New concepts for nanophotonics and nano-electronics

Molecular-scale electronics

Dominique Vuillaume

Molecular Nanostructures & Devices group, Institute for Electronics, Microelectronics and Nanotechnologies (IEMN),
Centre National de la Recherche Scientifique (CNRS), University of Lille, BP60069, avenue Poincaré, Villeneuve d'Ascq 59652 cedex, France

Available online 20 February 2008

Abstract

Molecular electronics is envisioned as a promising candidate for the nanoelectronics of the future. More than a possible answer to the ultimate miniaturization problem in nanoelectronics, molecular electronics is foreseen as a possible and reasonable way to assemble a large numbers of nanoscale objects (molecules, nanoparticles, nanotubes and nanowires) to form new devices and circuit architectures. It is also an interesting approach to significantly reduce the fabrication costs, as well as the energetical costs of computation, compared to usual semiconductor technologies. Moreover, molecular electronics is a field with a large spectrum of investigations: from quantum objects for testing new paradigms, to hybrid molecular-silicon CMOS devices. *To cite this article: D. Vuillaume, C. R. Physique 9 (2008).*
© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

Électronique à échelle moléculaire. L'électronique moléculaire est envisagée en tant que candidat prometteur pour la nano-électronique du futur. Plus qu'une réponse possible au problème ultime de miniaturisation en nanoélectronique, l'électronique moléculaire est envisagée comme une approche possible et raisonnable pour assembler un grand nombre d'objets nanométriques (des molécules, des nanoparticules, des nanotubes et des nanofils) pour étudier de nouvelles architectures de composant et circuit. C'est également une approche intéressante pour réduire de manière significative les coûts de fabrication, aussi bien que les coûts énergétiques de calcul, comparés aux technologies habituelles à semi-conducteur. Par ailleurs, l'électronique moléculaire présente un large champ d'investigation : des objets quantique, pour examiner de nouveaux paradigmes, aux dispositifs hybrides moléculaire–silicium CMOS. *Pour citer cet article : D. Vuillaume, C. R. Physique 9 (2008).*
© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Keywords: Molecular electronics; Nano-electronics; Hybrid devices

Mots-clés : Électronique moléculaire ; Nanoélectronique ; Dispositifs hybrides

1. Introduction

Molecular electronics, i.e. information processing at the molecular-scale, becomes more and more investigated and envisioned as a promising candidate for the nanoelectronics of the future. One definition is "*information processing using photo-, electro-, iono-, magneto-, thermo-, mechanico- or chemio-active effects at the scale of structurally and functionally organized molecular architectures*" (adapted from [1]). In the following, we will consider devices based

Nomenclature

List of acronyms

AFM	atomic force microscope	LOFO	lift-off float-on
AR	Aviram–Ratner	LUMO	lowest unoccupied molecular orbital
C-AFM	conducting atomic force microscope	MmM	metal–molecule–metal
CNT	carbon nanotube	MO	molecular orbital
CMOS	complementary metal oxide semiconductor	NDR	negative differential resistance
D–b–A	donor–bridge–acceptor	nTP	nanotransfer printing
DRAM	dynamic random access memory	RT	room temperature
HOMO	highest occupied molecular orbital	RTD	resonant tunneling diode
IETS	inelastic electron tunneling spectroscopy	SAM	self-assembled monolayers
IPES	inverse photoemission spectroscopy	STM	scanning tunnelling microscope
LB	Langmuir–Blodgett	UHV	ultra-high vacuum
		UPS	ultra-violet photoemission spectroscopy

on organic molecules with size ranging from a single molecule to a monolayer. This definition excludes devices based on thicker organic materials, referred to as organic electronics. Two works paved the foundation of this molecular-scale electronics field. In 1971, Mann and Kuhn were the first to demonstrate tunneling transport through a monolayer of aliphatic chains [2]. In 1974, Aviram and Ratner theoretically proposed the concept of a molecular rectifying diode, where an acceptor–bridge–donor (A–b–D) molecule can play the same role as a semiconductor p–n junction [3]. Since that, many groups have reported on the electrical properties of molecular-scale devices from single molecules to monolayers.

In this article, after a brief overview of the nanofabrication of molecular devices, we review the electronic properties of several basic devices, from simple molecules such as molecular tunnel junctions and molecular wires, to more complex ones such as molecular rectifying diodes, molecular switches and memories.

2. Nanofabrication for molecular devices

To measure the electronic transport through an organic monolayer, we need a test device as simple as possible. The generic device is a metal/monolayer/metal or metal/molecules/metal (MmM) junction (for simplicity, we will always use this term and acronym throughout the paper even if the metal electrode is replaced by a semiconductor). Organic monolayers and sub-monolayers (down to single molecules) are usually deposited on the electrodes by chemical reactions in solution or in the gas phase, using molecules of interest bearing a functional moiety at the ends which is chemically reactive to the solid surface considered (for instance, thiol group on metal surfaces such as Au, silane group on oxidized surfaces, etc.)—Fig. 1. However, Langmuir–Blodgett (LB) monolayers have also been used for device applications early in the 1970s (see a review in a text-book [4]). Some important results are, for instance, the observation of current rectification behavior through LB monolayers of hexadecylquinolinium tricyanoquinodimethanide [5–11] and the fabrication of molecular switches based on LB monolayers of catenanes [12–16]. The second method deals with monolayers of organic molecules chemically grafted on solid substrates, also called self-assembled monolayers (SAM) [4]. Many reports in the literature concern SAMs of thiol terminated molecules chemisorbed on gold surfaces, and to a less extent, molecular-scale devices based on SAMs chemisorbed on semiconductors, especially silicon. Silicon is the most widely used semiconductor in microelectronics. The capability to modify its surface properties by the chemical grafting of a broad family or organic molecules (e.g. modifying the surface potential [17–19]) is the starting point for making almost any tailored surface useful for new and improved silicon-based devices. Between the end of the silicon road-map and the envisioned advent of fully molecular-scale electronics, there may be a role played by such hybrid-electronic devices [20,21]. The use of thiol-based SAMs on gold in molecular-scale electronics is supported by a wide range of experimental results on their growth, structural and electrical properties (see a review by F. Schreiber [22]). However, SAMs on silicon and silicon dioxide surfaces were less studied and were more difficult to control. This has resulted in an irreproducible quality of these SAMs with large time-to-time and lab-to-lab variations. This feature may explain the smaller number of attempts to use these SAMs in molecular-scale electron-
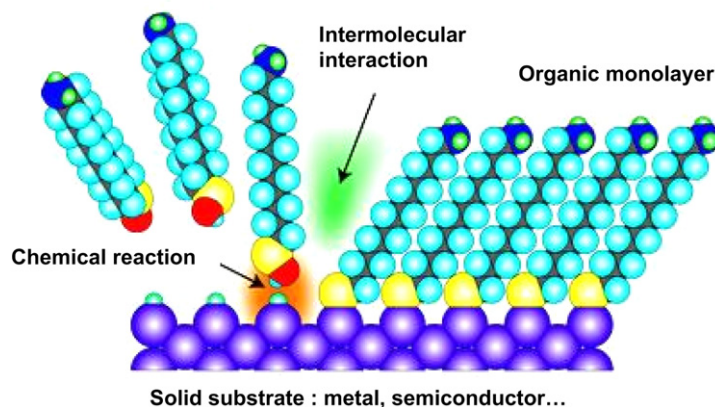
Fig. 1. A schematic description of the formation of an organic monolayer on a solid substrate, showing the chemical reaction between a functionalized end of the molecule and the substrate, and the interactions between adjacent molecules (from Sugimura Hiroyuki, www.mtl.kyoto.u.ac.jp/groups/sugimura-g/index-E.html).

ics than for the thiol/gold system. Since the first chemisorption of alkyltrichlorosilane molecules from solution on a solid substrate (mainly oxidized silicon) introduced by Bigelow, Pickett and Zisman [23] and later developed by Maoz and Sagiv [24], further detailed studies [25–28] have led to a better understanding of the basic chemical and thermodynamical mechanisms of this self-assembly process. For a review of these processes, see Refs. [4,22].

In their pioneering work, Mann and Kuhn used a mercury drop to contact the monolayer [2], and this technique is still used nowadays [29–32] at the laboratory level as an easy technique for a quick assessment of the electrical properties. Several types of MmM junctions have been built. The simplest structure consists of depositing the monolayer onto the bottom electrode and then evaporating a metal electrode on top of the monolayer through a masking technique. These shadow masks are fabricated from metal or silicon nitride membranes and the dimensions of the holes in the mask may range from few hundreds of μm to few tens of nanometers. Chen and coworkers [33,34] have used nanopores (about 30 nm in diameter in a silicon nitride membrane), in which a small numbers of molecules are chemisorbed to fabricate these MmM junctions. From $\sim 10^{10}$ to $\sim 10^2$ molecules can be measured in parallel with these devices. The critical point deals with the difficult problem of making a reliable metal contact on top of an organic monolayer. Several studies [35–40] have analyzed (by X-ray photoelectron spectroscopy, infra-red spectroscopy, ...) the interaction (bond insertion, complexation ...) between the evaporated atoms and the organic molecules in the SAM. When the metal atoms are strongly reactive with the end-groups of the molecules (e.g. Al with COOH or OH groups, Ti with COOCH$_3$, OH or CN groups ...) [35–40], a chemical reaction occurs, forming a molecular overlayer on top of the monolayer. This overlayer made of organometallic complexes or metal oxides may perturb the electronic coupling between the metal and the molecule, leading, for instance, to partial or total Fermi-level pinning at the interface [41]. In some cases, if the metal chemically reacts with the end-group of the molecule (e.g. Au on thiol-terminated molecules), this overlayer may further prevent the diffusion of metal atoms into the organic monolayer [42]. The metal/organic interface interactions (e.g. interface dipole, charge transfer, ...) are very critical and they have a strong impact on the electrical properties of the molecular devices. Some reviews are given in Refs. [43,44]. If the metal atoms are not too reactive (e.g. Al with CH$_3$ or OCH$_3$ ...) [35–40], they can penetrate into the organic monolayer, diffusing to the bottom interface where they can eventually form an adlayer between this electrode and the monolayer (in addition to metallic filamentary short circuits). In a practical way for device application using organic monolayers, the metal evaporation is generally performed onto a cooled substrate ($\sim$100 K). It is also possible to intercalate blocking baffles on the direct path between the crucible and the sample, or/and to introduce a small residual pressure of inert gas in the vacuum chamber of the evaporator [10,11,45]. These techniques allow the reduction of the energy of the metal atoms arriving on the monolayer surface, thus reducing the damage.

To avoid these problems, alternative and soft metal deposition techniques have been developed. One, called nanotransfer printing (nTP), has been described and demonstrated [46]. Nanotransfer printing is based on soft lithographic techniques used to print patterns with nanometric resolution on solid substrates [47]. The principle is briefly described as follows. Gold electrodes are deposited by evaporation onto an elastomeric stamp and then transferred by mechanical

contact onto a thiol-functionalized SAM. Transfer of gold is based on the affinity of this metal for thiol function –SH forming a chemical bond Au–S. Loo et al. [46] have used the nTP technique to deposit gold electrodes on alkane dithiol molecules self-assembled on gold or GaAs substrates. Nanotransfer printing of gold electrodes was also deposited onto oxidized silicon surface covered by a monolayer of thiol-terminated alkylsilane molecules [48,49]. Soft depositions of pre-formed metal electrodes, e.g. lift-off float-on (LOFO) [50], have also been developed. Recently, another solution has been proposed in which a thin conducting polymer layer has been intercalated as a buffer layer between the organic monolayer and the evaporated metal electrode [51]. The use of a metallic electrode made of a 2D network of carbon nanotubes has also been reported [52]. Finally, another solution to avoid problems with metal evaporation is to cover a metal wire (about 10 µm in diameter) with a SAM and then to bring this wire in contact with another wire (crossing each other) using the Laplace force [53,54]. About 10^3 molecules can be contacted by this way.

