Chapter 8

Integration and up-scaling of large-area molecular junctions

Abstract
The route towards applications for molecular electronics requires a technology for fabricating molecular junctions with excellent reproducibility. Furthermore, integration of molecular electronics is encouraged when the processing of the molecular junctions is based on standard CMOS technology. Pursuing a complementary fabrication of both technologies might even result in hybrid semiconductor-molecular integrated circuits. Incorporation of an organic conductive layer on top of a self-assembled monolayer in large-area molecular junctions prevents direct top-down short circuit formation, resulting in a yield of almost 100 %. In this chapter the technology is presented to integrate and up-scale large-area molecular junctions onto 6-inch wafers, where over 22,000 junctions are fabricated simultaneously. Consequently, important parameters for molecular electronic devices, like device yield and spread in resistance, are automatically obtained. We show that our technology allows for unprecedented reproducibility, reliability and scalability in the field of molecular electronics.

REFERENCES
8.1 Introduction

Device integration is a major bottleneck for future applications of nanodevices and passive nanostructures [1]. Therefore, potential applications in the near future based on molecular electronics are limited by the quest for suitable molecules with specific electronic functionalities [2] but also, and perhaps all the more, by a reliable technology to fabricate and integrate reproducible molecular junctions with a high yield. In the previous chapters discrete devices were fabricated by the incorporation of an organic conductive layer on top of a self-assembled monolayer to prevent direct top-down short circuit formation, resulting in a yield of almost unity [3,4]. Although all processing techniques used for the fabrication of the large-area molecular junctions are fully compatible with standard IC fabrication processes, certain steps in the processing need to be done differently when the molecular junctions are integrated. For example, as described in chapter 2, the fabrication of the Au electrodes of the discrete devices on 4-inch wafers is done by thermal evaporation through a shadow mask. Shadow mask evaporation strongly hinders the decrease in lateral size of the Au leads, the accuracy of top-bottom electrode alignment and the automation of the fabrication process. Therefore, bottom and top electrodes need to be defined by photolithography when the technology is integrated. This chapter will present the technology to integrate and up-scale the discrete large-area molecular junctions of the previous chapters onto 6-inch wafers, where over 1000 devices (or 22,000 molecular junctions) are fabricated simultaneously. The outcome of experiments on such a large number of individual devices provides us with important parameters like device yield and spread in resistance, with a proper statistical value. We show that our technology allows for unprecedented reproducibility, reliability and scalability.

To benchmark this technology for the fabrication of molecular junctions, series of alkanemonothiols and alkanedithiols with different lengths are used to assemble the molecular monolayer. As described in chapter 1, alkane(di)thiols are a perfect benchmark system for any new technology in molecular electronics due to their well-defined monolayer formation and close packing on Au, which, under applied bias, results in a tunneling current that decreases exponentially with increasing molecule length. Important process parameters within the technology, in particularly the self-assembly of the molecules, have been investigated thoroughly using numerous surface characterization techniques. The statistics and reliability of the electrical measurements provides us with a better understanding of the fundamental molecular charge transport properties in molecular devices. Factorization of charge transport is demonstrated with a dependence on process parameters, possibly reconciling current literature data in molecular electronics [5].

Finally, integration is crucial for any future application, and is demonstrated by connecting 200 molecular junctions in series. The use of functional molecular entities within this technology is envisaged for future applications.
8.2 Fabrication and analysis of integrated large-area molecular junctions

In the previous chapters the fabrication of discrete large-area molecular junctions was presented, which resulted in a device yield of nearly 100%. The key to this high yield is the incorporation of the highly conductive polymer PEDOT:PSS. This polymer interlayer between the evaporated Au top electrode and the self-assembled monolayer blocks the incoming Au atoms during evaporation and prevents short circuit formation, as commonly observed when metal atoms are directly evaporated on top of a self-assembled monolayer [6]. The high yield obtained for discrete devices makes the technology a promising candidate for the road towards potential applications, since a high yield of working devices is the main requirement for integrating any technology. The discrete devices of large-area molecular junctions, Au/SAM/PEDOT:PSS/Au, were fabricated in vertical interconnects in an insulating photoresist matrix, as shown in Figure 8.1.

