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The role of self-assembled monolayers in electronic devices

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Today, the self-assembled monolayer (SAM) approach for surface functionalization is regarded as highly versatile and compelling, especially in the immobilization of biomolecules and fabrication of novel supramolecular architectures. Most of the scientific articles recently published on biosensors use the concept of SAM to generate different surface functional groups for the immobilization of biomolecules such as antibodies, proteins, and enzymes. Due to the simplicity of the formation process and lack of requirement for costly instruments, this approach is prominent among researchers working in the field of surface functionalization and biosensing devices. Herein, we have reviewed a wide range of literature reports on electronic devices such as chemical sensors, biosensors and organic film transistors that use SAM concept for their purposes. In this review article, effort has been made to provide information about the SAM functionalization procedure, *i.e.* the technique used, the molarity of the SAM solution, and other physical/chemical conditions involved. Moreover, the fundamental concept of the monolayer, the types of monolayers on air/water interfaces, the techniques used for SAM formation on solid substrates and the use of SAMs for patterning are discussed.

1. Introduction

Self-assembled monolayers (SAMs) are highly oriented two-dimensional ordered molecular arrangements that form spontaneously on the surface of a variety of substrates.[1–3] Self-assembly is a unifying concept in nature.[4] Almost all biomolecules, such as proteins and peptides, interact and self-assemble to form organized and ordered structures according to their functionality. Proteins and peptides are used by nature as a platform to produce arrays of materials such as shells, pearls, and keratin.[4] In self-assembly molecules by molecules are assembled, that's the reason for ''bottom-up'' strategy terminology. It can be used to generate novel molecular architectures. Indeed, this approach is an

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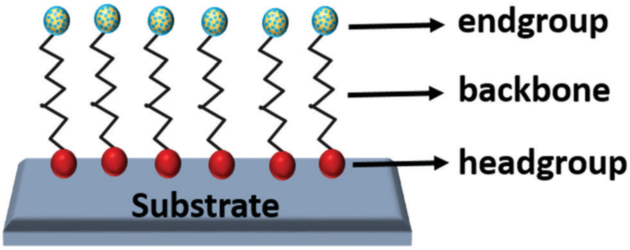

Fig. 1 Structure of a self-assembled monolayer.

essential part of nanomaterial manufacturing.[4] In particular, in chemistry, the molecular assembly approach is used to fabricate novel supramolecular architectures.[4] Recently, the concept of SAMs has been gaining considerable attention due to their use in electronic devices such as sensors,[5–7] thin film transistors,[2] and patterning.[8] The typical structure of a SAM, including its three main parts, is shown in Fig. 1.[9] The headgroup of the SAM binds to the surface, while the backbone is responsible for molecular ordering and is made up of an aromatic oligomer or aliphatic chain. The endgroup or terminal group defines the surface energy, topography, and functionality of the SAM and can be used for further functionalization, such as immobilization of biomolecules.[2,10]

In the field of surface modification with biomaterials, the concept of SAMs is gaining popularity every day.[1] In contrast to other physical surface modification techniques, such as plasma,[11] laser,[12] UV irradiation,[13] and electron beam,[14] the SAM technique has several advantages. One of the advantages is long shelf life because surface modification with SAMs allows the attachment of molecules through covalent bonding. Meanwhile, surface modification using the abovementioned physical methods shows poor stability and sometimes causes loss of surface chemical activity due to irradiation. Moreover, the SAM technique is now widely used for immobilization of biomolecules because conventional techniques such as physical adsorption, van der Waals interactions and cross-linking also suffer from stability issues. SAMs can be divided into two groups, *i.e.* SAMs of small molecules (thiols, silanes, *etc.*) and polymer SAMs (long chains of macromolecules).[2,15–18]

The deposition of a monolayer in the form of a thin film on a solid surface was first studied by Blodgett in 1935.[15] In this work, a long chain carboxylic acid monolayer was deposited on a solid substrate. The deposition of a monolayer on a solid surface opens the possibility to use this concept for molecular devices. One example is thiols on a gold surface; this is used to immobilize and detect different biomolecules, such as proteins and DNA.[19] The invention of microscopic characterization tools such as scanning probe microscopy and X-ray photoelectron spectroscopy has facilitated the analysis of monolayers; currently, increasing numbers of researchers are using this concept for their purposes, such as to immobilize biomolecules.