At the nanometer-scale, the top electrode can also be a STM tip. The properties of a very small number of molecules (few tens down to a single molecule) can be measured. If one assumes that an intimate contact is provided by the chemical grafting (in case of a SAM) at one end of the molecules on the bottom electrode, the drawback of these STM experiments is the fact that the electrical 'contact' at the other end occurs through the air-gap between the SAM surface and the STM tip (or vacuum in case of an UHV-STM). This leads to a difficult estimate of the true conductance of the molecules, while it is possible through a careful data analysis and choice of experimental conditions [55,56]. Recently, some groups have used a conducting-atomic force microscope (C-AFM) as the upper electrode [57–59]. In this case, the metal-coated tip is gently brought into a mechanical contact with the monolayer surface (this is monitored by the feed-back loop of the AFM apparatus) while an external circuit is used to measure the current–voltage curves. The advantage over the STM is twofold: (i) tip-surface position control and current probing are physically separated (while the same current in the STM is used to control the tip position and to probe the electronic transport properties); and (ii) under certain conditions, the molecules may be also chemically bounded to the C-AFM tip at the mechanical contact [60]. The critical point of C-AFM experiments is certainly the very sensitive control of the tip load to avoid excessive pressure on the molecules [61] (which may modify the molecule conformation and thus its electronic transport properties, or can even pierce the monolayer). On the other hand, the capability to apply a controlled mechanical pressure on a molecule to change its conformation is a powerful tool to study the relationship between conformation and electronic transport [62]. A significant improvement has been demonstrated by Xu and Tao [63] in measuring the conductance of a single molecule by repeatedly forming a few thousand Au–molecule–Au junctions. This technique is a STM-based break junction, in which molecular junctions are repeatedly formed by moving back and forth the STM tip into and out of contact with a gold surface in a solution containing the molecules of interest. A few molecules, bearing two chemical groups at their ends, can bridge the nanogap formed when moving back the tip from the surface. Due to the large number of measurements, this technique provides statistical analysis of the conductance data. This technique has been recently used to obtain new insights on the electronic transport through molecular junctions, e.g. on the analysis of the variability of the conductance [64,65], on the role of the chemical link between the molecule and the metal electrode [65,66] (for instance, it has been shown that the amine group gives a better defined conductance than thiol [65]), on the influence of the atomic configuration of the chemical link [67]. Changes in the electrical conductance of a single molecule as function of a chemical substitution [68] and a conformational change were also demonstrated [69].

The second type of MmM junctions uses a 'planar' configuration (two electrodes on the same surface). The advantage over a vertical structure is the possibility to easily add a third gate electrode (3-terminal device) using a bottom gate transistor configuration. The difficulties are: (i) to make these electrodes with a nanometer-scale separation; and (ii) to deposit molecules into these nanogaps. Alternatively, if the monolayer is deposited first onto a suitable substrate, it would be very hard to pattern, with a nanometer-scale resolution, the electrodes on top of it. The monolayers have to withstand, without damage, a complete electron-beam patterning process for instance. This has been proved possible for SAMs of alkyl chains [70,71] and alkyl chain functionalized by π-conjugated oligomers [72] used in nanoscale (15–100 nm) devices. However, recently developed soft-lithographies (micro-imprint contact . . .) can be used to pattern organic monolayers or to pattern electrodes on these monolayers [47]. Nowadays, 30 nm width nanogaps are routinely fabricated by e-beam lithography and 5 nm width nanogaps are attainable with a lower yield (a few tens of %) [73–75]. However, these widths are still too large compared to the typical molecule length of 1–3 nm. The smallest nanogaps ever fabricated have a width of about 1 nm. A metal nanowire is e-beam fabricated and a small gap is created by electromigration when a sufficiently high current density is passing through the nanowire [76]. These gold nanogaps were then filled with few molecules (bearing a thiol group at each ends) and Coulomb blockade and
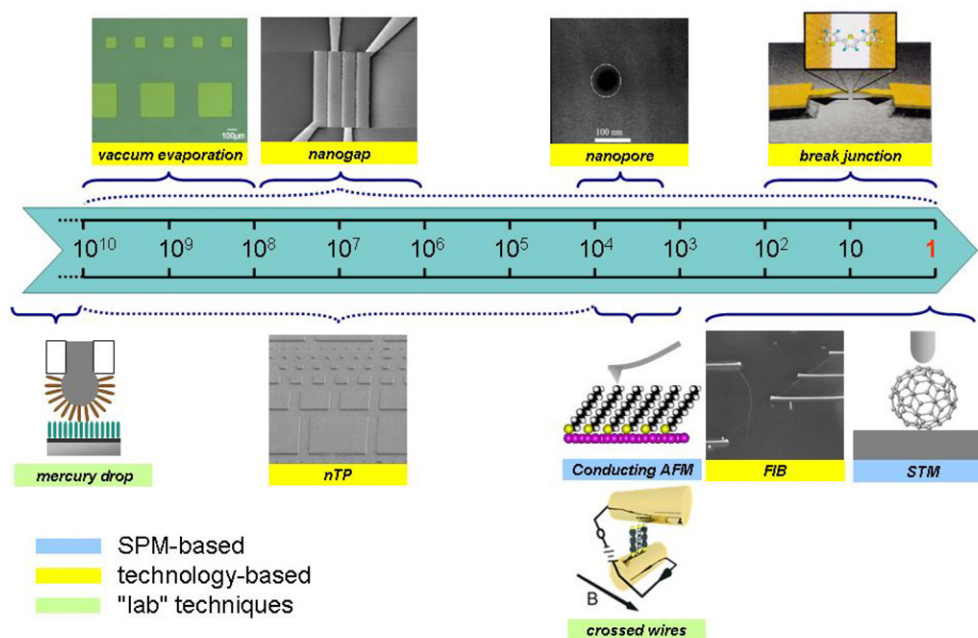
Fig. 2. A schematic overview of the different test-beds used to electrically contact organic molecules. The scale gives the approximate number of molecules contacted from monolayer (left) to single molecule (right). The techniques are (from left to right, upper part of the figure): microme-ter-scale metal evaporation, nanogap patterned by e-beam lithography, nanopores, break-junction, and (from left to right, lower part of the figure): mercury drop, nanotransfer printing, conducting AFM, crossed wires, metal deposition by FIB, STM (courtesy of S. Lenfant, IEMN-CNRS).

Kondo effects were observed in these molecular devices [77,78]. A second approach is to start by making two elec-trodes spaced by about 50–60 nm, then to gradually fill the gap by electrodeposition until a gap of a few nanometers has been reached [79–81]. Recently, carbon nanotubes (CNT) have been used as electrodes separated by a nanogap (<10 nm) [82]. The nanogap is obtain by a precise oxidation cutting of the CNT, and the two facing CNT ends which are now terminated by carboxylic acids, are covalently bridged by molecules of adapted length derivatized with amine groups at the two ends. It is also possible to functionalize the molecule backbone for further chemical reactions allow-ing the electrical detection of molecular and biological reactions at the molecule-scale [82,83]. Another approach is to use a breaking junction, bridged by few dithiol-terminated molecules. Reed and coworkers [84] and Kergueris and coworkers [85] have used these breaking junctions to fabricate and to study some MmM junctions based on dithiolben-zene and bisthiolterthiophene, respectively, and this technique was further used with others short oligomers [86,87]. However, these MmM breaking junctions are not stable over a very long period of time (no more than 20–30 min) while the vertical MmM junctions and the 'planar' ones based on nanofabricated nanogaps are stable over months. Weber et al. reported some improvements allowing stable MmM breaking junction measurements at low tempera-ture [88,89]. Finally, we mention that Au nanoparticles (NP) can be used to connect a few molecules, these NP (tens of nm in diameter) being themselves deposited between electrodes or contacted with a STM [60,90,91]. Microspheres metallized by Ni/Au can also be magnetically trapped between micro-lithographically patterned electrodes covered by a monolayer of molecules forming two molecular junctions in series [91]. These approaches allow the measurement of a small number of molecules and avoid the difficult fabrication of few nm size gaps.

To conclude this section, many technological solutions are available to measure the electronic transport properties of molecular monolayers with lateral extension from few molecules to $\sim 10^{10}$ (Fig. 2). A comparison between electri-cal measurements at the molecular-scale and those on macroscopic devices will be helpful to understand the effect of intermolecular interactions on the transport properties. As a result of these various approaches for making the organic monolayers and the MmM junctions, the nature of the interfaces, and thus the electronic coupling between the mole-cules and the electrodes are largely dependent on the experimental conditions and protocols. This feature requires a multi test-bed approach to assess the intrinsic properties of the molecular devices and not of the contacts [92]. In the following sections, we illustrate and discuss the effects of this molecule/electrode coupling on the electronic transport properties of some molecular devices.

3. Molecular tunneling barrier

It has long been recognized that a monolayer of alkyl chains sandwiched between two metal electrodes acts as a tunneling barrier. Mann and Kuhn [2], Polymeropoulos and Sagiv [93,94] have demonstrated that the current through LB monolayers of alkyl chains follows the usual distance-dependent exponential law, $I = I_0 \exp(-\beta d)$, where d is the monolayer thickness and β is the distance decay rate. They have found $\beta \sim 1.5$ Å^{-1}. More recently, we found [95] $\beta \sim 0.7$–0.8 Å^{-1} for n^+-Si/native SiO$_2$/SAM of alkyl-1-enyltrichlorosilane/metal (Au or Al) junctions and Whitesides's group [29] found $\beta \sim 0.9$ Å^{-1} for Hg/SAM of alkylthiol/Ag junctions. All these experiments were done with macroscopic-size electrodes. Data taken for alkanethiols in a nanopore junction gave ~ 0.8 Å^{-1} [96]. Recently, C-AFM experiments were also performed, addressing the properties of a small number of molecules. Again, a tunneling law was observed with $\beta \sim 0.9$–1.4 Å^{-1} for Au/SAM of alkylthiols/Au-covered AFM tip junctions [57,58, 97,98]. A smaller value ($\beta \sim 0.5$ Å^{-1}) was reported for Au/SAM of alkyldithiol/Au-covered AFM tip junctions [99], but another work reported no significant variation of β between alkanethiols and alkanedithiols, but only a contact resistance 1 or 2 decades lower for the alkanedithiols. A more complete review of these data and others is given in Ref. [100]. The β value is related to the tunneling barrier height (Δ) at the molecule/electrode interface and to the effective mass (m^*) of carriers in the monolayer, $\beta = \alpha(m^*/m_0)^{1/2}\Delta^{1/2}$, with m_0 the rest mass of the electron and $\alpha = 4\pi(2m_0 e)^{1/2}/h = 10.25$ eV$^{-1/2}$ nm^{-1} (e is the electron charge and h Planck's constant). The tunneling barrier height may be measured independently by internal photoemission experiment (IPE) [101] where carriers in one of the electrodes are photoexcited over the tunneling barrier and collected at the other electrode (under a small applied dc bias). Threshold energy of the exciting photons allows the measurement of Δ. We have found an electron tunneling barrier of about 4.3–4.5 eV at the silicon/native SiO$_2$/SAM and aluminum/SAM interfaces in the case of densely packed, well-ordered, SAMs of alkyl chains [102], a larger value than ~ 1.4 to 3 eV found in other experiments on LB monolayers and alkylthiol SAM on Au [2,29,94,96]. This high value (~ 4.5 eV) is in agreement with theoretical calculations [103]. For the same alkyl chains directly chemisorbed on Si (no native oxide), lower values have been reported from a combination of electrical (~ 1–1.5 eV) and UPS/IPES (2.5–3.5 eV) experiments [104,105]. The discrepancy between electrical and spectroscopy data is due to the fact that charge carrier transport is dominated by the presence of interface states localized between the molecular HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) and the Si band edges [105].