![Schematic representation of the discrete large-area molecular junctions](image)

**Figure 8.1** Schematic representation of the discrete large-area molecular junctions, as presented in the previous chapters of this thesis. The basic cross-sectional layout for these molecular junctions is the metal/SAM/conducting polymer/metal stack configuration.

In this chapter, a 6-inch technology is presented to integrate these large area molecular junctions with lateral dimensions down to 1 µm. To benchmark the technology, self-assembled monolayers of alkane(di)thiols were used as the molecular component within the molecular junction. In contrast to the fabrication of the discrete devices, both bottom and top electrode have to be structured by photolithography when the technology is integrated. The implementation of additional processing steps needs to be investigated and optimized to realize an integration of the technology. In detail, a proper quality of the bottom electrode, the self-assembled monolayer and the top contact needs to be pursued, as these parameters strongly determine the electrical characteristics of the device (reference 5, and references therein).
The process flow chart for a 6-inch technology for integrated large-area molecular junctions is divided into 3 parts:

1. The fabrication of the bottom electrode and the definition of vertical interconnects.
2. Assembling a densely packed and well-ordered monolayer, *i.e.*, the molecular component that determines the electrical output characteristics.
3. Fabrication and defining the PEDOT:PSS interlayer and Au top electrode.

The quality and the properties of each step were characterized using a variety of techniques like Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), Contact Angle goniometry (CA), Ellipsometry, Kelvin Probe measurements (KPM), Focused Ion Beam Transmission Electron Microscopy (FIB-TEM), and Low-Energy Ion Scattering (LEIS). Discussing the results of all the analytical studies performed is beyond the scope of this thesis. These analyses were performed to come to a reliable process flow chart for reproducible integrated molecular junctions.

### 8.2.1 Bottom electrodes and via definition

**Figure 8.2** Process flow chart for structured Au bottom electrodes and via definition. (a) 50 nm Au layer is deposited on top of a 2 nm Ti adhesion layer on a 6-inch Si/SiO$_2$ wafer. (b,c) A positive photoresist is deposited onto the Au and structured by photolithography. (d) The structured Au bottom electrode is obtained by etching away the exposed Ti/Au layer. In addition the cross-linked photoresist is removed. (e,f) A negative photoresist layer is spincoated, which is patterned by photolithography. The non cross-linkable photoresist is developed to define the vertical interconnect area (via).
After having established a low surface roughness of 50 nm sputtered Au (~ 0.6 nm RMS for a 1 µm² area), the bottom electrode has to be structured to realize the integration of molecular devices on 6-inch wafers. The structuring of the bottom electrode was performed by photolithography as depicted in Figure 8.2 (a–d). On top of the sputtered Au layer, a positive photoresist is spincoated with a layer thickness of 500 nm and by photolithography the desired pattern is created in the photoresist. The Au layer is etched away with gold etchant TFA (KI/I₂) in H₂O (1:3). Etching the Ti adhesion layer is done with a wet etch of H₂O/HNO₃/HF, resulting in the patterned bottom electrodes. Subsequently, the protecting photoresist on top of the bottom electrodes is stripped with acetone. Finally, organic residuals on the bottom electrode were removed with fuming HNO₃, and rinsed thoroughly with de-ionized water.

