

Single molecule electrical transport using self-assembled-monolayers

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Abstract

The understanding of current flow through molecular conductors requires an interdisciplinary approach to molecular electronics. New reproducible experiments with better assembling, including more sophisticated fabrication processes and structural control as a feedback for assembling of molecular devices, and designing molecular electronic devices with pre-defined properties are essential for this goal. Any interpretation of molecular transport experimental data requires information on the number of molecular wires per device, device structure and geometry, and the nature of the molecular-electrode bonding. The lack of this knowledge is the pivotal problem in molecular electronics. We have thus embarked in developing approaches to fabricate molecular electronic devices through self-assembled-monolayer (SAM) of molecular wires and insulating molecules in solid-state solutions that enable fine structural control, along with development of spectroscopic and electrical transport tools to study these structures. We used ellipsometry and reflectance spectroscopy to verify that the SAM films can be tuned by changing the ratio, r of molecular conductors (wires, such as Me-BDT) to insulating molecules (spacers, such as PT). We used surface titration for estimating the number of molecular wires per device. The single molecule electrical transport process in the vertical sandwich configuration SAM diodes with small r -value ($r < 10^{-3}$) that is based on isolated molecular wires, reveals a Fowler-Nordheim type tunneling injection mechanism. However this behavior is not observed in devices fabricated with large r -values.

Keywords: Self-assembled monolayers, single molecule transport, single molecule diodes, organic/inorganic interfaces, reflection spectroscopy, ellipsometry

1. Introduction

Molecular devices have impacted a large number of research areas of modern science [1]. The optimization of hybrid molecular electronic devices comprised from diverse organic and inorganic materials ultimately depends upon the precise control of the organic structure and electronic properties at the monomolecular level and is the prerequisite for the successful design of supra-molecular systems [2]. The spin-dependent electron transport properties of organic thin films and molecular magnetic systems offer the prospect of new types of high performance magnetic memory devices, sensors and other types of new organic spintronic devices whose functionalities depend on the electron spin as well as its charge. To understand the physics underlying these properties and to develop them for possible applications will require extensive efforts with the aim to manipulate and characterize the properties of organic heterostructures and magnetic materials with nanoscale dimensions. Our research has been focused on using sophisticated thin film techniques to produce ultra-thin films with desired electronic and magnetic properties, and characterizing the fabricated devices by state-of-the-art tools including

spectroscopy and extensive electronic transport measurements.

The electron transfer process across organic monolayers (ML) has been studied extensively in the past decade. However, single molecule conduction mechanism is still not very well understood. Contrary to the conventional electrical circuits, where adding one branch does not change the electronic properties of the others, formation of inter-molecular circuits by adding to the molecule new molecular wires effectively creates a ‘new’ molecule, known as macro-molecule that may have a different electronic transport mechanism than the starting molecules [3]. We initiate research with solid-state self-assembled-monolayer (SAM) solutions of molecular wires and dielectric spacers, using different experimental tools borrowed from the fields of microbiology and biochemistry. Here we report on the spectroscopic evidence of tuning the structure of the solid-state SAM solutions using surface chemistry. In addition, we also show a way of counting the isolated molecular wires in the SAM solutions using surface titration of amino groups. The results are used for calculating the isolated molecular transparency and electrical resistance in order to better understand the magneto-transport processes [6].

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2. Experimental

We have used a solution self-assembling method that allows chemistry controlled self-limiting monolayer growth with interlayer covalent (*i.e.* sulfide) bonds. The SAM's were composed of solid solution mixtures of conductive molecular wires (1,4 benzenedimethanethiol, or Me-BDT) and dielectric spacers (1-pentanethiol, or PT) that were chemisorbed between two thin films of ferromagnetic cobalt electrodes. The general scheme of the SAM process as well as the molecular structure of the "wires" and "spacers" molecules that were used for the solid solutions and device structure is depicted in Fig. 1.

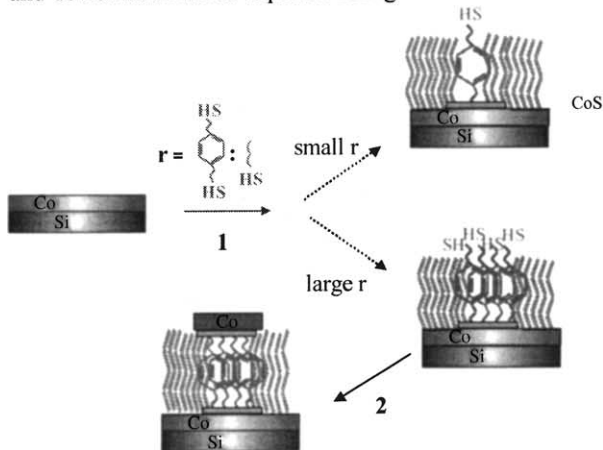


Fig. 1. General strategy of the SAM process for growing solid-state solutions of different BDT/PT molecular ratio, r . In step 1 reactive thiols form sulfide bonds with the bottom electrode. Step 2 shows sulfide bonding with the upper cladding electrode. Small r -values result in isolated molecular wires, whereas wire aggregates are formed for large r -values.

