Nanofabrication 2014; 1: 96–117 DE GRUYTER OPEN

Review Article **Open Access**

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Nanofabrication techniques of highly organized monolayers sandwiched between two electrodes for molecular electronics

Abstract: It is expected that molecular electronics, i.e., the use of molecules as critical functional elements in electronic devices, will lead in the near future to an industrial exploitable novel technology, which will open new routes to high value-added electronic products. However, despite the enormous advances in this field several scientific and technological challenges should be surmounted before molecular electronics can be implemented in the market. Among these challenges are the fabrication of reliable, robust and uniform contacts between molecules and electrodes, the deposition of the second (top) contact electrode, and development of assembly strategies for precise placement of molecular materials within device structures. This review covers advances in nanofabrication techniques used for the assembly of monomolecular films onto conducting or semiconducting substrates as well as recent methods developed for the deposition of the top contact electrode highlighting the advantages and limitations of the several approaches used in the literature. This contribution also aims to define areas of outstanding challenges in the nanofabrication of monomolecular layers sandwiched between two electrodes and opportunities for future research and applications.

Keywords: molecular junctions, monolayers, molecular electronics, nanofabrication

DOI 10.2478/nanofab-2014-0010
Received August 11, 2014; accepted Ocotber 27, 2014

Molecular electronics [1,2] is a promising field of research based on the idea that a single molecule or two dimensional assemblies of molecules (monomolecular films) can work as wires, switches, rectifiers, etc. Molecules are the smallest functional units and therefore it is expected that the use of molecules will permit to catch up with the limits of miniaturization (MM: more Moore), with an increase in device density by a factor of several orders of magnitude compared to today's state of the art. At the same time due to quantum effects novel and remarkable properties of organic and organometallic compounds at the nanoscale devices will result in increased performance (MtM: more than Moore) together with the appearance of new functions not possible with conventional semiconductors, and also cheaper devices due to the non-dependence of expensive materials used today in CMOS (complementary metal-oxide semiconductor) technology such as hafnium oxide. Nowadays, the number of research groups from different disciplines of science contributing to molecular electronics is gradually growing, and this field is becoming of great scientific and technological interest [1,3-8]. Since the seminal work of Aviram and Ratner in 1974 who firstly suggested that a single molecule could function as a rectifier [9], molecules have been experimentally demonstrated to work as switches, molecular wires or rectifiers, and a new field of opportunities is opened due to the understanding of electron transport through single entities or assemblies of molecules and expansion towards work on molecular spintronics, vibronic effects, excitation of the molecular junction with polarized light, quantum interference and decoherence, molecular chirality, molecular stretching and distortion as well as work on thermoelectric response in molecular junctions.

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These new opportunities could change the way in which technology approaches practical problems including solar-energy harvesting, thermoelectricity, catalysis, sensing, and environmental issues [1,2].

As mentioned above, the term molecular electronics is generally applied to devices designed to involve either a single molecule or a single layer of molecules oriented between two contacts with the critical distance between the contacts lying in the nanometer size range. The study of single-molecule junctions has enormously contributed to understand and control the electronic transport phenomena at the molecular level [6,10-20]. However, molecular-monolayer junctions offer an advantage over single-molecule junctions due to their crucial role in understanding the effect of intermolecular interactions, e.g., van der Waals interactions and polarization effects in electronic transport properties [21-23]. In addition, working with planar-sandwiched geometries is of large interest in electronic applications since two dimensional (2D) monomolecular structures up to 10^{15} molecules·cm^{-2} can be fabricated. Implementation of electrical devices that use molecules as the active basic units requires, among other challenges, ability to tailor the architecture of molecular assemblies on surfaces and at interfaces for which a comprehensive knowledge of the interactions between molecules and surfaces is critical. Furthermore, it is well-known that contact geometry between the organic terminal group and the conducting substrate together with the efficiency of electron transport in molecular junctions are key parameters to the construction of reliable molecular electronic devices with efficient electrical conduction properties. It is therefore the aim of this paper to briefly review the nanofabrication techniques explored so far for the assembly of a monolayer between two electrodes for molecular electronic applications (Figure 1) highlighting their advantages and limitations to obtain robust and reliable devices and occasionally suggest or speculate about issues that we feel that deserve further investigations. To achieve this goal, this paper has been divided into two parts. First, the principal methods used for the deposition of monomolecular films onto conducting electrodes will be revised. Second, the different fabrication methods employed for the deposition of the top-contact electrode onto organic monolayers will be presented.

1 Deposition of monomolecular films onto conducting electrodes.

A significant number of techniques for the deposition of mono or multi-layered films are used in the field of organic electronics (see differences between organic electronics and molecular electronics in reference [5]) including spin-coating, dip-coating, spray-coating, layer-by-layer (LbL), self-assembly (SA), Langmuir-Blodgett (LB), chemical vapour deposition (CVD), physical vapour deposition (PVD), liquid phase epitaxy (LPE), molecular

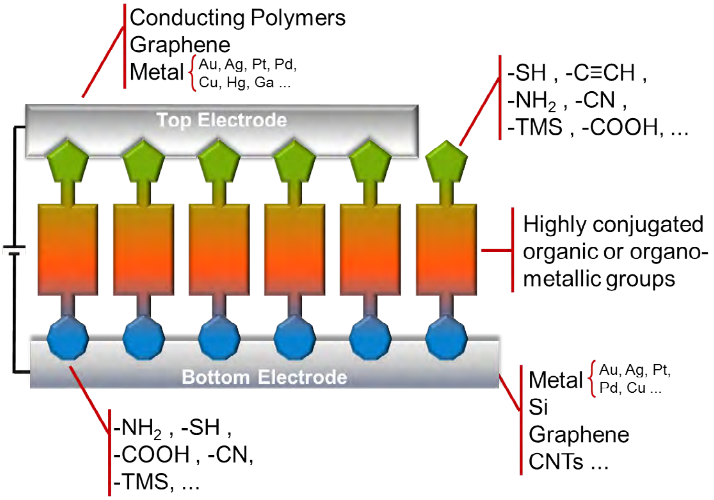


Figure 1: Scheme of an electrode-monolayer-electrode device, where the organic or organometallic monolayer is sandwiched between two electrodes. Typically these electrodes are metals but significant efforts are being made to connect molecules between organic electrodes to build up all carbon molecular electronic devices. Molecules have three main parts: (i) the head-group that anchors the molecule at the bottom electrode; (ii) the backbone of the molecule, generally, a highly conjugated skeleton that may also contain redox active groups; and (iii) the functional end-group that ideally should contain an appropriate functionality to ensure a good (chemical) contact to the top electrode.

beam epitaxy (MBE), molecular layer deposition (MLD), thermoevaporation, sputtering, etc. However, the main methods used for the fabrication of molecular electronic devices incorporating organic, organometallic or hybrid organic-inorganic materials onto conducting or semiconducting substrates have been so far limited to the self-assembly and the Langmuir-Blodgett techniques together with electrografting methods mainly based on the electroreduction of aryl diazonium salts. These techniques, which are described in this review, are included in the so called "bottom-up approaches" [24], which allow the construction of nanodevices from molecular building blocks. The unique capabilities of each of these methods are utilized by physicists, chemists, and molecular engineers in an effort to control the fabrication of well-ordered films, where the final architecture can be controlled by the operator.