Herein, we have reviewed the literature regarding the roles of SAMs in different electronic devices, such as biosensors, chemical sensors and organic field effect transistors (OFETs). A wide span of literature has been reviewed in this article. In the first part of this review, the fundamental concept of a monolayer is presented. Meanwhile, in the second part, the techniques used to deposit monolayers on solid surfaces, such as Langmuir–Blodgett (LB), dipping, and vapor phase, have been presented. In addition to these deposition techniques, post-deposition processes such as rinsing with solvents and heat treatment are discussed. In the last part, the role and use of SAMs in modern electronic devices such as chemical sensors, biosensors and OFETs, including the concept of patterning, are discussed in detail. While reviewing the literature, we focused mainly on the process of SAM functionalization, *i.e.* how the functionalization of SAMs on surfaces such as gold, oxides, *etc.* is performed. The techniques used for functionalization and other parameters, such as the molarity of the SAM solution, total time taken for functionalization, and heat treatment, have been presented.

Elisabetta Comini

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2. Types of monolayers

Amphiphilic compounds (chemical compounds which possess both hydrophilic (water-loving) and lipophilic (fat-loving) characteristics) can arrange themselves at a variety of interfaces, such as liquid/liquid, air/liquid, solid/liquid, and solid/air interfaces. Broadly speaking, in these types of compounds, two monolayer systems exist, *i.e.* Gibbs monolayers and Langmuir monolayers. Here, we will provide a brief introduction to this concept from a fundamental point of view.

2.1 Gibbs monolayer

A Gibbs monolayer is also called a soluble monolayer; it is formed by spontaneous adsorption of water-soluble compounds

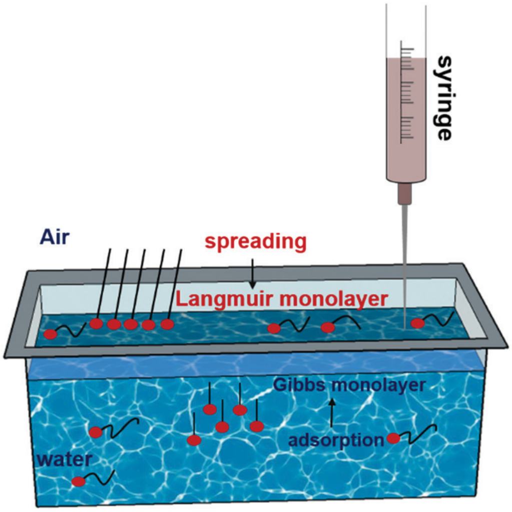

Fig. 2 Gibbs and Langmuir monolayers on the air/water interface.

such as surfactants from the bulk of an aqueous solution to the solution surface.[20]

Fig. 2 shows the Gibbs monolayer at the air/water interface. In the case of an amphiphile that is dissolved in water, it begins to be adsorbed at the air/water interface. This adsorption forms an ordered structure and gives rise to the Gibbs monolayer.[21] As shown in Fig. 2, a syringe supplies water-soluble amphiphiles such as surfactants to the water. As the density of the adsorbed molecules increases with time, the surface tension of the water-surfactant solution decreases from that of pure water, finally achieving a constant value. This constant surface tension represents the thermal equilibrium of the surfactant solution, which in turn depends on the temperature and bulk concentration of the surfactants. In order to form a highly ordered Gibbs monolayer, the amphiphiles should have the following features:

- Their solubility in water should be lower in comparison to that of normal surfactants.
- They should have powerful interactions between the hydrophilic groups of the amphiphiles.
- The amphiphiles should possess longer alkyl groups compared to common surfactants and consequently enable strong attractive interactions among the hydrophobic alkyl groups.