These puzzling data may be rationalized if we consider the nature of the molecule/electrode coupling. Fig. 3 shows some of these data in a β–Δ plot. The smallest β and Δ values are obtained for a good or 'intimate' coupling at both the two electrodes. This is the case for SAM of alkyldithiols chemisorbed at the two electrodes [29,99] and for SAM chemisorbed at one end and contacted at the other one by an evaporated metal [95]. This is also the case for alkyl
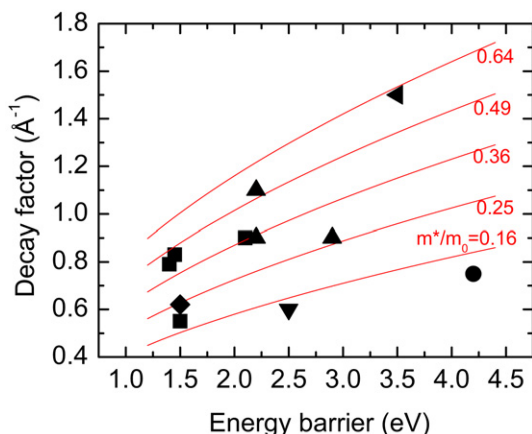

Fig. 3. Tunnel decay factor—energy barrier plot for several molecular tunnel junctions: (■) metal–alkylthiol or dithiol–metal (Au or Hg) junctions [29,60,96], (▲) Au–alkylthiol or dithiol–Au C-AFM junctions [58,59,98,107], (◄) LB monolayer [2], (◆) Si–alkyl–Hg junction [104,105], (●) Si-native SiO$_2$–alkylsilane–Al junction [102,103], (▼) Si-ative SiO$_2$–mercaptopropyltrimethoxysilane–Au junction [42]. Lines are calculated according to the classical equation (see text) for different values of the effective mass.

chains directly attached to Si without native oxide between the substrate and the molecules [104,105]. The largest values are obtained when at least one coupling is weak, as is the case for physisorbed LB monolayers [2,93,94] and SAM mechanically contacted by C-AFM tip [57,58] or chemisorbed on the native oxide of the Si substrate [102,103]. In this last case, the top metal electrode (Al or Au) was also weakly coupled with the CH_3-terminated molecules. The tunnel barrier height is lowered (2.2–2.5 eV) [42] if Au is used as the top electrode on thiol-terminated SAM of alkyl chains still grafted on naturally oxidized Si, probably due to a better molecule/metal coupling through the S–Au chemical link. This feature reveals that the nature of the molecule/electrode coupling strongly changes the electronic properties of the molecules. The HOMO–LUMO gap of the molecule, and therefore the tunnel barrier height, may be reduced by several eV for a chemisorbed molecule on metal compared to the gas phase molecule [106]. Charge transfer and interface dipole also move the position of the molecular orbitals with respect to Fermi energy of the electrodes. A review on these phenomena is given in Refs. [43,44]. The molecule/electrode contact is a key parameter in the overall transport properties of the MmM junctions. It was demonstrated that the conductance of a MmM junction is increased when the molecule is chemisorbed at its two ends (via a thiol link on gold for instance) compared to the situation when only one end is chemically connected to one electrode. An increase by a factor 10^3 was observed for a monolayer of octadecanedithiol molecules as compared to a monolayer of octadecanethiol [60,107]. Another experimental evidence is given by a comparison of two systems (Hg–S–alkyl and Hg/alkyl) where the sulfur linked molecules showed a better electrical conductivity [31].

Finally, these tunnel junctions are also good prototypal devices to study more detailed phenomena such as: electron–molecular vibration coupling using inelastic electron tunnel spectroscopy (IETS) [108–113], current-induced local heating in a molecular junction [114], dynamical charge fluctuations using noise measurements [115] and spin-polarized transport [116,117]. Beyond the first results, more of such experiments are now required to achieve a good agreement between a variety of different results, as well as with theoretical predictions. These approaches open very interesting pathway toward a better understanding of electronic transport in molecular junctions.

4. Molecular semiconducting wire

Contrary to the case of fully saturated alkyl chains, short oligomers of π conjugated molecules are considered as the prototype of molecular semiconducting wires. Bumm and coworkers [118] have studied the conductivity of prototypes of molecular wires. A few molecules of di(phenylene-ethynylene)benzenethiolate were inserted in a SAM of dodecanethiols (which are insulating molecules), and the difference in conductivity was investigated using the tip of a STM. With a STM working at a constant current, the tip is retracted when passing over a more conducting molecule than the surrounding matrix of alkyl chains. Thus the apparent amplitude height in the STM image is directly related to the conducting behavior of these molecules. Patrone and coworkers [119,120] have repeated these experiments for thiolterthiophene molecules, another prototype of molecular wires (Fig. 4). However, as explained above, the drawback of these experiments is the fact that the electrical 'contact' at the upper end of the molecules occurs through the air-gap between the SAM surface and the STM tip (or vacuum in case of an UHV-STM). This leads to a difficult estimation of the true conductance of the molecules. Reed et al. [84], Kergueris et al. [85], Weber et al. [86–88] have used breaking junctions to fabricate and to study some MmM junctions based on short conjugated
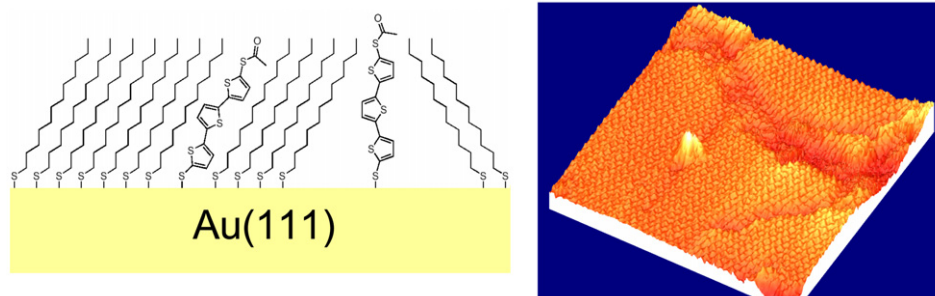

Fig. 4. Left, schematic view of a mixed monolayer where a few 'conducting' molecules (dithiol-terthiophene) are intercalated into 'insulating' ones (alkanethiol). Right, STM image (28 nm × 28 nm). The bump in the image is due to a higher current when the tip is passing over the more conducting terthiophene molecules. The background corresponds to the tunneling current through the alkanethiols [119,120].

oligomers. The current–voltage curves are strongly non-linear with steps (peaks in the first derivative) corresponding to resonant charge carrier transfer through the molecular orbitals (MO) of the molecules. The measured conductance corresponds to the conductance through the molecules and the conductance of the molecule/electrode contact. Thus, the influence of the chemical link between the molecules and the electrode is of a prime importance. A change from an asymmetric to a symmetric current–tension (with respect to the bias polarity) curve was observed when comparing MmM junctions of SAMs of monothiolate and dithiolate oligo(phenylene ethynylene) molecules [54]. The current increases by about a factor 10 when a sulfur atom attaches the molecule to the gold electrode compared to a mechanical contact. Today, the thiol group is the most used link to gold. However, theoretical calculations have recently predicted that selenium (Se) and tellurium (Te) are better links than sulfur (S) for the electronic transport through MmM junctions based on phenyl-based molecular wires [121,122]. This was recently demonstrated in a series of experiments using SAMs made of bisthiol- and biselenol-terthiophene molecules inserted in a dodecanethiol matrix [119,123]. Using both STM in ambient air and UHV-STM, the apparent height of the molecular wires above the dodecanethiol matrix (as in the Bumm et al. work quoted above [118]) is used to compare the electron transfer through the terthiophene molecule linked to the gold surface by S or Se atoms. Whatever the experimental conditions (air or UHV, tip-substrate bias, tunnel current set-point), the Se-linked molecules always appear higher in the STM images than the ones with a S linker. This feature directly demonstrates that a Se atom provides a better electron coupling between the gold electrode and the molecular wire than a S atom does (at least for the terthiophene molecule used in these experiments). From UPS experiments, this was attributed to a reduction of the energy offset between the highest occupied molecular orbital (HOMO) of the molecules (these molecules are mainly a better hole transport material than an electron transport material) and the Fermi energy of the gold electrode [119,120]. This offset reduction is in agreement with theory [121,122]. Similarly, comparing the electron transport through SAMs of alkylthiols and alkyl-isonitriles (C-AFM measurements), it was established that the contact resistance for the Au/CN link is about 10% lower than for the Au/S interface [107]. Further experiments have shown that: (i) the amine group (NH_2) gives better controlled conductance variability than thiol (SH) and isonitrile (CN) [65]; and (ii) the interface contact resistance is lower for amine than for thiol [66]. Further experiments are now required to deeply investigate all possible anchoring atom/electrode couples (S, Se, Te, CN, COOH etc., on one side and Au, Ag Pt, Pd, for instance, on the other side) and to determine to which extent the conclusions drawn for a peculiar molecule are valid for any other ones. With all these data on hand, one could optimize the design of future devices for molecular electronics. Electron-molecular vibronic coupling in short semiconducting oligomers has also been recently studied by IETS [108,113] for alkane molecules, as well as thermoelectricity in these molecular junctions [124]. In this latter case, the Seebeck coefficient of the single molecules has been determined, as well as a clear evidence of hole transport through the junctions. This result allows one to begin to explore thermoelectric energy conversion at the molecular-scale.