The electronic properties of the self-assembled components used in the solid solutions are known for many years [1]. Thus they have become natural candidates in the quest for conductivity control through monolayers. Me-BDT and PT precursors were mixed with a molar wires-to-spacers ratio r , diluted with distilled toluene at 3 mL solution and transferred to a home made high-vacuum based Shlenk line. The self-assembled process continued for 12 h in an Ar atmosphere at room temperature. The wires-to-spacers ratio r determines the conducting molecular structure to be governed either by isolated Me-BDT molecular wires in PT dielectric matrix at low r -values, or to form molecular aggregates at high r -values. Detail protocol of the SAM approach to these solid-state solutions is given in ref. [6].

3. Results and Discussion

The following methods were used to confirm the SAM growth process on the metallic films: progressive contact angle, ellipsometry, and UV-Vis spectroscopy. The contact

angles were 15.5° for the Si/SiO₂ substrate, 60° after Co evaporation, 65° for PT SAM, 70° for the aggregated BDT SAM, and intermediate values for their solid state mixtures. The solid-state solutions were organized into two motifs. At low r values, covalent intermolecular bonds held the individual structural units together. At high r formation of aggregates parallel to the surface, by interplane π -stacking of the BDT aromatic groups (see in-plane ordering in Fig. 2 A) usually occurs. The structural regularity of the resulting solid-state solutions was tested by variable angle spectroscopy ellipsometry (Woollam Co.) in the spectral range of 300–600 nm, and at 65° , 70° and 75° respect to the surface normal. (Fig. 2B). Normalized reflectivity spectra measured from samples with high r values having aggregate features indicate the formation of a new band in the visible spectral range compared with samples that contain only isolated Me-BDT wires.

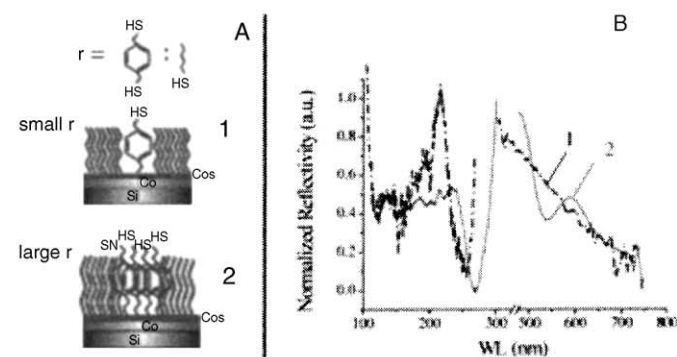


Fig. 2. Panel (A): structural organization in solid-state solution for different BDT/PT molecular ratio, r . (1) Small r showing isolated Me-BDT molecules. (2) Shows large r -values, where Me-BDT molecular aggregates are formed. Panel (B): normalized reflectivity spectra of samples 1 and 2 showing the appearance of a new band in the spectrum at ca. 600 nm due to the formation of Me-BDT aggregates in the film.

Fig. 3 shows the measured and fitted ellipsometric spectra for a SAM sample of isolated Me-BDT molecules in a matrix of PT molecules (Fig. 3 A), as well as a sample that contains some Me-BDT molecular aggregates (Fig. 3 B). The optical dielectric constant ($\epsilon(\lambda)$) was calculated from the reflectivity spectra; an example of $\epsilon(\lambda)$ is shown in Fig. 3B for model initialization. We used the fitting strategy that was developed for SAM growth in ref. [7]. Ex situ ellipsometry measurements reveal a thickness of 1.1 ± 0.05 nm for SAM aggregates of Me-BDT, and 1.0 ± 0.05 nm for SAM's that contain isolated Me-BDT in a PT matrix. We note that $\epsilon(\lambda)$ for aggregated Me-BDT samples follows the characteristic reflectivity spectra of SAM Me-BDT molecules (*i.e.* $r = 1$) (Fig 3 B, sample 2), which was also measured on a semitransparent glass [6]. Whereas $\epsilon(\lambda)$ for PT SAM does not have any of those features in UV-Vis spectral range since PT molecules are transparent (Fig 3 B, sample 1). The structural ordering of the aggregated system can be viewed

as a 2D “smectic-like” liquid crystal with the confinement of aromatic building blocks in a single monolayer.