2.2 Langmuir monolayer

A Langmuir monolayer[22] is formed on an aqueous subphase when a solution of a water-insoluble amphiphile in volatile organic solvent spreads. The spreading occurs when the amphiphile molecules possess long hydrophobic tails and hydrophilic heads and thus are attracted more to the water than to each other.[23] Fig. 2 shows a Langmuir monolayer on the air/water interface created by the spreading of insoluble amphiphiles. If the area of the liquid surface is large enough to accommodate the insoluble amphiphile molecules, a one-molecule-thick layer, *i.e.* a Langmuir monolayer, is formed.

The concept of an insoluble monolayer can also be found in ancient times, when Aristotle in ancient Greece described the effects of oil on the surface of water. In 1917, Irvin Langmuir[24] introduced a new breakthrough theoretical concept and experimental method to study these types of monolayers. Langmuir was awarded the Nobel Prize in 1932 for his contribution to surface chemistry. To fabricate solutions of water-insoluble amphiphiles, volatile organic solvents such as benzene and chloroform have been used. These solvents evaporate in a short period of time, leaving behind the water-insoluble molecules.

3. Mechanism of self-assembled monolayer formation and factors affecting their ordered assembly

Based on interactions between the substrate and SAM molecules, there are two different SAM formation processes, *i.e.* substrate-coupled and substrate-decoupled.[10,25] In the first process, such as alkanethiols on an Au(111) substrate, the headgroups of the SAM chemisorb on specific sites of the surface to form the ordered monolayer. In this type, the crystalline structure of the substrate plays an important role; generally, a single crystal such as Au(111) is used to prepare the ordered assembly. In the substrate-decoupled process, such as the formation of alkylsiloxanes on a hydrated silicon substrate, no direct interaction between the surface and SAM molecules is involved, and the monolayer formation process is purely driven by intermolecular forces.[25] Two of the most important classes of SAMs that are used for different device applications are thiols on gold surfaces and silanes on oxide surfaces. In particular, among SAMs, thiols on gold substrates have been explored immensely and have also been used to study the kinetics of SAM formation.[1,26,27] In the SAM formation process, surface-specific interactions lead to the development of a closely packed and highly ordered monolayer.[10] The interactions that lead to the formation of 2D ordered assemblies are surface-adsorbate interactions; intramolecular interactions such as torsion and bond stretches; electrostatic interactions between adsorbates; and van der Waals interactions. Finally, surface reorganization helps to attain the equilibrium structure of the assembly. A detailed discussion about these interactions can be found in the review article by Abraham Ulman.[10] Moreover, for deeper understanding of the theoretical approaches involved in SAMs and the interactions involved in SAM formation, one can refer to the review article by Jing Ma *et al.*[28] In order to form an ordered monolayer on the surface under consideration, SAM molecules should possess the following two characteristics:

- They must contain functional groups that react strongly to the surface, such as chemisorption of SAM molecules.
- The SAM molecules must self-assemble with high density and uniformly on the surface; their intermolecular interactions must form a unidirectional layer.

Kinetic studies of SAM formation reveal that the adsorption of SAMs on the substrate can be divided into two stages.[1,10] The first stage involves the formation of a thin monolayer due to the adsorption of SAM molecules from its bulk solution. This stage is very rapid and requires only a few minutes to complete. The second stage is a very slow process (10 to 20 hours) in which rearrangement and reorientation of the adsorbed SAM molecules occurs in order to achieve highly ordered structures. Over the years, a large number of papers have been published on the kinetic study of SAM formation. Concerning the rate of SAM formation, there is no consensus in the literature. Bain *et al.*[29] investigated the formation of octadecanethiol (10^{-4} to 1 mM SAM solution in ethanol) on gold substrate by exploring the relationship between the microscopic structures and macroscopic properties. In the first stage, fast formation of a thin monolayer with a thickness 80% to 90% of the final value occurs within a few minutes. Moreover, in the second stage, the process of SAM formation occurs at a very slow rate (10–20 hours) and the monolayer thickness approaches equilibrium to form a highly ordered and perfect monolayer. On the other hand, Shimadzu *et al.*[29] studied the formation of ferrocenylundecanethiol (0.5 mM solution in hexane) on gold substrate using an electrochemical quartz crystal microbalance (EQCM). Experimental investigation revealed that 40% to 50% of the monolayer is completed just in 10 seconds, while in the second stage, an ordered monolayer structure is achieved within 10–100 minutes. Indeed, the rate of SAM formation and its structure largely depend on the SAM solution molarity, type of solvent, temperature and conditions of the substrate, which we will discuss later in this section.