5. Molecular rectifying diode

A basic molecular device is the electrical current rectifier based on suitably engineered molecules. This molecular diode is the organic counterpart of the semiconductor p–n junction. At the origin of this idea, Aviram and Ratner (AR) proposed in 1974 to use D–σ–A molecules where D and A are respectively electron donor and acceptor, and σ is a covalent 'sigma' bridge [3]. Several molecular rectifying diodes were synthesized based on this AR paradigm, with donor and acceptor moieties linked by a short σ or even π bridge [5,7–11,125,126]. This D–b–A (b = bridge) group is also ω-substituted by an alkyl chain to allow a monolayer formation by the Langmuir–Blodgett (LB) method and this LB monolayer is then sandwiched in a metal/monolayer/metal junction. The first experimental results were obtained with the hexadecylquinolinium tricyanoquinodimethanide molecule ($C_{16}H_{33}$-Q-3CNQ for short)—Fig. 5 [5,7–11]. However, the chemical synthesis of this molecule was not obvious with several routes leading to erratic and unreliable results. A more reliable synthesis was reported with a yield of 59% [8]. More recently, other D–b–A molecules have been synthesized and tested [127,128] showing rectification with a ratio up to $\sim 2 \times 10^4$. We can also mention some other approaches using D–A diblock co-oligomers [129] or CNT asymmetrically functionalized by D and A moieties at their ends [130] with a rectification ratio of $\sim 10^3$ in this latter case. Even if these results represent an important progress to achieve molecular electronics, the physical mechanism responsible for the rectification is not clear. One critical issue is to know if the AR model can be applied to $C_{16}H_{33}$-Q-3CNQ because it is a D–π–A molecule [8], and due to the π bridge, the HOMO and LUMO may be more delocalized than expected in the AR model. On the theoretical side, these molecular diodes are complex systems, characterized by large and inhomogeneous electric fields,
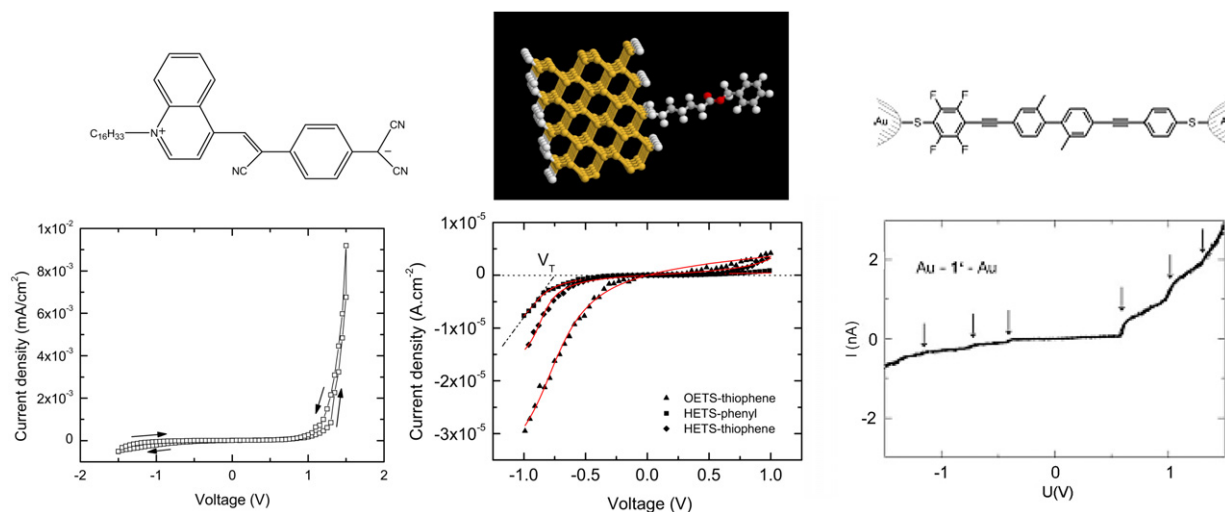
Fig. 5. Typical current–voltage characteristics of some molecular rectifying diodes. From left to right: LB monolayer of D–π–A molecules between metal electrodes, from [8,9], σ–π molecule grafted on Si, from [41,136], and D–A molecule inserted in a break-junction (at 30 K in this latter case), from [88].

which result from the molecular dipoles in the monolayer, the applied bias and the screening induced by the molecules themselves and the metallic electrodes. A theoretical treatment of these effects requires a self-consistent resolution of the quantum mechanical problem, including the effect of the applied bias on the electronic structure. Combining ab initio and semi-empirical calculations, it was shown [131] that the direction of easy current flow (rectification current) depends not only on the placement of the HOMO and LUMO relative to the Fermi levels of the metal electrodes before bias is applied, but also on the shift induced by the applied bias: this situation is more complex than the AR mechanism, and can provide a rectification current in an opposite direction. The electrical rectification results from the asymmetric profile of the electrostatic potential across the system [131,132]. In other words, this means that the molecule is more strongly coupled with one electrode than with the other (closer to one of the electrodes due to the presence of the alkyl chain). The alkyl tail in the $C_{16}H_{33}$-Q-3CNQ molecule plays an important role in this asymmetry, and a symmetric current–voltage curve in the case of molecules without the alkyl chain was predicted [131]. This asymmetry effect was further theoretically studied more extensively [133,134]. Generally speaking, any asymmetrical coupling of the molecules with the electrodes or any asymmetry in the molecule will result in a rectification effect [88, 135]—Fig. 5. This emphasizes the importance of the electrostatic potential profile in a molecular system and suggests that this profile can be chemically engineered to build new devices. For instance, based on these considerations, we have recently reported an experimental demonstration of a simplified and more robust synthesis of a molecular rectifier with only one donor group and an alkyl spacer chain [41,136]. We have used a sequential self-assembly process (chemisorption directly from solution) on silicon substrates. We have analyzed the properties of these molecular devices as a function of the alkyl chain length and for ten different donor groups. We have obtained rectification ratios up to 37 (Fig. 5). We have shown that rectification occurs from resonance through the HOMO of the π-group in good agreement with our calculations and internal photoemission spectroscopy. However, improvements are still required to suppress Fermi-level pinning at the molecule/metal interface [41] and to allow a clear design and tuning of the electrical behavior of the molecular diode through the right choice of the chemical nature of the molecule. This approach will allows us to fabricate molecular rectifying diodes compatible with silicon nanotechnologies for future hybrid circuitries.

6. Molecular switches and memories

Molecular switches and memories were also suggested at the early stage of the molecular electronics history [137–139]. We generally distinguish three approaches called 'resistive memory', 'capacitive memory' and 'RTD-based memory' (RTD is resonant tunneling diode). The first one relies on the idea of storing a data bit on two bistable

conformers of a molecule; the second on different redox states and the third on a negative differential resistance (NDR) due to resonant tunneling through molecular orbitals.

6.1. Resistive memory

One of the most interesting possibilities for molecular electronics is to take advantage of the soft nature of organic molecules. Upon a given excitation, molecules can undergo conformational changes. If two different conformations are associated with two different conductivity levels of the molecule, this effect can be used to make molecular switches and memories. Such an effect is expected in π-conjugated oligomers used as molecular wires, if one of the monomer is twisted away from a planar conformation of the molecule [69]. Twisting one monomer breaks the conjugation along the backbone, thus reducing the charge transfer efficiency along the molecule. This has been experimentally observed for a small molecular wire where the central unit was substituted with redox moieties. With the nanopore configuration to fabricate the MmM junction, Chen and coworkers [33,34] have observed that molecules with a nitroamine redox center (2′-amino-4,4′-di(ethynylphenyl)-5′-nitro-1-benzenethiol) exhibit a negative differential resistance behavior. In other words, they have observed that for a certain voltage range (typically between 1.5 and 2.2 V) applied on the MmM junction, the conductivity of the junction increased by a factor 10^3 (at 60 K, while the on/off ratio dropped to 1 at about 140 K). Other molecules with some changes of the redox moieties have exhibited on/off ratio of about 1.5 at RT [34]. They have also reported the feasibility of molecular random access memory cell using these molecules [140]. The switching behavior of these compounds inserted in an alkanethiol SAM was also observed by STM [141]. To separate the intrinsic behavior of the molecules from the molecule/metal interface, the same type of molecules have been measured on various test-beds (Fig. 6) [92]. These experiments demonstrated a clear bias-induced switching, while with a large statistical variability. However, it is not firmly established that this switching behavior is solely due to the molecules. Recently, the Lindsey's group showed that another possible mechanism is a random and temporary break in the chemical link between the molecule and the gold surface [142] and this point is still a subject of debate.

Catenane and rotaxane are a class of molecules synthesized to exhibit a bistable bahavior. In brief, these molecules are made of two parts, one allowed to move around or along the other one (e.g. a ring around a rod, two interlocked rings). These molecules adopt two different conformations depending on their redox states, changing the redox state triggers the displacement of the mobile part of the structure to minimize the total energy. This kind of molecule was used to build molecular memories. A MmM junction using a LB monolayer of these molecules mixed with phospholipid acid showed a clear electrical bistable behavior at room temperature [13,14,143]. A voltage pulse of about 1.5–2 V was used the switch the device from the 'off' state to its 'on' state. The state was read at a low bias (typically 0.1–0.2 V). The on/off ratio was about a few tens. A pulse in reverse bias (−1.5 to −2 V) returned the device to the 'off' state. Using these molecular devices, Chen and coworkers [15,16] have demonstrated a 64 bits non-volatile molecular memory cross-bar with an integration density of 6.4 Gbit/cm^2 (a factor ∼10 larger than the today's state-of-the-art silicon memory chip). The fabrication yield of the 64 bits memory is about 85%, the data retention is about 24 h and about 50–100 write/erase cycles are possible before the collapse of the on/off ratio to 1. Recently a 160 kbit based on the same class of molecules has been reported, patterned at a 33 nm pitch (10^{11} bits/cm^2) [144]. About 25% of the tested memory points passed an on/off ratio larger than 1.5 with an average retention time of ∼1 h. However, it has also been observed that similar electrical switching behaviors can be obtained without such a class of bistable molecules (i.e. using simple alkyl chains instead of the rotaxanes) [145]. The switching behavior is likely due to the formation and breaking of metallic micro-filaments introduced though the monolayer during the top metal evaporation. The presence of such filaments is not systematic (see discussion above), and caution has to be taken before to definitively ascribing the memory effect as entirely due to the presence of the molecules. While having rather poor performance at the moment, these demonstrations allow us to envision the coming era of hybrid-electronics, where molecular cross-bar memories like these ones, will be addressed by multiplexer/demultiplexer and so one fabricated with standard semiconductor CMOS technologies [15]. The advantage of such molecular cross-bar memories are: (i) a low cost; (ii) a very high integration density; (iii) a defect-tolerant architecture; (iv) an easy post-processing onto a CMOS circuitry; and (v) a low power consumption. For instance, it has been measured that an energy of ∼50 zJ (or ∼0.3 eV) is sufficient to rotate the dibutyl-phenyl side group of a single porphyrin molecule [146]. This is ∼10^4 lower than the energy required to switch a state-of-the art MOSFET, and near the kTLn2 (2.8 zJ at 300 K, or 0.017 eV) thermodynamic limit.
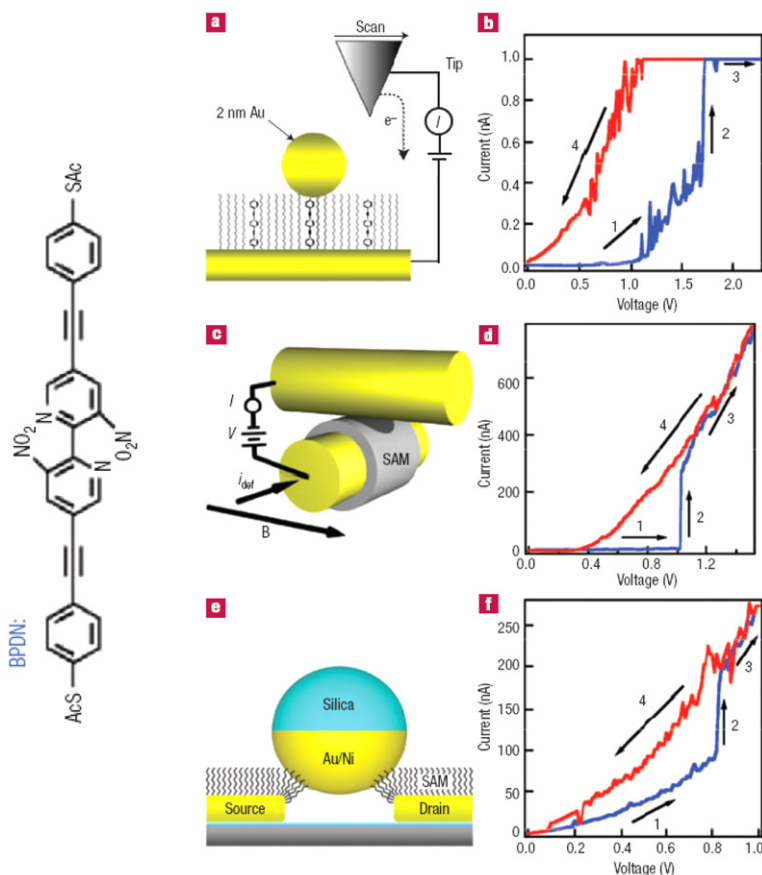
Fig. 6. Current–voltage characteristics of bipyridyl-dinitro oligophenylene-ethynylene dithiol connected by Au electrodes using different test-beds, from [92]: Au nanoparticle with STM, crossed-wires put in contact by the Lorentz force and Ni/Au metallized microsphere used as a magnetic bead junction. These experiments demonstrate a clear bias-induced switching behavior, while with a large variability.