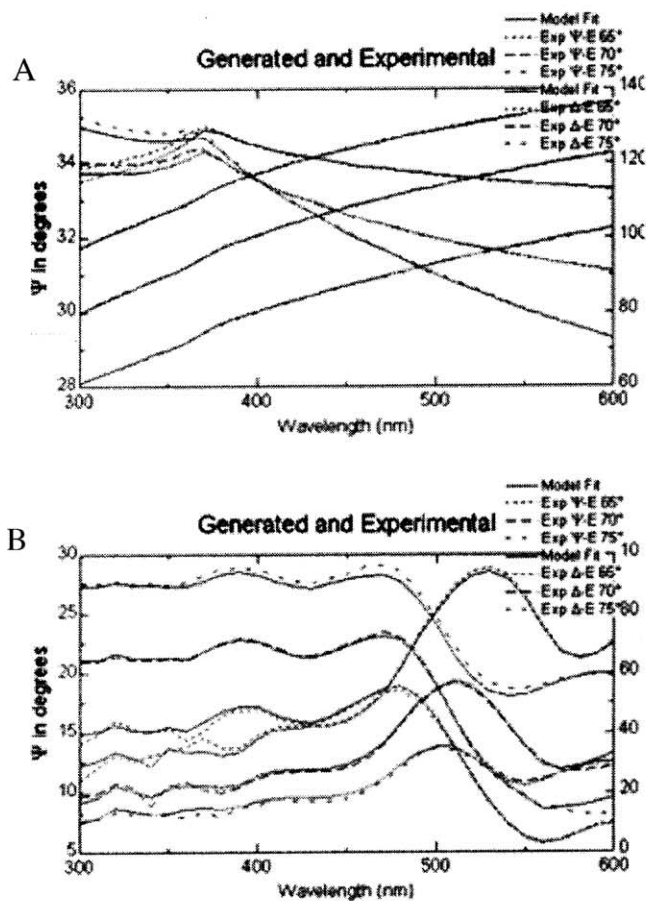


Fig. 3. Variable angle spectroscopic ellipsometry (VASE) of SAM's that contain (A) isolated Me-BDT molecular wires, and (B) Me-BDT forming molecular aggregates. The dashed lines through the data points in the Δ and ψ optical spectra correspond to a model fit.

Counting the number of single wire molecules on the SAM surface is not trivial because the low electronic density of the organic molecules that leads to lack of experimental detection techniques. We have borrowed experimental tools from biochemistry that are routinely used for measuring the number of thiol groups by titration. The main explicit assumption is that counting the number of thiol groups that are connected to the molecular wires, is equivalent to the number of molecular wires within the experimental error. The problem for the applications of these approaches in our case is that they have never tried on SAM surfaces. The surface chemistry and analytical tools for counting the thiol groups on SAM substrates may be very different from “conventional” chemistry. Therefore we have started our studies with titration of amino groups on the surface, which is an established method for

measuring the number of active sites and surface density of closed packed structures [7, 8].

We have performed a similar test in diluted solid-state solutions of the same concentration range of 4-aminophenylthiol molecules that are similar to Me-BDT molecules, but have amino group on top of the obtained SAM instead of a thiol group. We could obtain the density of aminobenzthiol molecules on the surface following protocols of surface titration procedures [7, 8] as shown in Fig. 4A.

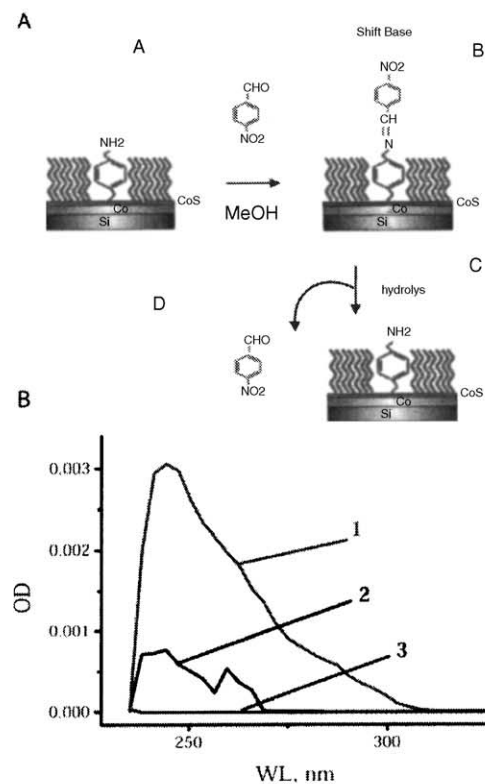


Fig. 4. (A) Schematic representation of the surface titration process of amines in solid-state solutions. (B) Absorption spectra measured at stage D above, at molecular wire concentrations of: (1) $r = 10^{-3}$, (2) $r = 10^{-4}$ and (3) $r = 10^{-5}$.