In the following processing step the vertical interconnects (vias) are defined, in which the monolayer will be self-assembled on the bottom electrode. The vertical interconnects are fabricated within an insulating photoresist matrix. Instead of using photoresist for the insulating layer, inorganic isolators like SiO₂ or Si₃N₄ can be used [6,7]. The requirements for the vertical interconnects are the same as for the discrete molecular junctions, as described in paragraph 2.2.2., i.e., preferably a wedge-shaped profile of the via and the surface of the Au bottom electrode should be indistinguishable from a clean as-deposited Au layer. The vertical interconnects were fabricated in a negative photoresist as insulating matrix (MA1407, micro resist technology GmbH). MA1407 is a Novolac based photoresist, which can be developed in aqueous media and baked at 200 °C to improve on chemical resistivity. This negative photoresist was spincoated on top of the structured Au bottom electrodes and by photolithography the vertical interconnects were created, as depicted in Figure 8.2 (e) and (f). The unexposed regions of the photoresist were developed, resulting in vias ranging from 1 to 50 µm in diameter.
8.2.2 PEDOT:PSS and top electrodes

The top electrode is formed by the conductive polymer PEDOT:PSS and a Au layer, which are structured using photolithography. The process flow chart for the top electrode is schematically depicted in Figure 8.3. On top of the SAM layer PEDOT:PSS is processed, which acts as the conductive layer that protects the SAM upon vapor deposition of the Au top electrode. A wide range of commercially available PEDOT:PSS is on the market from different companies with different conductance properties. A highly conductive PEDOT:PSS layer is required, since the active component is a self-assembled monolayer of only a few nanometers. Therefore, PEDOT:PSS with a ratio of 1:1 is used. In addition a high boiling solvent, like DMSO, is added (5 vol %) to increase the conductivity. The PEDOT:PSS is dried in vacuum at room temperature for ~ 1 hour.

After coverage of the SAM by the PEDOT:PSS layer, the top contact is formed by vapor deposition or sputtering of a 150 nm layer of Au. The top contact is then structured by photolithography. As the stack contains the vulnerable SAM and a water-soluble PEDOT:PSS layer, the fabrication of the top contact requires a dry process at room temperature or low temperatures, as demonstrated in chapter 2 and 6. A positive photoresist is spun on top of Au, and dried in vacuum at room temperature. Subsequently, photolithography is performed and the exposed Au is removed by dry Argon etching. To prevent lateral conductive pathways through the
PEDOT:PSS from the top to bottom electrode, the redundant PEDOT:PSS is etched using a STS Reactive Ion Etcher (RIE) with a 30 Watt O2/N2 plasma. Finally, the protective photoresist is stripped with acetone. Figure 8.4 shows the final result, a fully processed 6-inch wafer (a), the layout of Kelvin structures (b) and strings, i.e., a large number of devices in series (c).

Figure 8.4  (a) A 6-inch wafer is shown after fabrication, containing 62 dies. Every die contains a large inventory of devices, among which are 4-point probe Kelvin structures (b) and strings, i.e., a large number of devices in series (c).
To analyze the quality of all deposited layers in the vertical interconnect, Focused Ion Beam Transmission Electron Microscopy (FIB-TEM) was used. A FIB uses Ga ions to remove material with a very high spatial resolution. A thin slice of the sample is cut out and transferred to the TEM. Cross-sections of completed molecular junctions with different via dimensions were analyzed with TEM. The cross-section was studied by tilting the samples by 45°. In Figure 8.5 two FIB-TEM images show the cross-sections for the left and right side of a 10 µm via. Due to the difference in electron density, the SiO$_2$ layer, Au bottom electrode, photoresist layer, PEDOT:PSS and Au top electrode are visible. Unfortunately, the SAM layer cannot be distinguished between the Au bottom electrode and the PEDOT:PSS layer. The edges of the vertical interconnects have a positive slope of about 30 degrees, which is suitable for the processing of the PEDOT:PSS to fabricate a homogenous top contact. This slope of the resist profile was confirmed by AFM measurements.

![FIB-TEM images of the cross-section of a large-area molecular junction. Separate layers of SiO$_2$, Au, photoresist, PEDOT:PSS, and Au/Pt are visualized.](image)

**Figure 8.5** FIB-TEM images of the cross-section of a large-area molecular junction. Separate layers of SiO$_2$, Au, photoresist, PEDOT:PSS, and Au/Pt are visualized.
8.3 Results on integrated large-area molecular junctions

We developed a 6-inch wafer technology for large-area molecular junctions, which yields fully patterned process evaluation modules (PEMs) designed for automated measurements (Figure 8.4). These evaluation modules contain numerous structures, typical for large scale integrated circuits, to monitor various steps within the process technology. Vertical interconnects (vias) were used for the electrical characterization of the molecular junctions.