6.2. Capacitive memory

Redox-active molecules, such as mettalocene, porphyrin and triple-decker sandwich coordination compounds attached on a silicon substrate have been found to act as charge storage molecular devices [147–150]. The molecular memory works on the principle of charging and discharging of the molecules into different chemically reduced or oxidized (redox) states. It has been demonstrated that porphyrins: (i) offer the possibility of multibit storage at a relatively low potentials (below ∼1.6 V); (ii) can undergo trillions of write/read/erase cycles; (iii) exhibit charge retention times that are long enough (minutes) compared with those of semiconductor DRAM (tens of ms); and (iv) are extremely stable under harsh conditions (400 °C – 30 min) and therefore meet the processing and operating conditions required for use in hybrid molecule/silicon devices [150]. Moreover, the same principle works with semiconducting nanowires dressed with redox molecules in a transistor configuration [151–153]. Optoelectronic memories have also been demonstrated with polymer-functionalized CNT transistors [154,155]. However, in all cases, further investigations on the search of other molecules and, understanding the factors that control parameters such as, charge transfer rate, which limit write/read times, and charge retention times, which determines refresh rates, are needed.

6.3. RTD-based memory

Memory can also be implemented from RTD devices following cell architecture already used for semiconductor devices. Memory cell based on RTD can be set up with 2 RTD and 2 transistors in a cross-bar architecture [156]. The advantages compared to 'resistive' and 'capacitive' molecular memories are fast switching times and possible long

retention times. RTD devices are characterized by a NDR behavior in their current–voltage curves; however, a NDR may be also induced by other physical phenomena such as conformational changes already discussed above. The principle of a RTD molecular device is similar to that of its solid state counter-part (a potential well separated from the electrodes by two tunnel barriers). In the molecular analogue, the barriers should consist of aliphatic chains (of variable length) and the well should be made up of a short conjugated oligomer. Even if NDR behavior has been observed from STM results on a single molecule attached to Si [157] and has been ascribed to resonance through the molecular orbitals, in agreement with a theoretical result [158], this interpretation has been ruled out both experimentally [159] and theoretically [160]. The exact origin of the molecular NDR behavior is still an open question, and therefore the RTD molecular device has not yet been clearly demonstrated.

7. Conclusions

We have described several functions and devices that have been studied at the molecular scale: tunnel barrier, molecular wire, rectifying and NDR diodes, bistable devices and memories. However, a better understanding and further improvements of their electronic properties are mandatory and need to be confirmed. These results suffer from a large dispersion and more efforts are now required to improve reproducibility and repeatability. For viable applications, more efforts are also mandatory to test the integration of molecular devices with silicon-CMOS electronics (hybrid molecular-CMOS nanoelectronics). Moreover, most of these devices are 2-terminal; what about a true/fully molecular 3-terminal device? We have also pointed out that the molecule-electrode coupling and conformation strongly modify the molecular-scale device properties. Molecular engineering (changing ligand atoms, for example) may be used to improve or adjust the electrode-molecule coupling. Nevertheless, a better control of the interface (energetics and atomic conformation) is still compulsory. Beyond the study of single or isolated devices, more works towards molecular architectures and circuits are required. Up to now, mainly the 'cross-bar' architecture has been studied. Is it sufficient? More new architectures must be explored (e.g. non-von Neuman, neuronal, quantum computing, . . .). Open questions concern the right approaches for inter-molecular device connections and nano-to-micro connections, the interface with the outer-world, hybridation with CMOS and 3D integration [161–164]. Beyond the CMOS, probability bets on non-charge based devices. Molecular devices using other state variables (e.g. spin, molecule conformation, . . .) to code a logic state are still challenging and exciting objectives. Finally, other reviews, current status and challenges on charge transfer on the nanoscale can be found in [165–168].

Acknowledgements

References

[1] J.-M. Lehn, Supramolecular chemistry-scope and perspectives. Molecules, supermolecules and molecular devices (Nobel lecture), Angew. Chem. Int. Ed. Engl. 27 (1988) 89–112.
[2] B. Mann, H. Kuhn, Tunneling through fatty acid salt monolayers, J. Appl. Phys. 42 (11) (1971) 4398–4405.
[3] A. Aviram, M.A. Ratner, Molecular rectifiers, Chem. Phys. Lett. 29 (2) (1974) 277–283.
[4] A. Ulman, An Introduction to Ultrathin Organic Films: From Langmuir–Blodgett to Self-Assembly, Boston, Academic Press, 1991.
[5] G.J. Ashwell, J.R. Sambles, A.S. Martin, W.G. Parker, M. Szablewski, Rectifying characteristics of Mg/(C16H33-Q3CNQ LB film)/Pt structures, J. Chem. Soc. Chem. Commun. 19 (1990) 1374–1376.
[6] N.J. Geddes, J.R. Sambles, A.S. Martin, Organic molecular rectifiers, Adv. Mater. Opt. Electron. 5 (1995) 305–320.
[7] A.S. Martin, J.R. Sambles, G.J. Ashwell, Molecular rectifier, Phys. Rev. Lett. 70 (2) (1993) 218–221.
[8] R.M. Metzger, B. Chen, U. Höpfner, M.V. Lakshmikantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T.V. Hughes, H. Sakurai, J.W. Baldwin, C. Hosch, M.P. Cava, L. Brehmer, G.J. Ashwell, Unimolecular electrical rectification in hexadecyquinolinium tricyanoquinodimethanide, J. Am. Chem. Soc. 119 (43) (1997) 10455–10466.
[9] D. Vuillaume, B. Chen, R.M. Metzger, Electron transfer through a monolayer of hexadecylquinolinium tricyanoquinodimethanide, Langmuir 15 (11) (1999) 4011–4017.
[10] T. Xu, I.R. Peterson, M.V. Lakshmikantham, R.M. Metzger, Rectification by a monolayer of hexadecylquinolinium tricyanoquinodimethanide between gold electrodes, Angew. Chem. Int. Ed. Engl. 40 (9) (2001) 1749–1752.

[11] R.M. Metzger, T. Xu, I.R. Peterson, Electrical rectification by a monolayer of hexadecylquinolinium tricyanoquinodimethanide measured between macroscopic gold electrodes, J. Phys. Chem. B 105 (30) (2001) 7280–7290.

[12] C.P. Collier, E.W. Wong, M. Belohradsky, F.M. Raymo, J.F. Stoddart, P.J. Kuekes, R.S. Williams, J.R. Heath, Electronically configurable molecular-based logic gates, Science 285 (1999) 391–394.

[13] C.P. Collier, G. Mattersteig, E.W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. Raymo, J.F. Stoddart, J.R. Heath, A [2]catenane-based solid state electronically reconfigurable switch, Science 289 (2000) 1172–1175.

[14] A.R. Pease, J.O. Jeppesen, J.F. Stoddart, Y. Luo, C.P. Collier, J.R. Heath, Switching devices based on interlocked molecules, Acc. Chem. Res. 34 (6) (2001) 433–444.

[15] Y. Chen, G.-Y. Jung, D.A.A. Ohlberg, X. Li, D.R. Stewart, J.O. Jeppesen, K.A. Nielsen, J.F. Stoddart, R.S. Williams, Nanoscale molecular-switch crossbar circuits, Nanotechnology 14 (2003) 462–468.

[16] Y. Chen, D.A.A. Ohlberg, X. Li, D.R. Stewart, R.S. Williams, J.O. Jeppesen, K.A. Nielsen, J.F. Stoddart, D.L. Olynick, E. Anderson, Nanoscale molecular-switch devices fabricated by imprint lithography, Appl. Phys. Lett. 82 (10) (2003) 1610–1612.

[17] M. Bruening, E. Moons, D. Yaron-Marcovitch, D. Cahen, J. Libman, A. Shanzer, Polar ligand adsorption controls semiconductor surface potentials, J. Am. Chem. Soc. 116 (7) (1994) 2972–2977.

[18] R. Cohen, S. Bastide, D. Cahen, J. Libman, A. Shanzer, Y. Rosenwaks, Controlling surfaces and interfaces of semiconductors using organic molecules, Opt. Mat. 9 (1998) 394–400.

[19] R. Cohen, N. Zenou, D. Cahen, S. Yitzchaik, Molecular electronic tuning of Si surfaces, Chem. Phys. Lett. 279 (1997) 270–274.

[20] R. Compano, L. Molenkamp, D.J. Paul, Technology roadmap for nanoelectronics, European Commission, IST Programme, Future and Emerging Technologies, Brussels, 2000.

[21] C. Joachim, J.K. Gimzewski, A. Aviram, Electronics using hybrid-molecular and monomolecular devices, Nature 408 (2000) 541–548.

[22] F. Schreiber, Structure and growth of self-assembling monolayers, Prog. Surf. Sci. 65 (5–8) (2000) 151–256.

[23] W.C. Bigelow, D.L. Pickett, W.A. Zisman, J. Colloid Sci. 1 (1946) 513–538.

[24] R. Maoz, J. Sagiv, On the formation and structure of self-assembling monolayers, J. Colloid Interface Sci. 100 (2) (1984) 465–496.

[25] J.B. Brzoska, N. Shahidzadeh, F. Rondelez, Evidence of a transition temperature for optimum deposition of grafted monolayer coatings, Nature 360 (1992) 719–721.

[26] J.B. Brzoska, I. Ben Azouz, F. Rondelez, Silanization of solid substrates: a step toward reproducibility, Langmuir 10 (11) (1994) 4367–4373.

[27] D.L. Allara, A.N. Parikh, F. Rondelez, Evidence for a unique chain organization in long chain silane monolayers deposited on two widely different solid substrates, Langmuir 11 (7) (1995) 2357–2360.

[28] A.N. Parikh, D.L. Allara, I. Ben Azouz, F. Rondelez, An intrinsic relationship between molecular structure in self-assembled *n*-alkylsiloxane monolayers and deposition temperature, J. Phys. Chem. 98 (1994) 7577–7590.

