Chapter

7

Upscaling and integration of molecular junctions

Abstract

The ultimate target of molecular electronics is to combine discrete junctions with functional molecules into integrated circuits. The formation should be autonomous, hence by self-assembly. Charge transport perpendicular through self-assembled monolayers (SAM) has been investigated. Reliability and yield are the main issues. Electric shorts are formed upon vapour deposition of the top electrode. Short-circuit formation in discrete junctions can be prevented by applying a conducting polymer as barrier layer between the SAM and top electrode. Here, we present a technology to fabricate and integrate molecular junctions on 150 mm wafers. On a single wafer over 20000 molecular junctions are fabricated simultaneously. Integration is demonstrated in strings where up to 200 junctions are connected in series with a yield of unity. The statistical analysis on these molecular junctions, for which the processing parameters were varied and the influence on the junction resistance was measured, allows for the tentative interpretation that the electrical transport through these monolayer junctions is factorised.*

7.1 Introduction

Molecular electronics is the study of charge transport through single molecules or through a monolayer of molecules. The transport has been measured with a variety of techniques such as break junctions and conducting AFM. The current-voltage characteristics have shown useful phenomena such as bistability and rectification. The ultimate target of molecular electronics is to combine different types of functional molecules into integrated circuits of which the formation should be autonomous, hence by self-assembly.

The most studied systems in molecular electronics are self-assembled monolayers (SAMs) of alkane(di)thiols on gold. The resistance of gold / SAM / gold junctions is independent of temperature and exponentially dependent on the length of the molecule: the charge transport mechanism is non-resonant tunneling. A fair agreement between experimentally measured and theoretically calculated resistances can be obtained for molecular junctions with two chemisorbed thiol-gold contacts, taking into account that different contact geometries can lead to an order of magnitude difference in the computed results.

Progresses in the study of discrete devices, not to mention the integration into circuits thereof, is severely hampered by limited reliability, stability and, especially, yield. Electrical shorts in the SAM are readily formed upon vapour deposition of the top electrode. This has limited the diameter of the first reported molecular junctions to several tens of nm. Recently, a statistical analysis has been reported for manually measured molecular junctions with diameter of $2 \mu m$, which resulted in a yield of functional junctions of $1.2\%$ (156 out of 13440). The formation of shorts can be prevented by applying a conducting barrier layer between the SAM and the top electrode. A yield of unity has been reported for discrete large-area junctions by using the conducting polymer poly(3,4-ethylenedioxythiophene) stabilised with polystyrene sulphonic acid, henceforth abbreviated as PEDOT:PSS, as a barrier. To prevent cross talk, the discrete junctions were processed in vertical interconnect holes, lithographically defined in photoresist. Integration of discrete molecular junctions, however, requires additional patterning of both the bottom and top electrode as well as a second layer of interconnects. A bottleneck is the limited processing window; the process tem-
temperature had to be limited to only 50 °C to prevent deterioration of the SAM. Here we present a default process flow chart for processing simultaneously over 20000 molecular junctions on 150 mm substrates. Integration is demonstrated in strings where up to 200 junctions are connected in series. The layout allows semi-automatic measurements of electrical transport properties. The yield of unity for such a large number of identically processed junctions enables us to statistically analyse the reliability and reproducibility. Furthermore, the statistics obtained by varying the processing parameters and measuring the influence on the junction resistance, allows for the tentative interpretation that the electrical transport through these monolayer junctions is factorised.

### 7.2 Fabrication of molecular junctions

![Figure 7.1](image)

**Figure 7.1:** Schematic presentation of the process flow chart. a) deposition of Au bottom electrode; b) patterning Au bottom electrode using photolithography; c) spin coating of negative photoresist; d) photolithographically definition of vertical interconnect; e) SAM formation; f) spin coating of PEDOT:PSS; g) deposition Au top electrode; h) patterning of top electrode using photolithography.