Vias are present in the so-called 4-point probe Kelvin structures, see Figure 8.4 (b). The electrical characterization of large-area molecular junctions was performed using these 4-point probe Kelvin structures with diameters ranging from 1 up to 50 micrometer. The 6-inch wafer contains 62 identical dies. Each die contains 8 Kelvin structures with varying surface area. Thus each wafer produces nearly 500 different devices for a certain molecular junction, and provides us with proper statistics about the electrical characteristics of the self-assembled monolayer. The resistance of the Kelvin structures is measured at 0.5 V with an automated probing set-up. The complete $I-V$ characteristics from –1 V up to +1 V were recorded for Kelvin structures with a diameter of 10 µm. For these tunnel junctions the current changes from a linear increase with applied voltage at low bias (up to 100 mV) to an exponential increase of the current with voltage at higher bias. Therefore, we use the ratio of the resistances at 10 mV and 0.5 V as a measure of the non-linearity for the charge transport through a self-assembled monolayer. The transversal conductivity is displayed as a normalized resistance value, where the resistance at a specific voltage is multiplied with the surface area.

Integration is benchmarked by fabricating large numbers of molecular junctions in series in the so-called string structures, Figure 8.4 (c). Each die contains several different types of strings. The strings contain 20, 40, 100, and 200 molecular junctions in series with a diameter varying between 1, 2, and 5 µm. Finally, additional structures were present on each process evaluation module to monitor the process technology. Typically, we used so-called van der Pauw and leakage structures to inspect the quality of the bottom and top contact, as well as the bond pads and leakage currents.

The use of process evaluation modules allows us to obtain information on reliability, reproducibility, scalability and uniformity all at once. The amount of Kelvin and string structures on a wafer is sufficient to obtain statistics about the process technology and the molecular properties. Importantly, the fabrication of these molecular junctions is based on standard technology. Automated equipment and routine based procedures under controlled conditions were used. Therefore, the fabrication of these 6-inch wafers was done in a reproducible way. The combination of these aspects is crucial in the development of a technology to fabricate large-area molecular junctions.
8.3.1 Large-area molecular junctions in 4-point probe Kelvin structures

After establishing the process flow chart, the molecular junctions were fabricated and characterized by $I-V$ measurements. We investigated the electrical performance of our molecular devices with respect to different process parameters within our technology. The most important process parameters are the type of PEDOT:PSS (conductivity, formulation, additives), and the molecules (mono or dithiols, and molecule length). Unless stated otherwise, the measurements were performed in air at room temperature. Additional measurements were performed in vacuum to check the influence of water and oxygen. About 20 Kelvin structures per wafer were measured manually in a vacuum of $1 \times 10^{-7}$ mbar. Similar $I-V$ characteristics were obtained for these molecular junctions when measured in air or under vacuum with the exception that the absolute normalized resistance ($R_S$) value in vacuum of $10^{-7}$ mbar slowly drops in time, as shown in chapter 2. The $R_S$ value equilibrates roughly after a few hours to a constant value, which is a factor ~2 lower compared to the original $R_S$ value in air. This factor was observed for all molecular devices irrespective of the molecular length. Even for PEDOT:PSS-only devices similar results were obtained. Likely, this effect is due to water absorbed by the PEDOT:PSS under ambient conditions.