3.1 Surface modification of gold using thiol SAMs

Due to the unique properties of gold, such as its inertness, ease of patterning and biocompatibility, it is widely used for the preparation of SAMs for different applications, such as biosensors, gas sensors and microfabrication.[29] In order to modify the gold surface with SAMs, the bottom-up approach has been used. The adsorption of various sulfur-containing groups of SAM molecules on the gold surface is achieved *via* chemical bonding. Indeed, gold has high affinity toward sulfur-containing molecules, and its surface can be modified by the adsorption of compounds that contain organosulfur groups, such as thiols (HS–R–X).[10,30] In the process of alkanethiol formation on the surface of Au (Fig. 3a), chemisorption of sulfur-containing molecules occurs and Au–S bonds are formed. The bond strength of the Au–S bond is around 40 kcal mol^{-1}.[1] Specifically, the head groups of alkanethiol on the Au surface undergo a chemical reaction that involves oxidative addition of the S–H bond to the Au surface followed by reductive elimination of the hydrogen, as shown in eqn (1):[10]

$$\mathrm{R-S-H+Au}_n^0 \rightarrow \mathrm{R-S^-Au^+\cdot Au}_n^0+\frac{1}{2}\mathrm{H}_2 \qquad (1)$$

This chemisorption process leads to the formation of alkanethiol on the Au surface, as shown in Fig. 3(a). In this figure, X represents the end groups, such as amine or carboxylic groups, of the SAM molecules, which determine the functional properties of the surface.

Furthermore, instead of using a single or mono SAM for the modification of a substrate, a mixture of SAMs can be used to modify the surface. With the selection of an appropriate molar ratio, a mixture of SAMs can be prepared in the same solvent and can be used for further studies, such as cell adhesion and adsorption of proteins, due to the gradient of the interfacial composition. In the preparation of mixed SAMs, the choice of solvent, the chain length of the SAM molecules and the molar ratio play very important roles. Moreover, thiol-based mixed SAMs are found to be more stable compared to those prepared from disulfides and dialkylsulfides (X–R1–S–R2–X).[1] A mixed SAM formed on a Au surface is shown in Fig. 3b.

3.2 Oxide surface modification with organosilanes

Organosilanes such as octadecyltrichlorosilane (OTS) require hydroxylated (–OH) surface groups to form SAMs on oxide surfaces such as silicon oxides (SiO_2). For the generation of –OH groups, the silicon surface is generally treated with piranha solution or oxygen plasma. This type of surface containing –OH groups is hydrophilic in nature, which helps to form a highly ordered monolayer of organosilanes. The reaction involves the formation of polysiloxane, which attaches to the silanol groups (–SiOH) present on the surface *via* Si–O–Si bonds. Not only silicon but other surfaces, such as alumina, glass, zinc oxide, indium oxide, mica and germanium oxide, can be modified using organosilanes. Fig. 4 shows the formation of a silane SAM on the surface of silicon. First, the silicon substrate is treated with piranha solution in order to create –OH groups on its surface. Afterward, the hydroxyl-terminated silicon substrate is either dipped in SAM solution or treated with SAM vapors for a prolonged time to form the monolayer.[1,10]

3.3 Factors affecting the formation of SAMs

In order to use SAMs for particular applications, such as biosensors, the reproducibility of the SAM formation process is an important factor that requires control and knowledge of various experimental parameters. The type of solvent, concentration of the SAM solution, temperature and presence of moisture majorly affect the formation of the SAM on the surface. Self-assembly is a

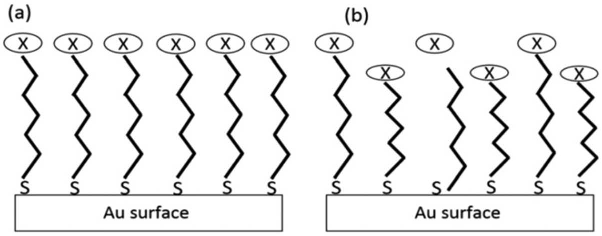

Fig. 3 (a) Formation of a mono/single SAM of thiols on an Au surface and (b) formation of a mixed monolayer of mixtures of two different thiols on the Au surface.

