the current in [28] can qualitatively be explained by the more rigid sample design, which suppresses thermal changes of the contact geometry.

5. Conclusion

A novel method for the fabrication of metal–molecule–metal contacts was presented based on the micro-contact printing technique. The technique results in reliable, long-lived devices with reproducible transport behavior. The reproducibility is demonstrated by small variations of current–voltage characteristics of different contacts and by comparison to results with different contact techniques from other groups. We used this technique to characterize decanedithiol molecules electrically, revealing a transport mechanism which consists of two main contributions: tunneling between the metallic electrodes (either through the molecules or vacuum states), which becomes temperature dependent because of conformational changes of the molecules with temperature, and transport through molecular states, which is temperature independent at the temperatures used in this study (5–100 K). This is in agreement with previous experiments using different techniques, which showed a similar complexity of the transport behavior of alkane systems, although different in detail. The μ TP technique allows use of various metals and molecular endgroups and will therefore be used in the future to test different combinations.

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