![Figure 8.6](image_url)  
**Figure 8.6** Resistance values at 0.5 V bias for a C20-monothiol SAM in Kelvin structures of 1–50 µm in diameter, plotted for 57 dies on a 6-inch wafer. The molecular junctions were fabricated using MAI-407 as the photoresist and AGFA ICP new type PEDOT:PSS 1:1 with 5% DMSO.
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Figure 8.6 depicts the resistance at 0.5 V bias for Kelvin structures with diameters ranging from 1–50 µm, containing eicosanethiol (HS-C$_{20}$H$_{41}$, C20-monothiol) as the self-assembled monolayer and MA1407 as the photoresist. All Kelvin structures with a different vertical interconnect area show a more or less constant value throughout the whole wafer. The resistance increases with decreasing diameter. For devices with a diameter of 50 µm the resistance at 0.5 V is about 10 kΩ, while for the Kelvin structures of 2 µm in diameter the resistance at the same voltage is about 2 MΩ. The absolute resistance value at 0.5 V bias varies within a factor 3 to 4 for a certain device area for all Kelvin structures. The error of our electrical data can be expressed by the standard deviation. Occasionally, a low resistance value is obtained, like the 50 µm Kelvin at die number 32 in Figure 8.6. Furthermore, due to a fabrication failure at the top side of this wafer, 57 dies are shown instead of the total 62 dies. The remaining 5 dies were short circuited due to this fabrication failure. The Kelvin structures with a diameter of 1 and 2 µm are displayed to show that we are able to fabricate devices down to these small lateral sizes. However, these structures deal with some reliability issues concerning the lithography, and data extracted from these small vias have to be taken with caution.

Figure 8.7  The normalized resistance values ($R_S$) at 0.5 V for a C20-monothiol SAM of ~ 400 Kelvin structures ranging from 2 up to 50 µm in diameter are plotted for 57 dies. Clearly, rescaling the data from Figure 8.6 to $R_S$ values results in a perfect overlap for different device areas and an excellent reproducibility is obtained.
When the resistance values shown in Figure 8.6 are multiplied with the device area, the normalized resistance value ($RS$) is obtained. The $RS$ at 0.5 V is expressed in $\Omega \mu m^2$ and is presented in Figure 8.7 for all ~ 400 Kelvin structures containing a C20-monothiol SAM. Irrespective of the diameter of the contact hole, or device area, the same normalized resistance is obtained for the large-area molecular junctions, with an average value at 0.5 V of $RS \approx 1 \times 10^7 \Omega \mu m^2$. This clearly demonstrates that the $I-V$ characteristics of the large-area molecular junctions per unit area are perfectly overlapping, although the difference between the largest and the smallest device area is more than 2 orders of magnitude.

To study the length dependence of these large-area molecular junctions processed with automated fabrication methods, alkanemonothiols with a different length, e.g., C14, C16 and C18, were incorporated in these molecular devices as the self-assembled monolayer. In a similar way as for the C20 monothiol devices, the resistance at 0.5 V for the different Kelvin structures was measured. In Figure 8.8 the averaged $RS$ values at 0.5 V are presented for the alkanemonothiol devices, ranging in length from C14 to C20. The normalized resistance values are averaged over all dies. In addition, an error bar is given, showing the standard deviation. The yield and scalability with area for these devices are comparable. Virtually all Kelvin structures reveal the same electrical characteristics. The normalized resistance values for a specific molecule are similar within the error of measurement. At 0.5 V bias the average normalized resistance values for C14-, C16-, C18- and C20-monothiol are $8 \times 10^4$, $6.2 \times 10^5$, $4.2 \times 10^6$ and $1.2 \times 10^7 \Omega \mu m^2$, respectively. When the molecular length is increased from C14 up to C20, and thus the SAM layer thickness, an exponential increase in resistance is observed, as shown in Figure 8.8 and Figure 8.9. In addition, the measurement for a PEDOT:PSS-only device is shown. The resistance of a PEDOT:PSS-only device is much lower than the molecular junctions with an $RS$ value of $\sim 3 \times 10^3 \Omega \mu m^2$, for larger device areas. The trend for the PEDOT:PSS-only devices, where an increase of the resistance is observed with decreasing device area, is likely related to an area dependent wetting of PEDOT:PSS on gold in vertical interconnects.
Figure 8.8  Normalized resistance ($R_S$) at 0.5 V bias plotted as a function of the device diameter for molecular junctions with different molecule lengths. In addition, the Agfa type ICP new type PEDOT:PSS-only devices are presented. The value is averaged over all 62 dies. The error bar represents the standard deviation.