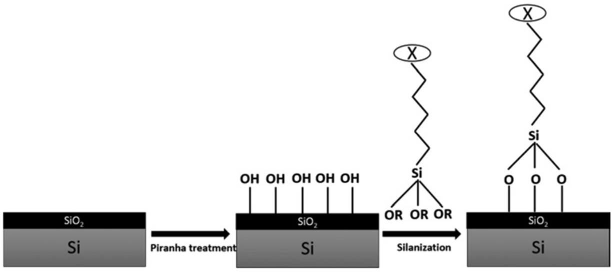

Fig. 4 Stepwise formation of organosilane on a silicon substrate.

spontaneous process and does not require any external intervention. However, in order to grow a perfect monolayer, suitable experimental conditions should be applied during the growth process.

3.3.1 Solvent. Ethanol is the most widely used solvent to prepare SAMs (both thiols and silanes) on gold and oxide surfaces. The reasons for this are its nontoxicity, low cost, high purity grade, and ability to solvate different SAMs; moreover, most of the surfaces used for SAM formation are stable under its effects.[1] SAM formation studies indicate that the solvent choice can affect the rate of SAM formation and the structure of the monolayers. In the case of alkanethiols, the rate of SAM formation is found to be higher in nonpolar solvents such as hexane compared to the rate when ethanol is used. However, the SAMs formed in these nonpolar solvents are poorly organized, while ethanol helps to form a highly organized monolayer. Moreover, thiol SAMs possess nucleophilic character; thus, a solvent should be selected that does not react with the nucleophile.[10,31]

As mentioned earlier, silanes require –OH groups on the oxide surface for their formation. Thus, the presence of moisture in the solvent and on the surface of oxides plays a crucial role. It has been found that solvents such as anhydrous toluene extract moisture from the oxide surface and help to form dense and ordered monolayers.[1]

3.3.2 Concentration of SAM solution and immersion time. The concentration of the SAM solution and the immersion time are related to each other. It has been suggested that a SAM solution with low concentration requires a longer immersion time. Meanwhile, a shorter immersion time may be required if a highly concentrated SAM solution is used. However, according to the kinetics of SAM formation, a longer immersion time is generally used because the reorganization of SAM molecules in the second stage requires more time.[1] Sometimes, when a high concentration of SAM solution is used, cross-linking of end groups can occur and decrease the surface reactivity. If the SAM-modified surfaces must be subjected to further treatment, such as immobilization of biomolecules, the selection of the concentration of SAM solution is more critical because both high and low concentrations can be detrimental to the ordered assembly as well as the reactivity. Thus, the optimization of both concentration and immersion time is required for the formation of reactive, densely packed and highly ordered SAMs.

3.3.3 Temperature. While studying the adsorption of oleophobic monolayers, W. Zisman *et al.*[32] discovered the existence of a critical temperature T_C above which the monolayer completely disappears. They found that monolayer formation is more favorable at lower temperatures, *i.e.* below the T_C. Indeed, with decreasing temperature, the rate of SAM formation decreases, resulting in a highly ordered monolayer with stronger van der Waals interactions. In another interesting study, the effects of the reaction temperature on the growth of OTS on a silicon substrate were investigated by Sunhyung Lee *et al.*[33] They found that in the low temperature region (5 °C to 20 °C), a highly ordered state of the SAM was present. Meanwhile, at high temperature (40 °C), an amorphous nature of the OTS SAM on the silicon substrate was observed. Thus, the temperature conditions should be chosen carefully during SAM formation.