[29] R.E. Holmlin, R. Haag, M.L. Chabinyc, R.F. Ismagilov, A.E. Cohen, A. Terfort, M.A. Rampi, G.M. Whitesides, Electron transport through thin organic films in metal–insulator–metal junctions based on self-assembled monolayers, J. Am. Chem. Soc. 123 (21) (2001) 5075–5085.

[30] M.A. Rampi, O.J.A. Schueller, G.M. Whitesides, Alkanethiol self-assembled monolayers as the dielectric of capacitors with nanoscale thickness, Appl. Phys. Lett. 72 (14) (1998) 1781–1783.

[31] Y. Selzer, A. Salomon, D. Cahen, Effect of molecule–metal electronic coupling on through-bond hole tunneling across metal–organic monolayer–semiconductor junctions, J. Am. Chem. Soc. 124 (12) (2002) 2886–2887.

[32] Y. Selzer, A. Salomon, D. Cahen, The importance of chemical bonding to the contact for tunneling through alkyl chains, J. Phys. Chem. B 106 (40) (2002) 10432–10439.

[33] J. Chen, M.A. Reed, A.M. Rawlett, J.M. Tour, Large on-off ratios and negative differential resistance in a molecular electronic device, Science 286 (1999) 1550–1552.

[34] J. Chen, W. Wang, M.A. Reed, A.M. Rawlett, D.W. Price, J.M. Tour, Room-temperature negative differential resistance in nanoscale molecular junctions, Appl. Phys. Lett. 77 (8) (2000) 1224–1226.

[35] G.C. Herdt, A.W. Czanderna, Metal overlayer on organic functional groups of self-organized molecular assemblies. V. Ion scattering spectroscopy and X-ray photoelectron spectroscopy of Ag/COOH interfaces, J. Vac. Sci. Technol. A 13 (3) (1995) 1275–1280.

[36] D.R. Jung, A.W. Czanderna, Chemical and physical interactions at metal/self-assembled organic monolayer interfaces, Crit. Rev. Solid State Mater. Sci. 191 (1994) 1–54.

[37] D.R. Jung, A.W. Czanderna, G.C. Herdt, Interactions and penetration at metal/self-assembled organic monolayer interfaces, J. Vac. Sci. Technol. A 14 (3) (1996) 1779–1787.

[38] G.L. Fisher, A.E. Hooper, R.L. Opila, D.L. Allara, N. Winograd, The interaction of vapor-deposited Al atoms with COOH groups at the surface of a self-assembled alkanethiolate monolayer on gold, J. Phys. Chem. B 104 (14) (2000) 3267–3273.

[39] G.L. Fisher, A.V. Walker, A.E. Hooper, T.B. Tighe, K.B. Bahnck, H.T. Skriba, M.D. Reinard, B.C. Haynie, R.L. Opila, N. Winograd, D.L. Allara, Bond insertion, complexation and penetration pathways of vapor-deposited aluminium atoms with HO- and CH$_3$O-terminated organic monolayers, J. Am. Chem. Soc. 124 (19) (2002) 5528–5541.

[40] K. Konstadinidis, P. Zhang, R.L. Opila, D.L. Allara, An in-situ X-ray photoelectron study of the interaction between vapor-deposited Ti atoms and functional groups at the surfaces of self-assembled monolayers, Surf. Sci. 338 (1995) 300–312.

[41] S. Lenfant, D. Guerin, F. Tran Van, C. Chevrot, S. Palacin, J.-P. Bourgoin, O. Bouloussa, F. Rondelez, D. Vuillaume, Electron transport through rectifying self-assembled monolayer diodes on silicon: Fermi level pinning at the molecule–metal interface, J. Phys. Chem. B 110 (28) (2006) 13947–13958.

[42] D.K. Aswal, S. Lenfant, D. Guerin, J.V. Yakhmi, D. Vuillaume, A tunnel current in self-assembled monolayers of 3-mercaptopropyltrimethoxysilane, Small 1 (7) (2005) 725–729.

[43] D. Cahen, A. Kahn, E. Umbach, Energetics of molecular interfaces, Mater. Today (July/August 2005) 32–41.

[44] A. Kahn, N. Koch, W. Gao, Electronic structure and electrical properties of interfaces between metals and pi-conjugated molecular films, J. Polymer Sci.: Part B: Polymer Phys. 41 (2003) 2529–2548.

[45] N. Okazaki, J.R. Sambles. New fabrication technique and current–voltage properties of a Au/LB/Au structure, in: International Symposium on Organic Molecular Electronics, Nagoya, Japan, 2000.

[46] Y.-L. Loo, D.V. Lang, J.A. Rogers, J.W.P. Hsu, Electrical contacts to molecular layers by nanotransfer printing, Nano Lett. 3 (7) (2003) 913–917.

[47] Y. Xia, G.M. Whitesides, Soft lithography, Angew. Chem. Int. Ed. Engl. 37 (1998) 550–575.

[48] Y.-L. Loo, R.L. Willet, K.W. Baldwin, J.A. Rogers, J. Am. Chem. Soc. 124 (2002) 7654.

[49] D. Guerin, C. Merckling, S. Lenfant, X. Wallart, D. Vuillaume, Silicon–molecules–metal junctions by transfer printing: chemical synthesis and electrical properties, J. Phys. Chem. C 111 (22) (2007) 7947–7956.

[50] A. Vilan, D. Cahen, Soft contact deposition onto molecularly modified GaAs. Thin metal film flotation: principles and electrical effects, Adv. Func. Mater. 12 (11–12) (2002) 795–807.

[51] H.B. Akkerman, P.W.M. Blom, D.M. De Leeuw, B. De Boer, Towards molecular electronics with large-area molecular junctions, Nature 441 (4) (2006) 69–72.

[52] J. He, B. Chen, A.K. Flatt, J.J. Stephenson, C.D. Doyle, J.M. Tour, Metal-free silicon–molecule–nanotube testbed and memory device, Nature Mater. 5 (2006) 63–68.

[53] J.G. Kushmerick, D.B. Holt, S.K. Pollack, M.A. Ratner, J.C. Yang, T.L. Schull, J. Naciri, M.H. Moore, R. Shashidhar, Effect of bond-length alternation in molecular wires, J. Am. Chem. Soc. 124 (36) (2002) 10654–10655.

[54] J.G. Kushmerick, D.B. Holt, J.C. Yang, J. Naciri, M.H. Moore, R. Shashidhar, Metal–molecule contacts and charge transport across monomolecular layers: measurement and theory, Phys. Rev. Lett. 89 (8) (2002) 086802.

[55] L.A. Bumm, J.J. Arnold, T.D. Dunbar, D.L. Allara, P.S. Weiss, Electron transfer through organic molecules, J. Phys. Chem. B 103 (38) (1999) 8122–8127.

[56] A.P. Labonté, S.L. Tripp, R. Reifenberger, A. Wei, Scanning tunneling spectroscopy of insulating self-assembled monolayers on Au(111), J. Phys. Chem. B 106 (34) (2002) 8721–8725.

[57] D.J. Wold, C.D. Frisbie, Formation of metal–molecule–metal tunnel junctions: Microcontacts to alkanethiol monolayers with a conducting AFM tip, J. Am. Chem. Soc. 122 (12) (2000) 2970–2971.

[58] D.J. Wold, C.D. Frisbie, Fabrication and characterization of metal–molecule–metal junctions by conducting probe atomic force microscopy, J. Am. Chem. Soc. 123 (2001) 5549–5556.

[59] D.J. Wold, R. Haag, M.A. Rampi, C.D. Frisbie, Distance dependence of electron tunneling through self-assembled monolayers measured by conducting probe atomic force microscopy: unsaturated versus saturated molecular junctions, J. Phys. Chem. B (2002), web 23-2-2002.

[60] X.D. Cui, A. Primak, X. Zarate, J. Tomfohr, O.F. Sankey, A.L. Moore, T.A. Moore, D. Gust, G. Harris, S.M. Lindsay, Reproductible measurement of single-molecule conductivity, Science 294 (2001) 571–574.

[61] K.-A. Son, H.I. Kim, J.E. Houston, Role of stress on charge transfer through self-assembled alkanethiol monolayers on Au, Phys. Rev. Lett. 86 (23) (2001) 5357–5360.

[62] F. Moresco, G. Meyer, K.-H. Rieder, H. Tang, A. Gourdon, C. Joachim, Conformational changes of single molecules induced by scanning tunneling microscopy manipulation: A route to molecular switching, Phys. Rev. Lett. 86 (4) (2001) 672–675.

[63] B. Xu, N.J. Tao, Measurement of single-molecule resistance by repeated formation of molecular junctions, Science 301 (2003) 1221–1223.

[64] J. Ulrich, D. Esrail, W. Pontius, L. Venkataraman, D. Millar, L.H. Doerrer, Variability of conductance in molecular junctions, J. Phys. Chem. B 110 (6) (2006) 2462–2466.

[65] L. Venkataraman, J.E. Klare, I.W. Tam, C. Nuckolls, M.S. Hybertsen, M.L. Steigerwald, Single-molecule circuits with well-defined molecular conductance, Nano Lett. 6 (3) (2006) 458–462.

[66] F. Chen, X. Li, J. Hihath, Z. Huang, N.J. Tao, Effect of anchoring groups on single-molecule conductance: comparative study of thiom-, amine-, and carboxylic-acid-terminated molecules, J. Am. Chem. Soc. 128 (49) (2006) 15874–15881.

[67] X. Li, J. He, J. Hihath, B. Xu, S.M. Lindsay, N.J. Tao, Conductance of single alkanethiols: conduction mechanism and effect of molecule-electrode contacts, J. Am. Chem. Soc. 128 (6) (2006) 2135–2141.

[68] L. Venkataraman, Y.S. Park, A.C. Whalley, C. Nuckolls, M.S. Hybertsen, M.L. Steigerwald, Electronics and chemistry: varying single-molecule junction conductance using chemical substituents, Nano Lett. 7 (2) (2007) 502–506.

[69] L. Venkataraman, J.E. Klare, C. Nuckolls, M.S. Hybertsen, M.L. Steigerwald, Dependence of single molecule junction conductance on molecular conformation, Nature 442 (2006) 904–907.

[70] J. Collet, O. Tharaud, A. Chapoton, D. Vuillaume, Low-voltage, 30 nm channel length, organic transistors with a self-assembled monolayer as gate insulating films, Appl. Phys. Lett. 76 (14) (2000) 1941–1943.

[71] J. Collet, D. Vuillaume, A nano-field effect transistor with an organic self-assembled monolayer as gate insulator, Appl. Phys. Lett. 73 (18) (1998) 2681–2683.

[72] M. Mottaghi, P. Lang, F. Rodriguez, A. Rumyantseva, A. Yassar, G. Horowitz, S. Lenfant, D. Tondelier, D. Vuillaume, Low-operating-voltage organic transistors made of bifunctional self-assembled monolayers, Adv. Func. Mater. 17 (2007) 597–604.

[73] S. Cholet, C. Joachim, J.P. Martinez, B. Rousset, Fabrication of co-planar metal–insulator–metal solid state nanojunction down to 5 nm, Eur. Phys. J. Appl. Phys. 8 (2) (1999) 139–145.

[74] A. Bezryadin, C. Dekker, Nanofabrication of electrodes with sub-5 nm spacing for transport experiments on single molecules and metal clusters, J. Vac. Sci. Technol. B 15 (4) (1997) 793–799.