The process flow chart is schematically presented in Fig. 7.1. We note that the junction resistance and scaling with surface area depend on processing conditions such as the type of photoresist, chemical composition of the monolayer, the use of surfactants, and drying conditions of the PEDOT:PSS. A detailed overview of experimental methods, technological details, junction characterisation and discussion is presented elsewhere. Here we discuss the default process flow chart in which alkane(di)thiols are used to benchmark the resistances versus literature data.
A 150 mm c-Si monitor wafer with a 1 µm thermally grown SiO₂ layer was used as substrate. A gold electrode is deposited and patterned by I-line projection photolithography to obtain the bottom contacts and the first layer of interconnects. Ti was used as an adhesion layer. The root mean square roughness for a 50 nm thick electrode amounted to 0.7 nm. To electrically isolate the junctions, processing is performed in vertical interconnects (vias) defined in photoresist. As default we use the epoxy based negative photoresist L6000.5. The diameter of the circular vias ranged from 1 to 50 µm. After developing the photoresist and cleaning of the gold, an alkanethiol monolayer is self-assembled from solution. The SAM coverage depends on temperature, concentration of the alkanethiol in solution and on the incubation time. To obtain a densely packed SAM we used 1 mM solutions and an incubation time of three days. To avoid any oxidation, the self-assembly took place in an inert atmosphere. As an empirical quality check for SAM formation we used complete de-wetting of the wafer by ethanol. The microstructure was investigated with AFM, XPS, Kelvin probe, ellipsometry and contact angle measurements. The process technology yields densely packed SAMs. On top of the SAM, a thin layer of PEDOT:PSS is spin coated. The electrically conducting PEDOT:PSS layer prevents the formation of top-down shorts upon deposition of a gold top electrode. The difference in surface tension between the hydrophobic SAM and the waterborne PEDOT:PSS prevents mixing thereof. We added 5% DMSO to PEDOT:PSS yielding a conductivity of 300 S/cm. Homogeneous PEDOT:PSS films were obtained when directly after spin coating the film is dried on a hot plate at 100 °C. However, SAMs of alkanethiols on gold are instable at elevated temperatures. To avoid any thermal deterioration of the SAM we limited the process window to 50 °C. Therefore, the PEDOT:PSS films were not dried at elevated temperatures but at room temperature in dynamic vacuum of 10⁻³ mbar. Unfortunately this drying procedure can lead to the formation of striations, i.e., radial thickness variations. Homogeneous PEDOT:PSS films could be made by careful adjustment of the processing conditions such as dispensing the solution over the whole 150 mm wafer and immediate drying of the film after spin coating. The wetting of PEDOT:PSS on hydrophobic surfaces can be dramatically improved by adding surfactants. Using a non-ionic, fluorinated surfactant, uniform PEDOT:PSS films
could be fabricated on SAMs with contact angles as large as $114^\circ$. The electrical resistance of the junction, however, is then comparable to that of PEDOT-only junctions, i.e. junctions without SAM. The gold top contacts and the second layer of interconnects are defined in the top gold electrode by photolithography and dry etching. To stay within the thermal budget and the top gold electrode layer was not sputtered but evaporated. Finally, by reactive ion etching with the patterned top gold electrodes as a self-aligned mask, the redundant PEDOT:PSS outside the junctions is removed to prevent cross talk. An optical micrograph

**Figure 7.2:** Cross section of a molecular junction. a) Optical micrograph showing a 4 point probe Kelvin leads to a circular molecular junction with a diameter of 50 µm. b,c) A (reconstructed) cross section of a molecular junction with a diameter of 10 µm. A 1 µm Pt layer is deposited on the region of interest to protect the sample during focused ion beam milling. Using 30 keV Ga-ions a hole is milled in the surface with one steep edge oriented perpendicular to the sample surface, and a step like construction at the opposite side. By tilting the sample at an angle of $45^\circ$ an image of the chemical composition is formed by detection of the secondary electrons. The SAM layer cannot be resolved. The image shows a conformal coverage of PEDOT:PSS in the via with a typical positive slope of $30^\circ$. An enlargement of the edges of the cross section of the via clearly demonstrating the PEDOT:PSS following the contours of the photoresist.

of a processed junction is presented in Fig. 7.2a. A cross section of a molecular junction is obtained with focused ion beam milling, as depicted in Fig. 7.2b and Fig. 7.2c. Both sides of the 10 µm junction are shown, and the chemical composition of the layers is indicated. From Fig. 7.2b and Fig. 7.2c the SAM
layer itself cannot be resolved, but the conformal coverage of the PEDOT:PSS following the contours of the via is clearly observed with the via having a typical positive slope of $30^\circ$.