Figure 8.9  Histogram of the obtained $R_S$ data at 0.5 V for different molecular lengths. The distribution is presented by bar statistics, with one length of the SAM per wafer. The wafers have been made using Novolac-based photoresist, Agfa ICP new type PEDOT:PSS with 5% DMSO for a series of alkanemonothiols, ranging in length from C14 to C20. The $R_S$ data for PEDOT:PSS-only devices are also presented.
8.3.2 Integration of large-area molecular junctions

Besides discrete 4-point probe Kelvin structures discussed in the previous paragraph, the Kelvin structures were also connected in series to demonstrate the feasibility of integration. A large number of these Kelvin structures in series are known as strings, shown in Figure 8.4 (c). Every die on the 6-inch wafers contains strings which represent the combination of 20, 40, 100, and 200 Kelvin structures in series with via diameters of 1, 2, and 5 µm. A typical result for strings of 5 µm in diameter is shown in Figure 8.10, where a dodecanethiol SAM (C12-SH) is measured in combination with AGFA (high ohmic) PEDOT:PSS. The resistance at 0.5 V bias is plotted versus die number. For every die depicted in Figure 8.10 strings were measured with 20, 40, 100 and 200 devices in series. Therefore, the plot represents the data obtained on a total of 21,600 molecular junctions. An increase in resistance is, logically, observed with increasing number of devices in series.

![Figure 8.10](image_url)

Figure 8.10  Resistance obtained for a C12-monothiol SAM on different string structures with 20, 40, 100 and 200 devices in series. An increase in resistance is observed with increasing number of devices in series. AGFA high ohmic PEDOT:PSS is used.
To compare the resistance per molecular junction (or the normalized resistance of the different strings) the resistance has to be divided by the number of devices and multiplied with device area. This is shown in Figure 8.11. For almost all strings, we obtain the same $R_S$ value as measured for a single Kelvin structure with a diameter of 5 µm. Moreover, the $R_S$ values for all strings are similar, irrespective of the amount of Kelvin structures in series (e.g. 20, 40, 100, and 200). Again, these data show that the yield of working devices is close to unity when PEDOT:PSS is used as a conducting interlayer between the SAM and the Au top electrode. For the first time, integration of molecular junctions within an existing fabrication technology is demonstrated. The $R_S$ value for C12-monothiol in Figure 8.11 seems to contradict the data shown in Figure 8.8. However, the higher $R_S$ value for C12 in this plot is due to a different high ohmic PEDOT:PSS layer. This change in absolute value for resistance, by changing the processing parameters is the subject of the next paragraph.

**Figure 8.11** Normalized resistance ($R_S$) for a total of 21,600 junctions of C12-monothiol. When rescaled to the resistance of a single device, an excellent reproducibility is obtained on integrated large-area molecular junctions.
8.4 Influence of process parameters on charge transport

In the low voltage regime, the currents obtained for both the alkanemonothiol and alkanedithiol molecular junctions depend exponentially on the molecular length. This confirms that the currents are specific for the molecules in the junctions. Furthermore, it demonstrates that non-resonant, through-bond tunneling is the transport mechanism in these metal–insulator–metal junctions, since no temperature dependence was observed for lower temperatures, as demonstrated in chapter 3 and 6.