1.1 The Self-Assembly technique

1.1.1 Self-Assembled monolayers on metal surfaces

In the year 1983, Nuzzo and Allara [25] published their investigations on the formation of dialkyl disulphide monolayers on gold. This spontaneous chemisorption of organic compounds onto metal surfaces was the first report on the SA method. Since then, many materials have been successfully self-assembled onto different solid supports for a wide range of applications and excellent reviews on the field have been published [26-33]. The SA technique is a quick, cheap, versatile, and simple method that permits the fabrication of high quality self-assembled monolayers (SAM). In SAMs grown in solution molecules attach themselves by means of an end group to a specific substrate to form a densely packed monomolecular film. Therefore, no special equipment is needed to fabricate a SAM, which results in low production costs, since the molecules assemble themselves at the designated surface without any external influence, and also because only small quantities are required to cover large areas, making SAMs very appealing for industrial uses. The experimental procedure for the fabrication of a SAM consists in (Figure 2): (i) immersion of a well-cleaned substrate (Au, Ag, Pt, Cu, Pd, GaAs, InP,...) into an organic solution containing the molecules of interest (typically in the 10 mM to 10 µM range); the immersion time depends on the nature of the molecule, the interface, and the concentration of the solution, varying between minutes and days; (ii) non-adsorbed molecules are removed by rinsing thoroughly with the same solvent. In SA, chemisorption

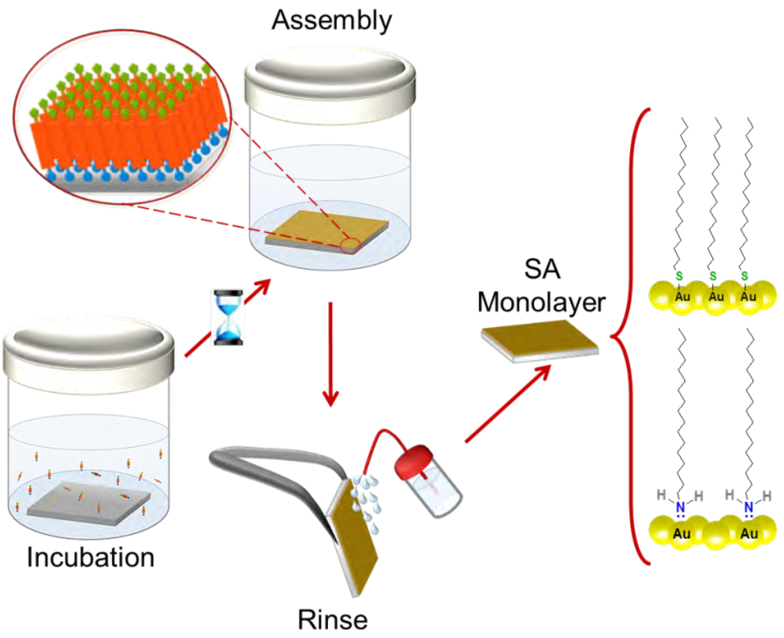


Figure 2: Scheme of the experimental procedure for the fabrication of SAMs. First, the substrate is incubated in a solution containing the molecules for a period of time, which depends on the nature of the material, the interface, and the solution concentration. Second, a thorough rinsing of the substrate is used to remove the non-adsorbed material. As indicated in the text, a relatively strong chemical bond between the molecule and the substrate may occur as in the case of thiols adsorbed on gold. Also donor-acceptor bonds (e.g. N-Au) are possible.

of the material onto the substrate comes first, and it is followed by molecular organization driven by lateral forces (typically van der Waals, π-π and hydrophobic forces between neighbouring molecules). SAMs have been described [31] as the interface between two different worlds: contacting metals, semiconductors or inorganic compounds with organic or biological materials, i.e., materials with totally different physical and chemical properties. This is the reason why the nature and strength of the interaction between the functional organic material and the underlying conducting substrate is crucial in achieving an efficient electron transport from the bottom electrode to the molecule and subsequently to the top-contact electrode (or vice versa) since junctions, in which the molecule is chemically contacted with both electrodes, are less resistive than junctions with only one chemisorbed contact [11]. Formation of SAMs and information about the molecule-electrode interaction can be obtained by means of a wide variety of methods including quartz crystal microbalance, cyclic voltammetry, impedance spectroscopy, ellipsometry, surface plasmon resonance imaging, infrared reflection absorption spectroscopy, scanning electron and scanning force microscopies, etc.

Most of the research done so far on molecular electronics of SAMs is focused on thiolate-SAMs deposited onto metal substrates, especially onto gold, that results in excellent quality films formed by the relatively strong gold-sulfur linkage [25,27,34,45]. In particular, thiolate-SAM surfaces can be formed by employing monothiols (R-SH), thioethers (R-S-R) or disulfides (R-SS-R), where R represents an alkyl or an aryl group. The thiolate-gold bond formation requires a deprotonation of the sulfhydryl group to form a thiyl radical ($RS^{\cdot}$) [46] and subsequent formation of a covalent RS-Au bond, which has been demonstrated by DFT calculations in combination with photoelectron spectroscopy [47-52]. However, in the last years many other functional groups have been studied for the assembly of organic compounds with potential applications in the field of molecular electronics since several drawbacks of the S-Au bond have been highlighted. First, deposition problems due to the tendency of organic thiols to oxidize to disulfides have been noticed [53]. Although protected thiols can alleviate this problem, the incorporation of extraneous material within the monolayer has also been reported when in situ deprotection steps are used [54]. Second, X-ray photoelectron spectroscopy (XPS) experiments [55] together with theoretical studies [56,57] suggest the presence of different hybridization/bonding states of the sulphur head-group resulting in conductance instabilities. Third, the S-Au bond is rather fluxional, and changes in the Au-S interaction are known to be largely responsible for the dynamic switching of conductivity [54,58-60]. Fourth, a serious limitation for the applicability of thiols in molecular electronic devices is the low energy barrier for molecular diffusion and desorption [61]. Fifth, thiols do not provide an efficient platform for charge transport due to the local character of the sulphur 3p orbitals involved in the thiolate–metal bond [62,63].

Among functional groups explored for the fabrication of SAMs in molecular electronics, other sulfur-containing materials can be highlighted, e.g., dithiocarbamates ($R-NCS_2H$) that form chelate complexes with metals [64,65]. Dithiocarbamate monolayers have been demonstrated to be thermally more stable than thiolate monolayers. In addition, dithiocarbamates strongly couple to metals resulting in a mixture of discrete molecular levels with metal states, which leads to a reduction of the metal-molecule charge injection barrier and, consequently, in a lower contact resistance than thiols at the metal-molecule interface [64,66]. Recently, n,n-dialkyl dithiocarbamate monolayers have been used to decrease the work function of gold surfaces, which plays a crucial role in determining the size of this barrier. Thus, Schulz *et al.* [67] demonstrated that the packing-density, the polarization along the N-C bond, and the charge rearrangement associated with chemisorption are responsible of the low work function observed in gold surfaces incorporating dithiocarbamates. Selenols, (-SeH) have also been studied on Hg and Au contacts and compared with thiols (-SH) [68,69]. n-alkanethiol monolayers have a lower tunnelling barrier height than n-alkaneselenol SAMs, and, therefore, a higher conductance and electron tunneling rates larger than the rates measured across n-alkaneselenol monolayers containing the same number of carbon atoms.