[75] M.A. Guillorn, D.W. Carr, R.C. Tiberio, E. Greenbaum, M.L. Simpson, Fabrication of dissimilar metal electrodes with nanometer interelectrode distance for molecular electronic device characterization, J. Vac. Sci. Technol. B 18 (3) (2000) 1177–1181.

[76] H. Park, A.K.L. Lim, P.A. Alivisatos, J. Park, P.L. McEuen, Fabrication of metallic electrodes with nanometer separation by electromigration, Appl. Phys. Lett. 75 (2) (1999) 301–303.

[77] W. Liang, M.P. Shores, M. Bockrath, J.R. Long, H. Park, Kondo effect in a single-molecule transistor, Nature 417 (2002) 725–729.

[78] J. Park, A.N. Pasupathy, J.I. Goldsmith, C. Chang, Y. Yaish, J.R. Petta, M. Rinkoski, J.P. Sethna, H.D. Abrunas, P.L. McEuen, D.C. Ralph, Coulomb blockade and the Kondo effect in single-atom transistors, Nature 417 (2002) 722–725.

[79] S. Boussaad, N.J. Tao, Atom-size gaps and contacts between electrodes fabricated with a self-terminated electrochemical method, Appl. Phys. Lett. 80 (13) (2002) 2398–2400.

[80] C.Z. Li, H.X. He, N.J. Tao, Quantized tunneling current in the metallic nanogaps formed by electrodeposition and etching, Appl. Phys. Lett. 77 (24) (2000) 3995–3997.

[81] Y.V. Kervennic, H.S. Van der Zant, A.F. Morpurgo, L. Gurevitch, L.P. Kouwenhoven, Nanometer-spaced electrodes with calibrated separation, Appl. Phys. Lett. 80 (2) (2002) 321–323.

[82] X. Guo, J.P. Small, J.E. Klare, Y. Wang, M.S. Purewal, I.W. Tam, B.H. Hong, R. Caldwell, L. Huang, S. O'Brien, J. Yan, R. Breslow, S.J. Wind, J. Hone, P. Kim, C. Nuckolls, Covalently bridging gaps in single-walled carbon nanotubes with conducting molecules, Science 311 (2006) 356–359.

[83] X. Guo, A.C. Whalley, J.E. Klare, L. Huang, S. O'Brien, M.L. Steigerwald, C. Nuckolls, Single-molecule devices as scaffolding for multi-component nanostructure assembly, Nano Lett. 7 (5) (2007) 1119–1122.

[84] M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, J.M. Tour, Conductance of a molecular junction, Science 278 (1997) 252–254.

[85] C. Kergueris, J.P. Bourgoin, S. Palacin, D. Esteve, C. Urbina, M. Magoga, C. Joachim, Electron transport through a metal–molecule–metal junction, Phys. Rev. B 59 (19) (1999) 12505–12513.

[86] J. Reichert, R. Ochs, D. Beckmann, H.B. Weber, M. Mayor, H.v. Löhneysen, Driving current through single organic molecules, Phys. Rev. Lett. 88 (17) (2002) 176804.

[87] H.B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs, H.v. Löhneysen, Electronic transport through single conjugated molecules, Chem. Phys. 281 (2002) 113–125.

[88] M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H.B. Weber, M. Mayor, A single-molecule diode, Proc. Natl. Acad. Sci. USA 102 (25) (2005) 8815–8820.

[89] J. Reichert, H.B. Weber, M. Mayor, H.v. Lölneysen, Low-temperature conductance measurements on single molecules, Appl. Phys. Lett. 82 (23) (2003) 4137–4139.

[90] T. Dadosh, Y. Gordin, R. Krahne, I. Khrivrich, D. Mahalu, V. Frydman, J. Sperling, A. Yacoby, I. Bar-Joseph, Measurement of the conductance of single conjugated molecules, Nature 436 (2005) 677–680.

[91] D.P. Long, C.H. Patterson, M.H. Moore, D.S. Seferos, G. Bazan, J.G. Kushmerick, Magnetic directed assembly of molecular junctions, Appl. Phys. Lett. 86 (2005) 153105.

[92] A. Szuchmacher Blum, J.G. Kushmerick, D.P. Long, C.H. Patterson, J.C. Yang, J.C. Henderson, Y. Yao, J.M. Tour, R. Shashidhar, B.R. Ratna, Molecularly inherent voltage-controlled conductance switching, Nature Mater. 4 (2005) 167–172.

[93] E.E. Polymeropoulos, Electron tunneling through fatty-acid monolayers, J. Appl. Phys. 48 (6) (1977) 2404–2407.

[94] E.E. Polymeropoulos, J. Sagiv, Electrical conduction through adsorbed monolayers, J. Chem. Phys. 69 (5) (1978) 1836–1847.

[95] S. Lenfant, Monocouches organiques auto-assemblées pour la réalisation de diodes moléculaires, PhD, Univ. of Lille, 2001.

[96] W. Wang, T. Lee, M.A. Reed, Mechanism of electron conduction in self-assembled alkanethiol monolayer devices, Phys. Rev. B 68 (2003) 035416.

[97] H. Sakaguchi, A. Hirai, F. Iwata, A. Sasaki, T. Nagamura, E. Kawata, S. Nakabayashi, Determination of performance on tunnel conduction through molecular wire using a conductive atomic force microscope, Appl. Phys. Lett. 79 (22) (2001) 3708–3710.

[98] V.B. Engelkes, J.M. Beebe, C.D. Frisbie, Length-dependent transport in molecular junctions based on SAMs of alkanethiols and alkanedithiols: Effects of metal work function and applied bias on tunneling efficiency and contact resistance, J. Am. Chem. Soc. 126 (43) (2004) 14287–14296.

[99] X.D. Cui, A. Primak, X. Zarate, J. Tomfohr, O.F. Sankey, A.L. Moore, T.A. Moore, D. Gust, L.A. Nagahara, S.M. Lindsay, Changes in the electronic properties of a molecule when it is wired into a circuit, J. Phys. Chem. B 106 (34) (2002) 8609–8614.

[100] A. Salomon, D. Cahen, S.M. Lindsay, J. Tomfohr, V.B. Engelkes, C.D. Frisbie, Comparison of electronic transport measurements on organic molecules, Adv. Mat. 15 (22) (2003) 1881–1890.

[101] R.J. Powell, Interface energy barrier determination from voltage dependence of photoinjected currents, J. Appl. Phys. 41 (6) (1970) 2424–2432.

[102] C. Boulas, J.V. Davidovits, F. Rondelez, D. Vuillaume, Suppression of charge carrier tunneling through organic self-assembled monolayers, Phys. Rev. Lett. 76 (25) (1996) 4797–4800.

[103] D. Vuillaume, C. Boulas, J. Collet, G. Allan, C. Delerue, Electronic structure of alkylsiloxane self-assembled monolayer-silicon heterostructure, Phys. Rev. B 58 (24) (1998) 16491–16498.

[104] A. Salomon, M. Boecking, C.K. Chan, F. Amy, O. Girshevitz, D. Cahen, A. Kahn, How do electronic carriers cross Si-bound alkyl monolayers? Phys. Rev. Lett. 95 (2005) 266897.

[105] A. Salomon, M. Boecking, O. Seitz, T. Markus, F. Amy, C.K. Chan, W. Zhao, D. Cahen, A. Kahn, What is the barrier for tunneling through alkyl monolayers? Results from n– and p–Si-alkyl/Hg junctions, Adv. Mat. 19 (2007) 445–450.

[106] T. Vondrak, C.J. Cramer, X.-Y. Zhu, The nature of electronic contact in self-assembled monolayers for molecular electronics: evidence of strong coupling, J. Phys. Chem. B 103 (42) (1999) 8915–8919.

[107] J.M. Beebe, V.B. Engelkes, L.L. Miller, C.D. Frisbie, Contact resistance in metal–molecule–metal junctions based on aliphatic SAMs: Effects of surface linker and metal work function, J. Am. Chem. Soc. 124 (38) (2002) 11268–11269.

[108] J.G. Kushmerick, J. Lazorcik, C.H. Patterson, R. Shashidhar, D.S. Seferos, G. Bazan, Vibronic contributions to charge transport across molecular junctions, Nano Lett. 4 (2004) 643.

[109] W. Wang, T. Lee, I. Krestchmar, M.A. Reed, Inelastic electron tunneling spectroscopy of an alkanedithiol self-assembled monolayer, Nano Lett. 4 (2004) 643.

[110] C. Petit, G. Salace, S. Lenfant, D. Vuillaume, Inelastic tunneling spectra of an alkyl self-assembled monolayer using a MOS tunnel junction as a test-bed, Microelectronic Engrg. 80 (2005) 398–401.

[111] D.K. Aswal, C. Petit, G. Salace, D. Guérin, S. Lenfant, J.V. Yakhmi, D. Vuillaume, Role of interfaces on the direct tunneling and the inelastic tunneling behaviors through metal/alkylsilane/silicon junctions, Phys. Stat. Sol. (a) 203 (6) (2006) 1464–1469.

[112] J.M. Beebe, H.J. Moore, T.R. Lee, J.G. Kushmerick, Vibronic coupling in semifluorinated alkanethiol junctions: Implications for selection rules in inelastic electron tunneling spectroscopy, Nano Lett. 7 (5) (2007) 1364–1368.

[113] D.P. Long, J.L. Lazorcik, B.A. Mantooth, M.H. Moore, M.A. Ratner, A. Troisi, Y. Yao, J.W. Ciszek, J.M. Tour, R. Shashidhar, Effects of hydration on molecular junction transport, Nature Mater. 5 (2006) 901–908.

[114] Z. Huang, B. Xu, Y. Chen, M. Di Ventra, N.J. Tao, Measurement of current-induced local heating in a single molecule junction, Nano Lett. 6 (6) (2006) 1240–1244.

[115] N. Clement, S. Pleutin, O. Seitz, S. Lenfant, D. Vuillaume, $1/f^\gamma$ tunnel current noise through Si-bound alkyl monolayers, Phys. Rev. B 76 (2007) 205407.

[116] J.R. Petta, S.K. Slater, D.C. Ralph, Spin-dependent transport in molecular tunnel junctions, Phys. Rev. Lett. 93 (13) (2004) 136601.

[117] W. Wang, C.A. Richter, Spin-polarized inelastic tunneling spectroscopy of a molecular magnetic tunnel junction, Appl. Phys. Lett. 89 (2006) 153105.

[118] L.A. Bumm, J.J. Arnold, M.T. Cygan, T.D. Dunbar, T.P. Burgin, L. Jones II, D.L. Allara, J.M. Tour, P.S. Weiss, Are single molecular wires conducting? Science 271 (1996) 1705–1707.

[119] L. Patrone, S. Palacin, J.-P. Bourgoin, J. Lagoute, T. Zambelli, S. Gauthier, Direct comparison of the electronic coupling efficiency of sulfur and selenium anchoring groups for molecules adsorbed onto gold electrodes, Chem. Phys. 281 (2002) 325–332.

[120] L. Patrone, S. Palacin, J. Charlier, F. Armand, J.-P. Bourgoin, H. Tang, S. Gauthier, Evidence of the key role of metal–molecule bonding in metal–molecule–metal transport experiments, Phys. Rev. Lett. 91 (9) (2003) 096802.

[121] M. Di Ventra, N.D. Lang, Transport in nanoscale conductors from first principles, Phys. Rev. B 65 (2001) 045402.