![Statistical representation of junction resistances](image)

**Figure 7.3:** Statistical representation of junction resistances. (a) Automatically measured resistances of $C_{18}H_{37} – SH$ SAM junctions with diameter between 1 and 50 $\mu$m as a function of die number. (b) The normalised resistance in $\Omega \mu$m$^2$ as a function of die number.
7.3 Electrical characterisation of molecular junctions

Current density-voltage (J-V) characteristics have been measured of alkane-mono-thiol junctions \( C_nH_{2n+1} - SH \) with \( n = 8 - 22 \). The current densities for \( n = 8, 10 \) and 12 are indistinguishable from PEDOT:PSS-only junctions. Only for the longer alkane chains the electrical transport is unambiguously dominated by the SAM. The transport is symmetric and independent of temperature and at low bias the resistance is constant. With increasing bias the resistance decreases, resulting in non-linear J-V characteristics. Here we focus on the resistance at low bias. In Fig. 7.3a the junction resistance of \( C_{18}H_{37} - SH \) SAMs are presented as a function of diameter and die number. A wafer consists of 62 identical die structures. Each die contains via holes with diameters ranging from 1-50 \( \mu m \), as indicated in the legend. The normalised resistances in \( \Omega \mu m^2 \) are presented in Fig. 7.3b. Two dies, \#30 and \#51 are shorted due to an artefact of the automatic prober and, therefore, are omitted. Fig. 7.3 shows that the reproducibility is good, and that the yield is almost unity. Furthermore, the resistance scales with area as expected for a parallel network of single molecule junctions. Careful inspection of Fig. 7.3 reveals a slight increase of resistance with device area.

If we define a junction as being electrically shorted when its resistance is equal to that of the PEDOT:PSS-only junction, then experimentally we find a yield of either about zero or unity. A yield of zero is obtained for fluorinated alkanethiols, and for alkane-mono-thiols onto which the PEDOT:PSS layer is processed with the use of a fluorinated surfactant. The reason for the low yield might be intermixing of SAM and PEDOT:PSS. Typically, however, the yield is about unity. Apparently, the technology is robust against imperfections in the SAM. We note that the bottom gold electrode is polycrystalline with a root mean square roughness of 0.7 nm, which is only slightly smaller than the length of the molecules, about 2-3 nm. The self-assembled monolayer is ordered but not single crystalline and, therefore, the monolayer contains a large number of structural defects distributed on a length scale smaller that the diameter of the junctions. The defects, however, do not lead to shorts, since the difference in surface tension between the SAM and PEDOT:PSS results in a poor wetting, which prevents intermixing. Consequently, PEDOT:PSS forms a badly adhering, but continuous film on top of the SAM.
Figure 7.4: Resistance as a function of process parameters. The normalised resistance of alkane-mono-thiol $C_nH_{2n+1}-SH$ SAM junctions with $n = 14 - 22$, averaged over all junctions on the wafer, on a semi-logarithmic scale as a function of the number of carbon atoms in the alkanethiol backbone, $n$. The dotted line represents the PEDOT:PSS-only value. The diamonds represent devices made with the default process flow chart using L6000.5 as a photoresist and with PEDOT:PSS from Agfa (ICP new-type) that contains 5% DMSO. The dotted line represents the PEDOT:PSS-only value. The diamonds represent devices made with the default process flow chart using L6000.5 as a photoresist and with PEDOT:PSS from Agfa (ICP new-type) that contains 5% DMSO. The squares represent the averaged normalised resistances when using a different type of PEDOT:PSS, PH500 with 5% DMSO. The squares represent the averaged normalised resistances when using a different type of PEDOT:PSS, PH500 with 5% DMSO. The squares represent the averaged normalised resistances when using a different type of PEDOT:PSS, PH500 with 5% DMSO. The squares represent the averaged normalised resistances when using a different type of PEDOT:PSS, PH500 with 5% DMSO. The three solid lines represent a fit to the data points. The resistance of the alkanethiol SAM junctions increases exponentially with the length according to $R_S \sim \exp(\beta n)$ with decay constant $\beta$ calculated as 0.9 per carbon atom, which corresponds to 0.73 Å$^{-1}$. The absolute values differ by an offset set by the technology, but the decay constants are comparable.