Amine ($R-NH_2$) [70,71] contact group has also been widely explored. For this group, the nitrogen lone electron pair is known to coordinatively bind to unsaturated surface gold atoms with the formation of an Au-N donor-acceptor (D-A) bond. The Au-N bond is considerably weaker than the Au-S covalent bond, but it is insensitive to the local structure of the bonding points and provides well-defined electronic coupling at Au-N contacts. Other coordinated molecule-gold bonds have been studied such as isocyanides (R-N≡C) [72], or nitriles (R-C≡N) [73]. Alkane isocyanide SAMs exhibit a 10% smaller contact resistance than those of thiol analogues [73]. On the contrary, aromatic isocyanide SAMs [72], show higher contact resistance than conjugated thiols, suggesting that not only the head-group nature and the work-function of the electrode influence the contact resistance [74,75]. Recently, Reddy *et al.* observed negative thermopower in isocyanide-terminated aromatic molecular junctions, which by means of computational calculations, was associated to charge transport primarily through the lowest unoccupied molecular orbital (LUMO); whereas in the junction with the same molecules terminating in thiol, positive thermopower was observed and attributed to charge transport primarily through the highest occupied molecular orbital (HOMO) [76,77].

Although reports on organic functional materials with a silane head-group chemisorbed on gold are scarce, it has been proved that SA of alkanes with silane terminal groups results in stable in-plane polymerized monolayers with Au-Si bonds [78], which makes them potential components for molecular electronic devices. Recent works on the trimethylsilylethynyl group ($R\text{-}C\equiv C\text{-}Si\text{-}(CH_3)_3$) have demonstrated chemisorption of this functional group on gold surfaces [79-81] with SAMs exhibiting a high surface coverage [82] and similar electrical characteristics to amine ($R\text{-}NH_2$) contacts. In addition, single molecules exhibit an unique conductance profile for this contacting group [82]. However, further work is needed to clarify the nature of this terminal group-metal interaction.

Only a few bidentate molecules in monomolecular films have been studied [39,64,65,83,84]. Multidentate molecules could provide additional stability to the monolayers, lower fluctuation effects and result in more efficient electronic coupling. Additionally, multiple anchoring elements to the substrate could represent a step towards a unique conductance signal. Our opinion is that this field should be explored in more detail.

At a single molecule level other contacts on metals have also been studied including acids (R-COOH) [23,85,86], carbodithioates ($R\text{-}CS_2H$) [87], dithiocarboxylic acids [87], pyridyl ($R\text{-}C_5H_4N$) [88,89], isothiocyanates (R-NCS) [90], dimethylphosphine ($R\text{-}PMe_2$) [91], 4-(methylthio)phenyl [92], dihydrobenzo[*b*]thiophene [93], thienyl ring [94] or diphenylphosphine ($R\text{-}PPh_2$) [95]. However, their electrical properties have hardly been studied in SAMs.

As mentioned above gold has been the most studied metal for SA deposition because of good fabricability, high conductivity and good stability of gold substrates. However, there is a need for the exploration of other metal surfaces driven by the search of an optimal electron transfer from the metal to the molecule since the electrode nature has a significant effect on the conductance of the molecular junction based on the electronic coupling between the molecular head-group and the electrode [96]. Thus, other metals such as Ag, Pd, Pt, Cu and Hg have been studied [68,96-98]. For instance, Engelkes *et al.* [96] analyzed the effect of the metal work-function on tunneling efficiency and contact resistance, showing that for SAMs of alkanethiol or alkanedithiol on Au, Pt and Ag electrodes, large resistances are observed for the low work-function metals, i.e. junction resistances are largest for Au contacts and smallest for Pt, with Au contacts showing resistances that are between that of Ag and Pt junctions.

1.1.2 Self-Assembled monolayers onto semiconductors or non-metallic conductors

Recently, there has been a growing interest in the use of semiconductors and non-metal electrodes due to the intrinsic technological limitations and high cost of metals. A few examples of SAMs-based junctions using ITO as the bottom electrode have been prepared [84] using a conductive polymer as the top contact electrode [99]. However, ITO electrodes, commercially available and widely used in the field of organic electronics are not exempted from significant limitations. One of the major issues is the scarcity of the indium supply and the resulting high costs. Additionally, ITO, together with its substitutes, fluorine-doped tin oxide (FTO) and aluminum zinc oxide (AZO) are brittle and thus unsuitable for future applications in flexible and stretchable electronic devices [100]. Metallic electrodes have been reported to exhibit a high atomic mobility and some of them also have a low chemical stability, which may result in destruction of the molecular junction upon oxidation or electromigration [101-106]. In addition, for certain fields of applications such as molecular optoelectronics, metallic electrodes may quench the excited states of the molecules and metal electrodes may limit optical access to the organic materials [107], generate light-induced plasmonic effects [108] or significant electrode expansion under visible light [109] masking the molecular optoelectronic properties. Metal-free junctions where both electrodes are non-metallic are highly desirable for such applications. These are some of the reasons why recently some world-leading researchers are suggesting a further effort towards the investigation of all-carbon based molecular electronic devices [110-112], following the roadmap already defined by organic electronics. Figure 3 indicates the research time line and market implementation followed by organic electronics and our vision of how molecular electronics research might evolve in the following years.

Glassy carbon and graphite electrodes have the advantage of not being subjected to electromigration or oxidation. Besides, they are more stable than metals in an electrochemical environment, are chemically inert and exhibit a density of states distribution similar to that of a metal. Deposition of monomolecular