[122] S.N. Yaliraki, M. Kemp, M.A. Ratner, Conductance of molecular wires: Influence of molecule–electrode binding, J. Am. Chem. Soc. 121 (14) (1999) 3428–3434.

[123] L. Patrone, S. Palacin, J.-P. Bourgoin, Direct comparison of the electronic coupling efficiency of sulfur and selenium alligator clips for molecules adsorbed onto gold electrodes, Appl. Surf. Sci. 212 (2003) 446–451.

[124] P. Reddy, S.-Y. Jang, R.A. Segalman, A. Majumdar, Thermoelectricity in molecular junction, Science 315 (2007) 1568–1571.

[125] R.M. Metzger, The unimolecular rectifier: Unimolecular electronic devices are coming..., J. Mater. Chem. 9 (1999) 2027–2036.

[126] R.M. Metzger, C.A. Panetta, The quest for unimolecular devices, New J. Chem. 15 (1991) 209–221.

[127] R.M. Metzger, J.W. Baldwin, W.J. Shumate, I.R. Peterson, P. Mani, G.J. Mankey, T. Morris, G. Szulczewski, S. Bosi, M. Prato, A. Comito, Y. Rubin, Electrical rectification in a Langmuir–Blodgett monolayer of dimethyanilinoazafullerene sandwiched between gold electrodes, J. Phys. Chem. B 107 (4) (2003) 1021–1027.

[128] J.W. Baldwin, R.R. Amaresh, I.R. Peterson, W.J. Shumate, M.P. Cava, M.A. Amiri, R. Hamilton, G.J. Ashwell, R.M. Metzger, Rectification and nonlinear optical properties of a Langmuir–Blodgett monolayer of a pyridinium dye, J. Phys. Chem. B 106 (47) (2002) 12158–12164.

[129] M.-K. Ng, D.-C. Lee, L. Yu, Molecular diodes based on conjugated biblock co-oligomers, J. Am. Chem. Soc. 124 (40) (2002) 11862–11863.

[130] Z. Wei, M. Kondratenko, L.H. Dao, D.F. Perepichka, Rectifying diodes from asymmetrically functionalized single-wall carbon nanotubes, J. Am. Chem. Soc. 128 (2006) 3134–3135.

[131] C. Krzeminski, G. Allan, C. Delerue, D. Vuillaume, R.M. Metzger, Theory of electrical rectification in a molecular monolayer, Phys. Rev. B 64 (2001) 085405.

[132] K. Stokbro, J. Taylor, M. Brandbyge, Do Aviram–Ratner diodes rectify? J. Am. Chem. Soc. 125 (13) (2003) 3674–3675.

[133] P.E. Kornilovitch, A.M. Bratkovsky, R.S. Williams, Current rectification by molecules with asymmetric tunneling barriers, Phys. Rev. B 66 (2002) 165436.

[134] J. Taylor, M. Brandbyge, K. Stokbro, Theory of rectification in Tour wires: the role of electrode coupling, Phys. Rev. Lett. 89 (13) (2002) 138301.

[135] S. Datta, W. Tian, S. Hong, R. Reifenberger, J.I. Henderson, C.P. Kubiak, Current–voltage characteristics of self-assembled monolayers by scanning tunneling microscopy, Phys. Rev. Lett. 79 (13) (1997) 2530–2533.

[136] S. Lenfant, C. Krzeminski, C. Delerue, G. Allan, D. Vuillaume, Molecular rectifying diodes from self-assembly on silicon, Nano Lett. 3 (6) (2003) 741–746.

[137] A. Aviram, C. Joachim, M. Pomerantz, Evidence of switching and rectification by a single molecule effected with a scanning tunneling microscope, Chem. Phys. Lett. 146 (6) (1988) 490–495.

[138] A. Aviram, C. Joachim, M. Pomerantz, Errata on "Evidence of switching and rectification by a single molecule effected by a scanning tunneling microscope", Chem. Phys. Lett. 162 (4–5) (1989) 416.

[139] A. Aviram, Molecules for memory, logic, and amplification, J. Am. Chem. Soc. 110 (1988) 5687–5692.

[140] M.A. Reed, J. Chen, A.M. Rawlett, D.W. Price, J.M. Tour, Molecular random access memory cell, Appl. Phys. Lett. 78 (23) (2001) 3735–3737.

[141] Z.J. Donhauser, B.A. Mantooth, K.F. Kelly, L.A. Bumm, J.D. Monnell, J.J. Stapleton, D.W. Price, A.M. Rawlett, D.L. Allara, J.M. Tour, P.S. Weiss, Conductance switching in single molecules through conformational changes, Science 292 (2001) 2303–2307.

[142] G.K. Ramachandran, T.J. Hopson, A.M. Rawlett, L.A. Nagahara, A. Primak, S.M. Lindsay, A bond-fluctuation mechanism for stochastic switching in wired molecules, Science 300 (5624) (2003) 1413–1416.

[143] C.P. Collier, J.O. Jeppesen, Y. Luo, J. Perkins, E.W. Wong, J.R. Heath, J.F. Stoddart, Molecular-based electronically switchable tunnel junction devices, J. Am. Chem. Soc. 123 (50) (2001) 12632–12641.

[144] J.E. Green, J.W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. Delonno, Y. Luo, B.A. Sherrif, K. Xu, Y.S. Shin, H.-R. Tseng, J.F. Stoddart, J.R. Heath, A 160-kilobit molecular electronic memory patterned at 10^{11} bits per square centimeter, Nature 445 (2007) 414–417.

[145] D.R. Stewart, D.A.A. Ohlberg, P.A. Beck, Y. Chen, R.S. Williams, J.O. Jeppesen, K.A. Nielsen, J.F. Stoddart, Molecule-independent electrical switching in Pt/organic monolayer/Ti devices, Nano Lett. 4 (1) (2004) 133–136.

[146] C. Loppacher, M. Guggiesberg, O. Pfeiffer, E. Meyer, M. Bammerlin, R. Lüthi, R.G. Schlitter, J.K.H. Tang, C. Joachim, Direct determination of the energy required to operate a single molecule switch, Phys. Rev. Lett. 90 (6) (2003) 066107.

[147] Q. Li, G. Mathur, M. Homsi, S. Surthi, V. Misra, V. Malinovskii, K.-H. Schweikart, L. Yu, J.S. Lindsey, Z. Liu, R.B. Dabke, A.A. Yasseri, D.F. Bocian, W.G. Kuhr, Capacitance and conductance characterization of ferrocene-containing self-assembled monolayers on silicon surfaces for memory applications, Appl. Phys. Lett. 81 (8) (2002) 1494–1496.

[148] K.M. Roth, J.S. Lindsey, D.F. Bocian, W.G. Kuhr, Characterization of charge storage in redox-active self-assembled monolayers, Langmuir 18 (10) (2002) 4030–4040.

[149] K.M. Roth, A.A. Yasseri, Z. Liu, R.B. Dabke, V. Malinovskii, K.-H. Schweikart, L. Yu, H. Tiznado, F. Zaera, J.S. Lindsey, W.G. Kuhr, D.F. Bocian, Measurements of electron-transfer rates of charge-storage molecular monolayers on Si(100). Towards hybrid molecular/semiconductor information storage devices, J. Am. Chem. Soc. 125 (2) (2003) 505–517.

[150] Z. Liu, A.A. Yasseri, J.S. Lindsey, D.F. Bocian, Molecular memories that survive silicon device processing and real-world operation, Science 302 (2003) 1543–1545.

[151] X. Duan, Y. Huang, C.M. Lieber, Nonvolatile memory and programmable logic from molecule-gated nanowires, Nano Lett. 2 (5) (2002) 487–490.

[152] C. Li, W. Fan, B. Lei, D. Zhang, S. Han, T. Tang, X. Liu, Z. Liu, S. Asano, M. Meyyappan, J. Han, C. Zhou, Multilevel memory based on molecular devices, Appl. Phys. Lett. 64 (11) (2004) 1949–1951.

[153] C. Li, J. Ly, B. Lei, W. Fan, D. Zhang, J. Han, M. Meyyappan, M. Thompson, C. Zhou, Data storage studies on nanowire transistors with self-assembled phorphyrin molecules, J. Phys. Chem. B 108 (28) (2004) 9646–9649.

[154] J. Borghetti, V. Derycke, S. Lenfant, P. Chenevier, A. Filoramo, M. Goffman, D. Vuillaume, J.-P. Bourgoin, Optoelectronic switch and memory devices based on polymer-functionalized carbon nanotube transistors, Adv. Mat. 18 (2006) 2535–2540.

[155] A. Star, Y. Lu, K. Bradley, G. Grüner, Nanotube optoelectronic memory devices, Nano Lett. 4 (9) (2004) 1587–1591.

[156] J.P.A. van der Wagt, A.C. Seabaugh, E.A. Beam, RTD/HFET low standby power SRAM gain cell, IEEE Electron Device Lett. 19 (1) (1998) 7–9.

[157] N.P. Guisinger, M.E. Greene, R. Basu, A.S. Baluch, M.C. Hersam, Room temperature negative differential resistance through individual organic molecules on silicon surfaces, Nano Lett. 4 (1) (2004) 55–59.

[158] T. Rakshit, G.-C. Liang, A.W. Ghosh, S. Datta, Silicon-based molecular electronics, Nano Lett. 4 (10) (2004) 1803–1807.

[159] J.L. Pitters, R.A. Wolkow, Detailed studies of molecular conductance using atomic resolution scanning tunneling microscopy, Nano Lett. 6 (3) (2006) 390–397.

[160] S.Y. Quek, J.B. Neaton, M.S. Hybertsen, E. Kaxiras, S.G. Louie, Negative differential resistance in transport through organic molecules on silicon, Phys. Rev. Lett. 98 (2007) 066807.

[161] A. Dehon, P. Lincoln, J.E. Savage, Stochastic assembly of sublithographic nanoscale interfaces, IEEE Trans. Nanotechnol. 2 (3) (2003) 165–174.

[162] J.M. Tour, W.L. van Zandt, C.P. Husband, S.M. Husband, L.S. Wilson, P.D. Franzon, D.P. Nackashi, Nanocell logic gates for molecular computing, IEEE Trans. Nanotechnol. 1 (2) (2002) 100–109.

[163] K.K. Likharev, D.B. Strukov, CMOL: Devices, circuits and architectures, in: G. Cuniberti (Ed.), Introduction to Molecular Electronics, Springer, 2005, pp. 447–477.

[164] S.C. Goldstein and M. Budiu, Nanofabrics: spatial computing using molecular electronics, in: Int. Symp. on Computer Architecture, 2001.

[165] D.M. Adams, L. Brus, C.E.D. Chidsey, S. Creager, C. Creutz, C.R. Kagan, P.V. Kamat, M. Lieberman, S.M. Lindsay, R.A. Marcus, R.M. Metzger, M.E. Michel-Beyerle, J.R. Miller, M.D. Newton, D.R. Rolison, O. Sankey, K.S. Schanze, J. Yardley, X. Zhu, Charge transfer on the nanoscale: Currents status, J. Phys. Chem. B 107 (28) (2003) 6668–6697.

[166] A. Nitzan, Electron transmission through molecules and molecular interfaces, Annu. Rev. Phys. Chem. 52 (2001) 681.

[167] N.J. Tao, Electron transport in molecular junctions, Nature Nanotechnol. 1 (2006) 173–181.

[168] A. Nitzan, M.A. Ratner, Electron transport in molecular wire junctions, Science 300 (5624) (2003) 1384–1389.