The normalised resistance averaged over all junctions on the wafer is presented on a semi-logarithmic scale in Fig. 7.4 as a function of the number of carbon atoms in the alkanethiol backbone, $n$. The dotted line represents the PEDOT:PSS-only value. The resistance of the alkanethiol SAM junctions increases exponentially with the length according to $R_S \sim \exp(\beta n)$. The decay constant $\beta$ is calculated as 0.9 per carbon atom which corresponds to 0.73 Å$^{-1}$. We investigated the influence of processing conditions on the junction resistance
by varying the type of PEDOT:PSS and the type of photoresist. Default jurisdictions were processed with L6000.5 as a photoresist and with PEDOT:PSS from Agfa (ICP new-type) that contains 5% DMSO. Junctions were also made with PEDOT:PSS from H.C. Starck, viz. PH500. After adding 5% DMSO the bulk conductivity is comparable to that of Agfa, about 300 S/cm. The yield of the junctions is again unity, but typically the wafers show more inhomogeneities, like striations. The scaling of the resistance with surface area is less perfect and the standard deviations are slightly larger than with the default process flow chart.

The averaged normalised resistances are presented in Fig. 7.4 as the dots. The resistances are about a factor of 5 higher than with using the default process flow chart, but the exponential dependence on length and thus the decay constant is comparable. A similar behaviour is found when replacing the photoresist. Fig. 7.4 shows the averaged normalised resistances when using MA1407 as photoresist instead of the standard L6000.5. The absolute values are larger than using the default process flow chart, but the exponential dependence and decay constant are comparable.

$\alpha, \omega$-Alkane-di-thiols are used in breakjunctions and conducting AFM measurements to obtain strongly bound chemisorbed Au-S contacts on both sides of the molecule. Since we use a physisorbed top contact consisting of PEDOT:PSS, replacing monothiols by dithiols is therefore not expected to improve the contact. Even though the use of dithiols might complicate the technology because $\alpha, \omega$-alkane-di-thiols are more prone to oxidation and sensitive to moisture, we fabricated dithiol junctions using the default process flow chart. The normalised resistances are comparable to that of the monothiols. However, depending on the processing conditions the absolute values of the normalised resistance can easily be offset by a factor of thousand. The process technology developed comprises patterned interconnects in both top and bottom electrode layers. Therefore strings can be fabricated in which a large number of molecular junctions are connected in series. The layout of strings as presented in Fig. 7.5a, shows that up to 100 sections, each containing two junctions, can be integrated. The normalised resistance per junction is given as function of the number of junctions in Fig. 7.5b using the default process flow chart. The normalised resistance does not depend on the number of junctions indicating a reproducible process technol-
Figure 7.5: Integration of junctions in series. a) Layout of strings in which a number of molecular junctions are connected in series. Each section contains two junctions. b) The normalised resistance of alkane-mono-thiol $C_nH_{2n+1} - SH$ SAM junctions with $n = 14 - 22$, integrated in strings using the default process flow chart. The junctions are $5 \mu m$ in diameter. The normalised resistance per via is presented as function of the number of junctions. Values for discrete single junctions are included as filled symbols for comparison.

...ogy with yield of unity. Values of Fig. 7.4 for the discrete junctions are included for comparison as filled symbols and typically a fair agreement is obtained. The molecular junction presented here consists of a chemisorbed Au-S bottom contact, an alkane backbone and a physisorbed SAM / PEDOT top contact. The junction thickness is smaller than the electron coherence length and, therefore, Ohm’s law is not obeyed and the junction resistance cannot be obtained from a simple equivalent series circuit. The transport mechanism is non-resonant tunnelling and the transmission of a junction can for instance be modeled with a multi-barrier tunnel model\textsuperscript{21}. Here we take the resistance of a single molecule,
7.3. Electrical characterisation of molecular junctions

At low bias according to Seminario and Yan\textsuperscript{22} as being factorised by:

\[
R = \frac{h}{2e^2} T^{-1} = 12.9 k \Omega T_{Au-S}^{-1} T_{mol}^{-1} T_{SAM PEDOT}^{-1}
\]

(7.1)

where \( T \) is the overall transmission probability and where \( T_{Au-S}, T_{mol} \) and \( T_{SAM PEDOT} \) are the transmission probabilities for the Au-S bottom contact, the molecule itself and the SAM / PEDOT top contact, respectively. Rewriting in practical terms yields:

\[
R = 12.9 k \Omega r_{Au-S} r_{mol} r_{SAM PEDOT}
\]