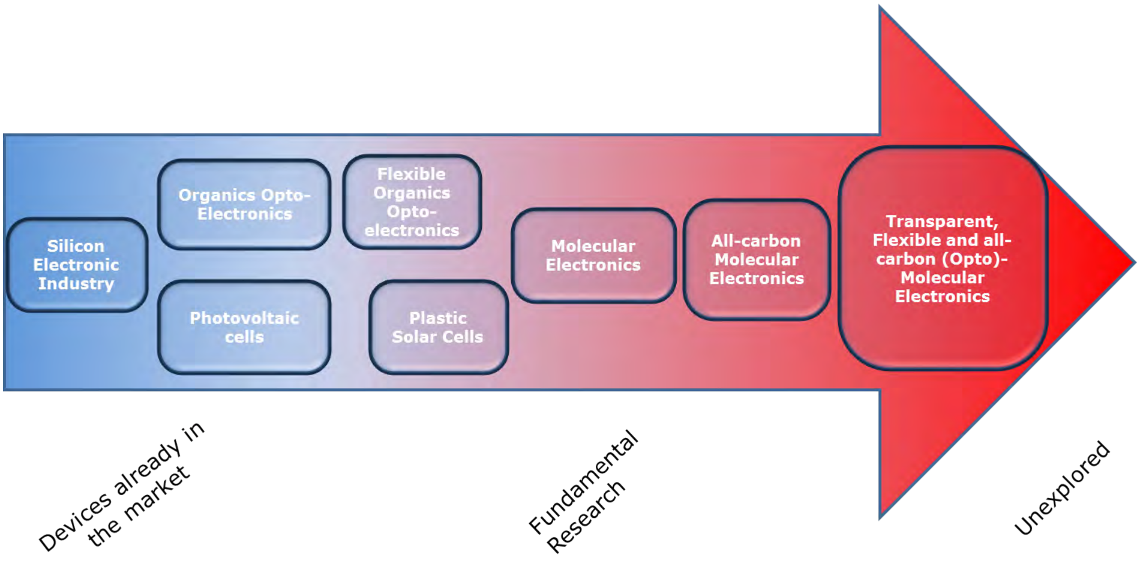


Figure 3: Scheme of the organic electronics and molecular electronics evolution.

films onto carbon electrodes has been mainly made by electrochemical methods (see section 1.3). Other examples of highly conductive organic materials include organic charge transfer salts (i.e. tetrathiafulvalene tetracyanoquinodimethane TTF-TCNQ salts) [113], PEDOT-PSS (poly-ethylene-dioxythiophene stabilized with poly-styrene-sulphonic acid) [114], and polypyrrole [115]. It is our opinion that these electrodes should be explored in more detail for applications in molecular electronics to give a step towards metal-free molecular electronic devices. Furthermore, flexible and transparent electrodes could also provide novel functionalities and properties to these nascent molecular electronic devices [111,116,117]. Graphene has emerged as an appealing electrode for molecular electronics due to its high electrical conductivity together with other properties such as high thermal conductivity, low thickness, chemical stability, flexibility and transparency. Graphene has also been demonstrated to be an amenable substrate for molecular self-assembly and to present the ability to pattern or create a desired size and shape of the film [118-121]. Excellent reviews in the field describe the fabrication techniques of graphene-based electrodes [119,121-124].

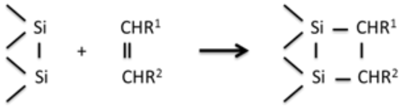
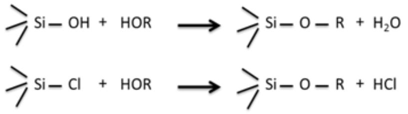
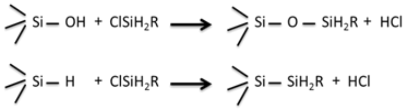
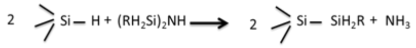
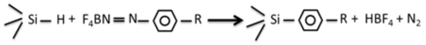
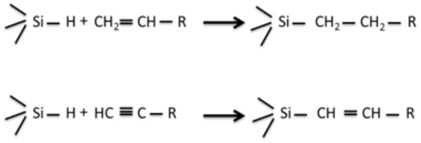
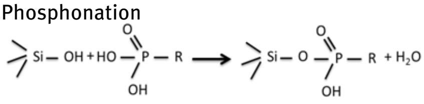
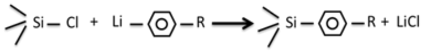
The use of silicon substrates has been widely explored in the microelectronic technology and recently some researchers have made significant efforts to export these ideas to the field of molecular electronics. Since implementation of molecular electronics in the market is neither an easy task nor an imminent event due to many unresolved technological problems and economic limitations, many voices have already claimed that a hybrid molecular electronics-CMOS technology could emerge soon, in which molecules are expected to add functionality to the already well-developed CMOS microelectronics [5,125-127]. Therefore, assembly of monolayers onto silicon or silicon oxide wafers might provide additional properties to our already massively produced microelectronic devices and is foreseen as a near future viable technology. Although a significant amount of work has been done to characterize the electrical properties of SAM-based devices on Si, the electronic properties of these Si-monolayer devices have been mainly studied separately by considering either the Si substrate or the adsorbed molecules, and there are relatively few examples of molecular electronic devices using silicon as the bottom electrode [128-134]. In addition, substantial care should be taken in the interpretation of the electrical properties of molecules deposited onto silicon surfaces since those properties could be the result of conduction from the substrate at a post soft-breakdown state and not due to the molecular components of the device [135]. Consequently, further investigations in this field are needed [133].

Commercially available single crystals of silicon contain a thin layer of silicon oxide with a thickness in the 1-1.5 nm range. This silicon oxide layer is spontaneously formed on exposure to ambient atmosphere. Taking this into account, monolayers on Si wafers can be deposited either by silanization of the native silicon oxide surface or by deposition onto bare silicon (by removal of the silicon oxide layer) with subsequent formation of Si-C bonds. Also modification of the silicon surface to form hydrogen, hydroxyl- or halogen-terminated more reactive silicon surfaces is a common procedure for the production of silicon-organic compound bonds [136]. These Si-C, Si-O-C, Si-Si, Si-O-P, etc. bonds are very strong (ca. 4 eV), which provide stability to the monolayer and yield good electrical junctions. Since the pioneering work of Lindford and Chidsay [137,138], multiple routes to fabricate monolayers onto silicon substrates have been demonstrated including chemical, thermal, photochemical and electrochemical methods. Table I shows a summary of the most relevant reactions utilized in the deposition of monomolecular layers onto Si.

1.2 The Langmuir-Blodgett technique

Although concepts such as nanoscience, bottom-up technologies, or molecular manipulation were experimentally demonstrated in the last quarter of the 20th century, the first investigations on floating monolayers on liquids are dated back to the 18th century when Benjamin Franklin [163] first prepared a monomolecular film of oil onto the surface of a pond in London. One century later, Agnes Pockels [164] described a method to manipulate layers of oil onto the water surface and ten years later Rayleigh [165] proposed that these oil layers were monomolecular films, providing the foundations

Table 1: Some of the most relevant reactions studied so far in the formation of monomolecular organic layers onto silicon surfaces.