As described in chapter 1, the interface or the contact between the molecules and the electrodes can be a chemisorbed or physisorbed contact [8]. For a chemisorbed contact, the end group of the molecule is chemically bonded to the electrode. Although the formation is not fully understood yet, the Au–S bond is known to be a chemisorbed contact [8,9,10,11]. The difference between a chemisorbed contact and a physisorbed contact can lead to a change of a few orders of magnitude in conduction of the junction [12,13,14]. This difference in conduction between physisorbed and chemisorbed contacts can be understood by describing the current through the molecular junction with the Landauer formula [15,16,17,18,19], stating that the conductance $G$ is given by:

$$G = \frac{2e^2}{h} \times T_l \times T_{mol} \times T_r,$$

where $e$ is the elementary charge, $h$ Planck’s constant and $T_l$, $T_r$ and $T_{mol}$ are the transmission coefficients of the left contact, right contact and the molecule, respectively. It is clear from this formula that a change in transmission of one of the contacts will change the absolute value of the current with the same factor. Therefore, to make a good comparison between the obtained currents per molecular junction, the differences in transmission of the second contact must be accounted for. This was shown in chapter 1 by comparing all literature data from recent years on alkane(dithiol molecules [5]. All data could be categorized in only 3 resistance groups, depending on the nature of the contacts: a low resistance group with two chemisorbed contacts, a medium resistance group with one chemisorbed and one physisorbed contact and a high resistance group with an extra resistive barrier present in the molecular junction.

Since all processing described in this chapter was automated for the fabrication of integrated large-area molecular junctions, it offers the unique opportunity to study the resistance of the molecular junctions as a function of processing parameters such as the type of PEDOT:PSS used. A change in the type of PEDOT:PSS might lead to a change in transmission of the molecule/PEDOT:PSS interface and, thereby, to a change in resistance.
Figure 8.12 summarizes the results obtained on alkane(mono/di)thiol SAMs. Here the obtained \( RS \) values are rescaled to resistance per molecule (at the low voltage regime, < 0.1 V) by assuming a maximum grafting density of alkanethiols on Au(111) of \( 4.6 \times 10^{18} \) m\(^{-2} \) [8]. By changing the types of PEDOT:PSS, which differ in conductivity and viscosity, the transmission coefficient at the molecule/PEDOT:PSS interface could be altered. This transmission was also influenced by changing from alkane/dithiol SAMs to alkane/monothiol, as described in chapter 7. Simply stated, Figure 8.12 summarizes our results obtained with PEDOT:PSS top electrodes and is similar to Figure 1.17, in which the recent literature data on series of alkane(di)thiols was rescaled to that of a single molecule and plotted versus the number of carbon atoms in the alkane backbone of the SAM. The main and important difference between both graphs is that the data in Figure 8.12 are obtained in a large-area molecular junction configuration, where only the processing parameters are varied. As discussed in chapter 1, in literature an average decay constant \( \beta_N \) of 0.92 (per methyl group) is obtained, with no clear reason for the higher or lower values that different research groups find in similar experimental testbeds. For the data represented in Figure 8.12, an exponential increase in resistance is obtained with increasing molecule length, with an average value of \( \beta_N = 0.70 \pm 0.15 \). The lowest value of \( \beta_N = 0.57 \) was obtained for discrete
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devices with alkanemonothiol molecules with Baytron® PH 500 type PEDOT:PSS. The highest value of $\beta_N = 0.87$ was obtained for an alkanemonothiol SAM in combination with AGFA ICP new type PEDOT:PSS. Clearly, no relationship between $\beta_N$ and processing parameters is observed.

More striking is the shift in absolute value of resistance. For the first time we demonstrate factorization of electrical transport in one type of experimental testbed, by simply changing the nature of the contacts due to different processing parameters. By modifying the molecule/PEDOT:PSS interface the resistance of the molecular junction can be modified. Moreover, the absolute $RS$ value obtained for similar molecules is shown to be dependent on technology. Molecular junctions of alkane(di)thiols with a different type of PEDOT:PSS display the same exponential behavior but with a different pre-factor, see Figure 8.12.