The extracted solution volume was 5 mL (± 0.1 mL) and the measured absorbance at a probe of $\lambda_{\max} = 244$ nm was 0.003 for $r = 10^{-3}$ (Fig. 4 B, spectrum 1). Given the molar extinction coefficient of the coupled dye we could estimate the number of molecular wires in solid-state solutions of Me-BDT assuming a similar packing density for 4-aminophenylthiol and Me-BDT molecules. The results of the titration were found to be in good agreement with surface titration of thiols (1.72×10^9 molecules/ mm^2 for $r = 10^{-6}$) and AFM detected surface density (4.4×10^8 molecules/ mm^2 for $r = 10^{-6}$) [6]. The obtained number of wire molecules in the device was then used for calculating

the electrical resistance of isolated molecular wires. Even through this initial rough estimate it is already evident that the transition from isolated molecules to clusters is governed by the wires-to-spacer ratio, r in the solid-state solutions as shown at Fig. 1.

In Fig.5 we show the room temperature I-V characteristic response of a diode fabricated with $r = 10^{-6}$ presented as a Fowler-Nordheim (FN) plot. The inter-electrode distance L used for calculating the field F ($F = V/L$) was estimated to be 1 nm, which is the linear dimension of the Me-BDT molecular wire. The FN plots show linear behavior at low bias, which

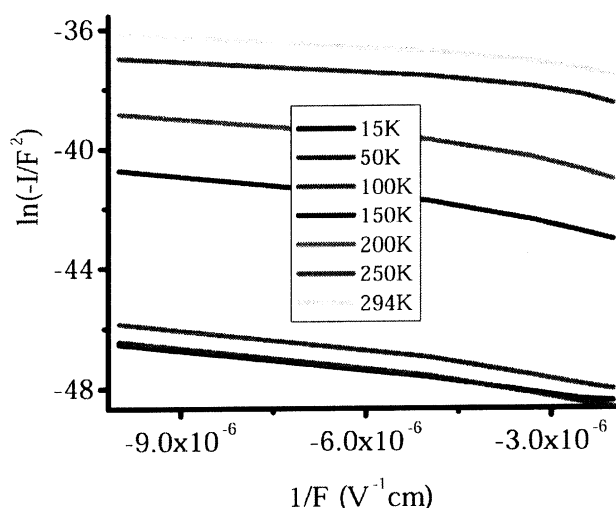


Fig. 5. Fowler-Nordheim plots for the I-V characteristic response of a SAM diode fabricated with $r = 10^{-6}$, measured at different temperatures. The field F was calculated using the rigid band approx. of $F = V/L$.

is characteristic of carrier injection by tunneling. The asymmetry of the plot is usually attributed to the different top and bottom interface heterojunction. We found, however that similar FN plots are not linear for diodes fabricated with higher r -values. The deviation from linearity, along with the critical changes that we found in the differential conductivity of such devices [6], indicates the contribution of aggregates to their electrical transport. Note that FN slope is almost temperature independent. FN transport model should describe charge injection from metal to molecules at low bias.

Even a brief review of the variety of experimental approaches to measurement of molecular conductivity and its theoretical explanation [9–15] shows the importance of interdisciplinary approach to molecular electronics. We need to refine our existing descriptions of the molecular

chemistry, device electrostatics, band structure, and surface physics for novel molecules and contacts, including spin and time-dependent effects.

4. Conclusions

In conclusion, we report the fabrication of SAM's from solid-state solutions having different ratio r of molecular wires (Me-BDT) to molecular spacers (PT) molecules. The value of r determines the SAM structure; it varies from isolated wires at low r ($r < 10^{-3}$), to aggregates of molecular wires at high r ($r > 10^{-3}$). We used reflection and ellipsometry spectroscopies to determine the thickness and structure of the solid-state solution SAM's. Surface titration of amino groups was used to obtain the surface density of isolated molecular wires in the device. Combining these approaches with additive surface studies [5, 6] we were able to count the isolated molecules in the mesoscopic devices and this helped us to obtain the electrical resistance of a single isolated Me-BDT molecule [6].

Acknowledgments

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