Reaction	Reference
Cycloaddition 	[139-143]
Condensation 	[144,145]
Silanization with chlorosilanes and trichlorosilanes  with azanes 	[146-148]
Arylation 	[149]
Hydrosilation 	[138,150-154]
Phosphonation 	[155-157]
Reaction with metal organic reagents/Grignard route 	[158-160]
Electrochemical deposition See Figure 5 in section 1.3 of this review	[161,162]

for the study of monolayers. In 1917 Irving Langmuir [166] developed the theoretical and experimental fundamentals that lead to the birth of a new method for the fabrication of ordered monomolecular films on a liquid surface, which are also known as Langmuir films. In 1935 Katherine Blodgett [167], working under Langmuir supervision, was able to transfer by the vertical deposition method, one of these monolayers fabricated at the air-liquid interface onto a solid substrate leading to mono- or multi-layered (after repeated passages of the substrate through the monolayer at the air-liquid interface) films, which are known as Langmuir-Blodgett films. Alternatively, very rigid monolayers can be transferred by a parallel contact of the solid substrate with the liquid subphase containing the Langmuir film (horizontal deposition) to yield Langmuir-Schaefer (LS) films [168]. The starting point, in terms of the type of chemical compounds studied, was the fabrication of films incorporating fatty acids. However, the real breakthrough in the study of LB films was due to Hans Kuhn [169], who in the 1970s synthetized and studied molecules specially designed for the construction of organized molecular buildings. Since then, many researchers have used the LB technique for the assembly of organic and hybrid organic-inorganic compounds into well-ordered films for different fields of applications. In fact, the Langmuir-Blodgett (LB) technique is one of the most sophisticated bottom-up methods for the assembly of molecular materials on surfaces [26,170,171].

Figure 4 illustrates the fundamentals of the LB technique. In the LB method, the material is first ordered at the air-liquid interface and then deposited onto the substrate in contrast to the SA method where the head group of the molecule is first attached to the substrate and the molecules are ordered later. The nature of the substrate-molecule interaction depends on both the nature of the surface and the functional group of the organic material. Thus, the monolayer can be either physisorbed onto the substrate surface or chemisorbed [172,173]. Therefore, by making use of the large variety of functional groups that can be physically or chemically adsorbed onto different electrodes, it is possible to use the LB technique to fabricate molecular junctions featuring any one of a large number of organic-electrode interfaces [174]. The LB method involves a detailed and relatively long experimental procedure which precludes its use as a manufacturing technique. However, it is an excellent scientific tool with a tremendous flexibility. This is the reason why it has widely been used in the literature for the fabrication of molecular junctions.

The LB technique has been successfully used to fabricate metal–monolayer–metal devices where the monolayer exhibits a high internal order and is free of three dimensional defects or pin-holes. In 1971 Kuhn [175] measured the current flowing through fatty acid LB films which were sandwiched between two metallic electrodes. In the 1990s Ashwell *et al.* [176,177] proved the rectification effect predicted theoretically by Aviram and Ratner in 1974 by studying the electrical properties of LB films incorporating hexadecylquinolinium tricyanoquinodimethanide and (4-dodecyloxy-phenyl)-carbamic acid-2-(4-bromo-3,6-bis-dicyanomethylene-cyclohexa-1,4- dienyloxyl)-ethyl ester. These experiments were first performed on asymmetrical electrodes and later on symmetrical electrodes of Al [178] and Au [179,180]. Recently, Zhou *et al.* have also demonstrated the rectifying behavior of LB films of an asymmetrically substituted dicyano-tri-tert-butylphtalocyanine [181]. Molecular switches based on LB monolayers of catenates have also been reported [182,183].

Oligo(phenylene-ethynylene) derivatives, OPEs, represent one of the most widely-investigated class of molecules in the nascent field of molecular electronics. Consequently they have also been assembled in LB monolayers and their electrical properties determined. A wide variety of functional groups have been employed to contact these molecules to metal substrates including nitriles (R-C≡N) [174], acids (R-COOH) [184-186], amines ($R\text{-}NH_2$) [85,187], esters ($R\text{-}COOCH_3$) [188], or trimethylsilane ($R\text{-}Si(CH_3)_3$) [22]. These monolayers have been proved to be either physisorbed or chemisorbed to the substrate depending on the anchoring group. Also asymmetrically bifunctionalized molecules have been studied by the LB technique which permits the fabrication of directionally-oriented monolayers. For instance, in SA films incorporating $HS\text{-}OPE\text{-}NH_2$ molecules, it was observed that 60% of the molecules were adsorbed onto the gold electrode by the thiol group whilst 40% of the molecules were adsorbed by the amine group [189]. In contrast, oriented LB monolayers with all the molecules arranged in the same direction were obtained, i.e. $Au\text{-}S\text{-}OPE\text{-}NH_2$ films when the substrate was immersed into the water subphase containing the Langmuir film, meanwhile $Au\text{-}H_2N\text{-}OPE\text{-}SH$ films were obtained when the gold substrate was withdrawn from the water subphase at the transference surface pressure [189]. Cruciform-structured OPE derivatives have also been assembled in LB films for probing intra- and inter-molecular exciton migration pathways revealing that assembly of these materials in well-organized LB films permits exciton migration control [190]. Other specific characteristics of molecular junctions fabricated by the LB technique have been reported including the possibility of modulating the electrical