In addition, the linear fits from Figure 1.17 to literature data on alkane(di)thiols are plotted. The dotted line represents the linear fit to all recent literature data with one chemisorbed and one physisorbed contact (medium resistance regime) and the solid line is the linear fit to the data from two chemisorbed contacts (low resistance regime, chapter 1). As demonstrated by the Landauer equation, the transmission through a monolayer depends on the two contacts and the properties (length, composition, etc.) of the molecule. The transmission through the contacts is minimized when two chemisorbed contacts between both electrodes and the molecules are present. In our technology the molecule/PEDOT:PSS contact is, most likely, a physisorbed contact. Logically, the data obtained on the discrete large-area molecular junctions is within the medium resistance regime, see Figures 1.15, 1.17 and 8.12. The data in Figure 8.12 obtained on the discrete molecular junctions with alkanedithiol molecules and Baytron® PEDOT:PSS type PHC V4 crosses the linear fit from Figure 1.17 to the complete medium resistance collection of data, due to a different $\beta_N$. However, by changing to alkanemonothiols in discrete devices and by changing the type of PEDOT:PSS to PH 500, the resistance can be decreased (see chapter 7). It was not possible to process the more viscous PHC V4 onto alkanemonothiol SAMs due to a bad wetting, resulting in PEDOT:PSS layers with many defects or pinholes and, therefore, in short circuit formation during the evaporation of the Au top electrode.

By further changing the type of PEDOT:PSS in the automated processing of large-area molecular junctions, the resistance can almost be decreased to a similar value of molecular junctions with two chemisorbed contacts. The fit to the low resistance collection of literature data with two chemisorbed contacts is given by the solid line in Figure 8.12. This fit is only slightly lower in resistance than the data obtained on alkanemonothiols and AGFA ICP new type PEDOT:PSS. This might imply that the electrical nature of the physisorbed top contact is almost comparable to the Au–S chemisorbed contact. Thus, for alkane(di)thiols a similar exponential length dependence is observed with a difference in the absolute value of the resistance, depending on the type of contacts between the molecules and the electrodes, and hence, on the technology used to fabricate the molecular junctions.
8.5 Summary and perspective

In this chapter a method to reliably fabricate integrated molecular junctions was presented using conventional technologies. Based on the technology for discrete devices, which was the subject of the previous chapters, an automated process was developed to fabricate over 22,000 large-area molecular junctions simultaneously on 6-inch wafers.

About 500 discrete 4-point probe Kelvin structures were fabricated with lateral dimensions down to 1 µm in diameter. A similar exponential increase in resistance with increasing molecule length was obtained and the normalized resistance, i.e., resistance of the junction multiplied by its area, was independent of the device area.

The feasibility of integration was demonstrated by fabricating a large number of molecular junctions in series in so-called string structures. With this method the yield and reproducibility of devices can be verified. An excellent yield of working devices was obtained for in total more than 21,000 junctions incorporated in strings. The reproducibility of the measured resistance for the different string lengths was excellent when rescaled to that of a single device.

For the first time the factorization of electrical transport was demonstrated within one experimental testbed. By changing process parameters like the type of PEDOT:PSS and/or molecules, a similar exponential length dependence was obtained but with a shift in absolute value of resistance. This clearly demonstrates the factorized nature of the tunneling transport through insulating molecules in molecular junctions. Furthermore, the obtained values for conduction of a specific molecular junction are dependent on the process parameters and can, therefore, be influenced by altering the technology to fabricate molecular junctions.

The integration of molecular junctions not only provides us with useful data like device yield, scalability and reproducibility, but offers routes towards applications in molecular electronics. When useful functional molecules will be designed and proven to show electrical functionality based solely on the molecular properties, this technology of integrating molecular junctions might pave the way to reliably assemble and interconnect large collections of functional molecular devices into the desired applications and/or, eventually, products. Since self-assembly is the key concept for ultimate low production costs, future electronics based on this concept might not only be smaller but, moreover, also a lot cheaper. Extremely low cost technology automatically implies that it will be used in any suitable application, at a colossal scale. Whether this will ever be reality is still uncertain. For now, the envisaged practical molecular electronics exists in the realm of thought and gives simply a lot of scientific pleasure to explore.
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