(7.2)

where \( r_{Au-S}, r_{mol} \) and \( r_{SAM PEDOT} \) are unitless resistance contribution factors accounting for the resistance contribution of the bottom contact, the molecule and the top contact, respectively. The molecule contribution is given by \( r_{mol} = \exp(\beta n) \), where \( \beta \) is the decay coefficient and \( n \) the number of carbon atoms in the backbone. The SAM junction resistance, assuming that cooperative effects can be disregarded\textsuperscript{23}, is given by the single molecule resistance divided by the grafting density. The factorisation of the resistance explains both the length dependence and the offset due to processing. The bottom contact is a chemisorbed Au-S bond that is the same for all junctions. When we vary the length of the molecule the resistance increases exponentially with the number of carbon atoms in the backbone by \( R \sim r_{mol} = e^{\beta n} \). The value for the decay constant \( \beta \) is about 0.9 per carbon or 0.73 Å\textsuperscript{-1} assuming 1.22 Å for the length of a methylene group. When we keep the length of the molecule fixed and vary the processing of the top contact, then the resistance is proportional to the top contact resistance factor \( r_{SAM PEDOT} \). Plotting the junction resistances on a semi-logarithmic scale as function of the length of the molecule therefore yields parallel straight lines where the slope gives the decay coefficient \( \beta \). The offset is determined by the technology via \( r_{SAM PEDOT} \) which is a measure of the electronic coupling strength between the SAM and PEDOT:PSS. The sets of parallel straight lines are clearly observed in Fig. 7.4. We note that the interpretation is only phenomenological. A microscopic explanation for the dependence of the electronic coupling of the top contact on for instance the type PEDOT:PSS cannot be presented. There might be relation with bulk conductivity but that could
not yet unambiguously be demonstrated. To benchmark the data obtained, we

\[
R \left( \Omega / \text{molecule} \right) = 10^d \text{ cm}^{-2}
\]

versus number carbon atoms in the backbone. Resistances were taken from Fig. 7.4 using the default process flowchart. Resistances of single molecule junctions obtained with mechanically controlled breakjunctions and conducting AFM measurements on \( \alpha, \omega \)-alkane-di-amines\(^2\) and \( \alpha, \omega \)-alkane-di-thiols\(^4\) with two chemisorbed contacts are included for comparison. The dotted line is calculated using Eq. 7.2 with a decay coefficient, \( \beta \), of 0.9 per carbon, using similar resistance contribution factors \( r_{\text{Au-S}} \) and \( r_{\text{SAM PEDOT}} \).

Present in Fig. 7.6 the resistance per molecule together with reported resistances from single molecule junctions. The resistance per alkane-mono-thiol using the default process flow chart is calculated from Fig. 7.4 assuming a grafting density of \( 4.6 \cdot 10^{14} \text{ cm}^{-2} \). As typical single molecule resistances we took the values obtained from mechanically controlled breakjunctions and conductive AFM on \( \alpha, \omega \)-alkane-di-thiols with two chemisorbed contacts.\(^1\)\(^-\)\(^6\) Fig. 7.6 shows a good agreement between the two data sets with a single decay coefficient of 0.9 per carbon, a typical value for a saturated chain.\(^24\),\(^25\). For the fit of Fig. 7.6 we use Eq. 7.2. We take \( r_{\text{Au-S}} \) similar to \( r_{\text{SAM PEDOT}} \) and slightly lower than the published estimated value of 18.721.\(^22\) This indicates that the SAM / PEDOT
contact behaves electrically as a strongly bound contact. However, we note that minor changes in processing of PEDOT:PSS lead to significant changes in the electronic coupling and hence to dramatic changes in the absolute value of the resistance. Therefore, a prerequisite to disentangle the contribution from the molecule and that of the processing to the transport is a systematic variation of the length of the molecule.

7.4 Conclusion

In summary we have presented a technology to fabricate and integrate molecular junctions on 150 mm wafers. The junction consists of a gold bottom electrode, a self-assembled alkanethiol monolayer, the conducting polymer PEDOT:PSS and a gold top electrode. On a single wafer more than 20000 molecular junctions with diameter between 1 and 50 µm are fabricated simultaneously. Integration is demonstrated in strings where up to 200 junctions are connected in series. The yield is about unity. The junction resistances depend exponentially on the length of the alkane backbone. However, the absolute value of the resistance shows a technology dependent prefactor: electrical transport through such junctions is factorised and the technology dependent prefactor reflects the electrical coupling at the PEDOT:PSS and SAM contact. To understand the electrical transport through self-assembled monolayers, a systematic variation of the length of the molecule together with uniform processing of PEDOT:PSS over the whole wafer is required.

7.5 References