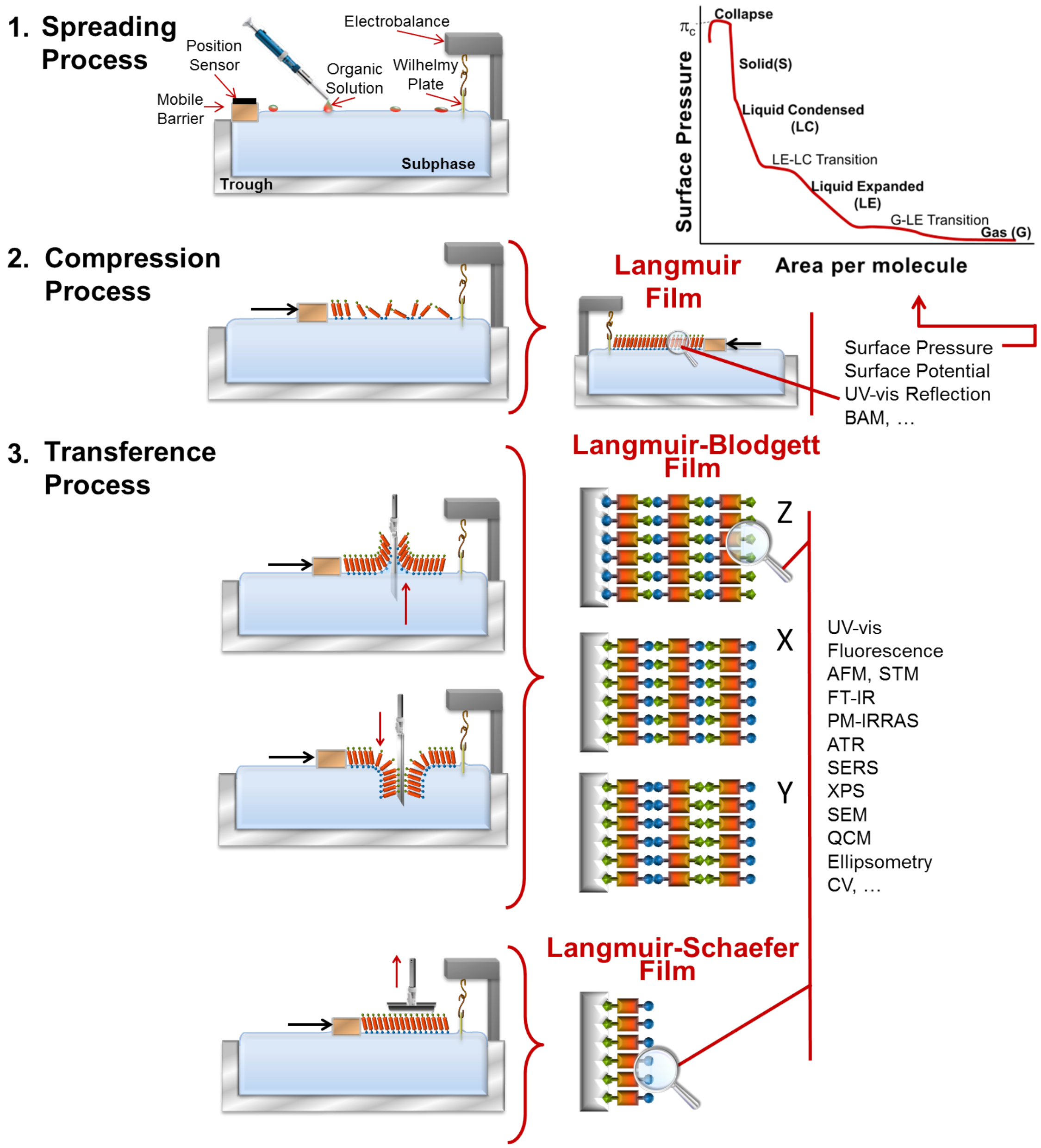


Figure 4: Schematic representation of the Langmuir-Blodgett and Langmuir Schaefer methods. The fabrication of a Langmuir film involves a first step in which a solution of the material is slowly and carefully spread onto the liquid surface. After a complete evaporation of the solvent, the compression process starts by means of a mobile barrier. Upon the compression process a surface pressure vs. area per molecule isotherm is obtained. This isotherm provides information about the phases and phase transitions of the monolayer. Once a stable monolayer has been formed at the air-liquid interface, the Langmuir film can be transferred onto a solid support. In the LB method a substrate is slowly immersed into and/or withdrawn from the subphase yielding to mono- or multi-layered films depending on the number of immersion and emersion cycles. Type Z, X or Y films can be obtained as indicated in the figure. In Y-type deposition the monolayer is transferred on both the emersion and the immersion of the substrate. X and Z-type films refer to situations where deposition only occurs on the immersion or on the emersion, respectively. In the LS method a substrate, situated in a horizontal position, is slowly put in contact with the liquid surface and subsequently lifted off the liquid surface. Different characterization techniques to determine the organization of the Langmuir films can be used including surface pressure vs. area per molecule isotherms (π-A), surface potential vs. area per molecule isotherms, Brewster Angle Microscopy (BAM), Ultraviolet-visible (UV-vis) reflection spectroscopy, etc. Also different characterization techniques can be used for the determination of the surface coverage, presence of holes, orientation of the molecules, physical or chemical interactions with the substrate, etc. Examples of these techniques include the Quartz Crystal Microbalance (QCM), ellipsometry, spectroscopies such as UV-vis, FTIR (Fourier Transform Infrared spectroscopy), PM-IRRAS (surface Polarization-Modulated Infrared Reflection-Absorption spectroscopy), ATR (Attenuated Total Reflectance spectroscopy), SERS (surface-enhanced Raman scattering), XPS (X-ray Photoelectron Spectroscopy), etc., electrochemical methods, for instance CV (Cyclic Voltammetry), Scanning Electron Microscopies (SEM), scanning probe microscopies (AFM: Atomic Force Microscopy; STM: Scanning Tunnelling Microscopy, …), etc.

properties of the junction by controlling the fabrication conditions (pH of the subphase) [23].

One of the most important features of the LB method is the large variety of substrates that can be employed including metals, carbon, conducting polymers, silicon, graphene-based electrodes, etc. Thus, LB layers of organic materials have not only been deposited onto metals but also onto other substrates. Donley *et al.* [191] deposited LB films onto silicon oxide to study the influence of the underlying substrate in the reactivity of the organic monolayer under the chemical vapor deposition of the top contact electrode. Additionally, in these devices the 1 nm thick native oxide layer provides a hydrophilic surface and a tunnel barrier that separates the monolayer and the underlying electrode [191].

In conclusion, although LB films are not as appealing as SA films for the industry due to the more complex fabrication method, and therefore higher production costs, they represent excellent platforms from which to explore different molecule-electrode interfaces, comparison of single molecule conductance with the electrical properties of the monolayer, study the influence of the surface pressure of transference (that is, the surface density) on the electrical properties of the films, and fabrication of multilayers, which is far more complex in SA films. In addition, as detailed in the next section, the incorporation of metal precursors in the LB films can also be used as a specific strategy of this technique for the fabrication of the top-contact electrode without the need of additional steps in the fabrication of a metal–monolayer–metal device. Finally, it is worth mentioning that another interesting application of the LB technique in molecular electronics is the fabrication of graphene electrodes [192,193] onto which a monolayer of organic molecules can be assembled. Graphene electrodes fabricated by the LB method could be used as the top contact electrode.

1.3 Electrochemical methods

Deposition by electrochemical methods has allowed a direct grafting of organic monolayers onto the bottom electrode. One of the best known examples is the electroreduction of diazonium salts that was first reported by Delamar *et al.* in 1992 [194]. Some excellent reviews can be found in the literature describing the diazonium modification of carbon (graphite carbon, GC, highly organized pyrolitic graphite (HOPG), pyrolized photoresist, pyrolized Teflon, carbon fibers, carbon nanotubes and boron-doped diamond), silicon, gallium arsenide, pyrolyzed photoresist film substrates, and metal surfaces (Au, Pt, Fe, Zn, Ni, Co, Cu, Pd, stainless steel, and metal oxides) [112,195-201]. Diazonium salts can be easily prepared from aromatic amines by reaction with $NaNO_2$ at low temperatures. The diazonium salt, usually isolated as a tetrafluoroborate salt, is dissolved either in an aprotic solvent with a supporting electrolyte or in an acidic aqueous medium. The diazonium salt is subsequently reduced using the surface to be covered by the monolayer as a cathode. This reduction results in the production of an aryl radical and nitrogen. The aryl radical reacts with the surface by coupling to an unsatisfied valency or adding to a double bond. Finally, a thorough rinsing of the substrate to remove the physisorbed material results in a layer which is chemically bond to the underlaying substrate. Demonstration of the deposition of an organic film onto the substrates, which is especially difficult onto carbon-based electrodes due to the similar chemical composition of both materials, has been achieved by using a wide variety of experimental techniques including XPS, AFM, PM-IRRAS (surface Polarization-Modulated Infrared Reflection-Absorption spectroscopy), SECM (scanning electrochemical microscope), CV (cyclic voltammetry), etc. [202]. One of the main advantages of the stepwise electroreduction of diazonium salts [196] is the formation of strong chemical bonds between the organic material and the substrate (Figure 5) with a bonding energy of ~4 eV vs. ~1.8 eV for the the S-Au bond. In addition, this deposition method results in a high surface coverage and these monolayers are stable at temperatures higher than 500 ºC [203]. The main drawback of this technique is that the monolayer is not as ordered as SAMs or LB films since molecules are not mobile once bonded. In addition, they are prone to multilayer formation [204]. The tendency to form multilayers depends on the nature of the electrode, the particular diazonium derivative employed, its concentration, and the deposition conditions (potential and scan rate).

Silane functionalized materials on Si via formation of Si-Si bonds is another good example of electrochemical deposition [126,205]. Vinil ($H_2C{=}CHR$) terminated molecules have also been electrochemically attached onto metal [206] and hydrogenated silicon surfaces [162] leading to metal-polymer and Si-C structures. Other electrochemical reactions for grafting of organic materials onto carbon-based electrodes have been reported, including oxidation of amines [207,208] and carboxylates [209]. Recently, investigations in molecular electronic applications have been focused on the formation of Au-C bonds in which the backbone of the molecules is directly bonded to the electrode without terminal functionalized groups, which results in an improved performance of the molecular device. In this way, Ricci *et al.* [210]

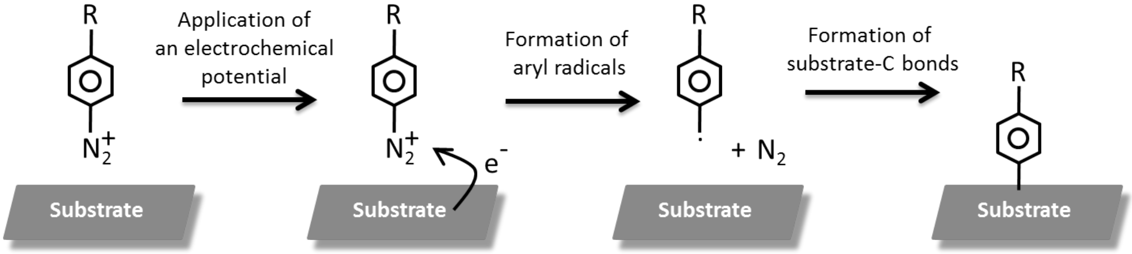


Figure 5: Scheme showing the attachment of organic layers to conducting or semiconducting substrates.

demonstrated by first time the formation of a direct C-Au bond by electrochemical reduction of the corresponding diazonium salt using chronoamperometry. In addition, Laurentius *et al.* [211] proved the formation of Au-C bonds in SAMs of a diazonium-derived aryl compound by using SERS (surface-enhanced Raman scattering).

2 Deposition of the top contact electrode

Once the monolayer has been assembled onto the bottom electrode, it is necessary to deposit a top contact electrode to close the circuit. Several approaches for the deposition of the top electrode have been used, and excellent reviews on this topic have been published [212-216]. However, despite intense investigations on the deposition of the top contact electrode onto monomolecular films a reliable control in the fabrication of molecular junctions remains rather limited. First works used a drop of a liquid metal such as mercury [175,217,218] together with other liquid metals such as a Ga/In eutectic [219], and some recent contributions have also made use of this method [220-222]. The use of liquid top contact electrodes has certain advantages including that they are cheap as well as easy and quick to assemble and they can also be employed onto all kinds of SAMs. However, liquid electrodes are not of interest for market implementations of electronic devices. STM (scanning tunneling microscopy) [37,186,214,223-226] or c-AFM (conducting-Atomic Force Microscopy) [96,227-230] tips have also been used to close the circuit and measure electrical properties of molecular electronic devices. In this case, the electrical properties of a small number of molecules (few tens down to a single molecule) are determined. However, from a practical point of view neither a liquid metal nor the tip of a scanning probe microscope is convenient to build a portable and stable device. In the search of fabricating an efficient top-contact electrode that does not damage the monolayer or form metallic filaments that yield short-circuits, several methods have been tested.

Evaporation of a metal onto the organic monolayer frequently results in penetration of the metal atoms through the monolayer which leads to a short circuit [231,232]. In order to minimize such an effect several approaches have been proposed including metal evaporation onto a cooled substrate (ca. 100 K) or intercalation of blocking baffles on the direct path between the crucible and the sample, which significantly reduce the number of short-circuits [179,180]. If the monolayer ends in a group capable to react with the metal atoms, an overlayer on top of the monolayer is formed. This overlayer, composed of metal oxides or organometallic complexes, may perturb the electronic coupling between the metal and the molecule leading to partial or total Fermi-level pinning at the interface [233]. Certain terminal groups in the monolayer may be efficient in reducing penetration of metal atoms through the monolayer [234-241]. Recently, thermally evaporated Pb [242] has been reported to limit the number of short-circuits. Atomic layer deposition (ALD) is a vapor phase technique that permits the deposition of a variety of thin film materials, including metals and metal oxides, from the vapour phase [243,244]. ALD metals form layers with chemical bonds to the organic molecules forming a thin protective film that can then be used for subsequent deposition of a thicker metal film using traditional methods such as CVD without damaging the organic film. ALD consists of sequential alternating pulses of gaseous chemical precursors that react with the substrate resulting in pinhole-free films that exhibit perfect conformity and thickness tolerances, which can be held to atomic-scale precision. Thus, films of Al_2O_3 or Cu have been deposited onto the monolayer to prevent penetration of metal atoms through the monolayer in a subsequent conventional evaporation technique [245,246]. Similarly, deposition of a conducting polymer layer, PEDOT:PSS, on top of the monomolecular film prior to the evaporation of a metal electrode has been proved as an efficient method to avoid penetration of metal atoms through the monolayer and metal filaments formation [247]. A significant reduction in the diffusion channels that result in penetration of metal atoms through the monolayer has been achieved by polymerization of the monomolecular film, which may be induced by irradiation [248-250] or by a chemical cross-linking [251]. However, these methods result in a chemical change in the molecular structure of the material that forms the monolayer, whose implications in the final electrical properties of the monolayer need evaluation.

Conventional electrochemical deposition (Cu, Ag, Au, ...) has so far been unsuccessful in the metallization of organic monolayers since it results in metal penetration into the monolayer (mushroom structures) or even penetration of the metal to the bottom electrode and formation of floating monolayers onto this new metal layer [252,253], although the use of certain terminal monolayer groups may reduce the metal penetration through the monolayer [254]. Overpotential deposition (OPD) of metals on monolayers results in metallic films that are above the organic film but are also frequently accompanied by metallic filaments that are in electrical contact with the bottom electrode rendering the device unusable [255]. Alteration of the monolayer integrity upon underpotential deposition (UPD) has also been described [253,256]. Recently, a successful electrochemical deposition of palladium onto a pyridine-terminated monolayer has been reported [257]. No evidence of penetration of the metal or formation of short-circuits was observed but only Pd nanoparticles and not a homogeneous metal layer was formed since a significant activation barrier appears and prevents further attachment of diffusing Pd adatoms [257].

Incubation of functionalized monolayers into a nanoparticle dispersion also results in the deposition of such nanoparticles forming thiol-gold bonds [11,258] or even strong carbon-gold bonds [259], which facilitate the electron transfer. Recently, fabrication of patterned arrays of gold nanoparticles onto a thiolated SAM by using scanning electrochemical microscopy has been reported [260]. In this method, an in situ electrosynthesis of gold nanoparticles by electrochemical reduction of an Au(III) salt is performed and the generated gold nanoparticles are locally deposited with the aid of a platinum ultramicroelectrode positioned on top of the SAM that permits the creation of a desired pattern onto the surface. However, none of these techniques result in a complete metallization of the organic film [11,258].

Alternative soft deposition techniques have also emerged in the literature. Nanotransfer printing (nTP) is a soft lithographic method in which patterns with nanometric resolution are created onto solid substrates. Thus, gold electrodes are evaporated onto an elastomeric stamp and are subsequently transferred by mechanical contact onto a monolayer that contains a group with chemical affinity to gold (e.g. a thiol group) [261-264]. Lift-off assisted approaches have also been used to fabricate the top contact electrode. The method, called lift-off, float-on (LOFO) permits the deposition of a metal layer by molecular adsorption on the monolayer with no discernible degradation of the organic film [265]. The method consists of two steps: (i) first, a metal leaf is detached from a solid support and this leaf is floated on a liquid (lift-off); (ii) second, the metal leaf is attached to the monolayer through a liquid-mediated process (float-on). The main drawbacks of this method are that the monolayer-metal contact areas are smaller in the LOFO technique than in the conventional evaporation technique [265-267], and the contacts have poor reproducibility [265,268]. Another interesting method for the deposition of the top contact electrode is the so called flip chip lamination (FCL). In this method a thin layer of metal is deposited onto a flexible substrate. Then, the monolayer is formed onto this gold layer. The flexible substrate allows an easy delamination and transference to another electrode to sandwich the organic film between the two conducting layers [269]. In the surface-diffusion-mediated deposition (SDMD) the top contact electrode is obtained by direct electron-beam evaporation of a metal onto a SiO_2 surface adjacent to although at a short distance of ca. 50 nm of the monomolecular layer. Surface diffusion of the metal adatoms deposited onto the SiO_2 surface allows migration of metal atoms onto the monomolecular film [270].

LB films of an organic compound incorporating a metal precursor, $AuCl_4^-$, from the subphase have been reported [271]. These LB monolayers were subsequently irradiated and photoreduction of the metal precursor results in gold nanoislands on top of the organic monolayer without destruction of the underlying organic film nor penetration of the nanoparticles. The photoreduction method is “contact” free and requires only optical illumination over the substrate area. However, a complete metallization of the monolayer would require the use of other complementary methods (see below electroless deposition).

Recently, our group [230] has reported the so-called TIDOC method or Thermal Induced Decomposition of an Organometallic Compound, in which an organometallic directionally oriented LB film is thermally decomposed resulting in functional metal–monomolecular organic film–gold nanoisland devices, see Figure 6. c-AFM experiments undoubtedly demonstrated that this method prevents penetration of the metal top contact electrode through the monomolecular film.

Metal nanoparticles or nanoislands deposited onto the organic film by making use of the different above-

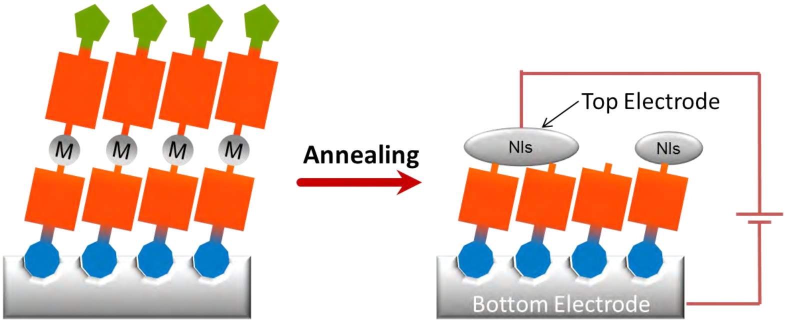


Figure 6: Scheme of the TIDOC method. A directionally oriented monomolecular film of an organometallic compound is annealed resulting in the thermal decomposition of this compound and formation of metal nanoislands (NIs) yielding Metal-monomolecular organic film-metal NIs conducting devices.

mentioned methods could be used as seeds for a complete metallization of the monolayer by electroless deposition (ELD). ELD is a simple, cheap and soft method in which metallization occurs via the chemically promoted reduction of metal ions without application of an externally applied potential [272-276].

Deposition of non-metallic electrodes is another interesting alternative that could not only avoid the above-mentioned problems involved in the use of metals but also provide other advantages such as the production of cheaper, flexible and transparent devices. In this context, some contributions are worth mentioning. For instance, McCreery's group reported the deposition of a top contact carbon electrode by electron-beam deposition [110]. Also graphene top contact electrodes have been deposited onto monomolecular films [277,278].

3 Conclusions and future directions

In the last forty years the emergence of synthetic routes for the production of functional organic materials, the development of sophisticated physical and chemical nanofabrication methods, and the accessibility to characterization techniques with molecular resolution have allowed scientists to experimentally demonstrate the fundamental idea behind the field of molecular electronics already suggested in the 1970s: functional organic molecules can work as basic components in electronic devices. However, there are still many challenges to be overcome before molecular electronics can begin the journey towards the market. Among these challenges, the fabrication of robust and reliable molecular junctions, minimization or elimination of the variability in the electrical response, and deposition of the top-contact electrode on monomolecular layers of active molecular components are of particular relevance. In this contribution, the most important methods for robust assembly of organic films onto electrodes, improved control over the molecule-substrate arrangement within junctions and the deposition methods for the top contact electrode developed to date have been summarized highlighting their advantages and limitations, commenting on future trends as well as gaps in the field, suggesting areas that require additional research.

A step forward the state-of-the-art in this field of research requires further improvement or development of new nanofabrication methods that:

(i) permit robust, reliable and efficient molecule-electrode contacts;

(ii) eliminate the variability in the conductance;

(iii) allow the deposition of the top contact electrode without damaging in the underlying organic molecular layer or penetration through the molecular layer that renders the device unusable;

(iv) construct new molecular electronic devices with reduced costs and improve performance (all carbon electronic devices, use of low cost, flexible and transparent electrodes, ...);

(v) permit a high degree of control in the size of the molecular electronic devices and distribution of these devices within the platform or wafer in which the device will be located (patterned structures with a few nm resolution).

Acknowledgements: Most of the work cited from the author's laboratory was supported by Ministerio de Economía y Competitivity (MINECO) from Spain and fondos FEDER (projects CTQ2012-33198, CTQ2009-13024, and CTQ2006-05236). Gobierno de Aragón and Fondo Social Europeo 'Construyendo Europa desde Aragón' also support the research activities of our research group (www.unizar.es/platon). We are also grateful to the European SUDOE TRAIN2 project and the Nanolito network through the MAT2011-13099-E project funded by MINECO. S.M. thanks his JIUZ-2013-CIE-05 grant. Finally, we acknowledge an Explora grant (2014-2016) from MINECO.

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