3.3.4 Water. Especially in the case of organosilanes, the presence of water plays an extremely important role because their formation requires hydroxyl groups on the surface of the substrate.[34] Both the deficiency and excess of water can be detrimental to the molecular assembly of the monolayer. Specifically, the presence of excess water results in facile polymerization in solution and its absence results in incomplete monolayer formation. Therefore, inert gases such as N_2 are sometimes continuously supplied during the SAM growth process to control moisture.[35]

4. Deposition of self assembled monolayers on solid substrates

A SAM should be deposited on a solid substrate to fabricate electronic devices such as transistors and biosensors. Langmuir Blodgett (LB) is a typical technique used to deposit monolayers on solid substrates. In this section, along with the LB technique, other simple techniques for SAM formation on solid substrates are presented. From a fundamental point of view, the mechanisms of LB film deposition and the types of LB films according to the arrangements of the monolayer molecules are discussed.

4.1 Langmuir–Blodgett (LB) trough

In 1935, Dr Katherine Blodgett (a student of Dr Irvin Langmuir) managed to deposit highly ordered monolayers of water-insoluble amphiphiles on a solid substrate. She used a movable Teflon barrier to compress the amphiphile molecules and fabricate a multilayer Langmuir–Blodgett (LB) film. The instrument used to make the LB film is called an LB trough (Fig. 5).

Basically, it consists of a container that holds water (liquid subphase) on which amphiphile molecules are. As described in Section 2.2, a Langmuir monolayer forms on the surface of water due to the spreading of the water-insoluble amphiphile molecules. This monolayer is transferred to the solid substrate by dipping the substrate through the monolayer. The dipping mechanism is used to transfer the Langmuir film onto a solid substrate at the desired packing density. The barriers are used to compress the monolayer. The barrier mechanism, which is shown in Fig. 5, represents the mechanism that is used for compression of the monolayer. Currently, in most LB troughs, barriers that move parallel to the walls of the trough and make contact with the top of the liquid subphase are used. The container and movable barriers must be made of a material

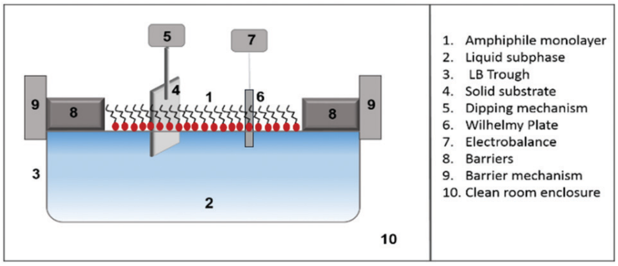

Fig. 5 Schematic of a Langmuir–Blodgett trough.

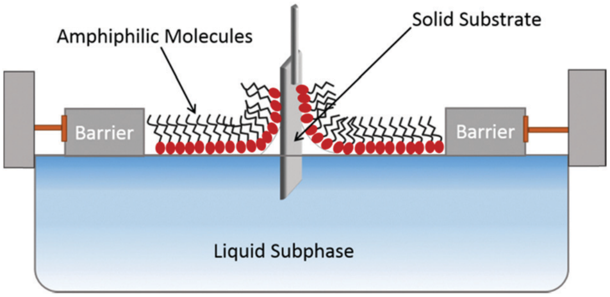

Fig. 6 Mechanism of Langmuir–Blodgett film formation on a solid substrate.

that does not contaminate the aqueous subphase. Generally, Teflon, which is an inert material, is used for this purpose. In an LB film, surface pressure is the most important parameter; during LB film formation, it should be maintained at a constant value. This pressure is measured using the Wilhelmy method, in which a Wilhelmy plate made of glass, filter paper, *etc.* is dipped into the liquid. This plate is connected to the electrobalance. The whole LB instrument is placed inside a clean room enclosure.

The LB film formation is typically carried out in solid phase. The value of surface pressure, which ensures ordering and cohesion in the monolayer, depends largely on the nature of the monolayer. When the substrate is hydrophobic in nature, the deposition starts from the air, and if the substrate is hydrophilic in nature, the first layer is deposited by raising the substrate from the aqueous subphase through the monolayer. Fig. 6 shows the mechanism of LB film deposition on the solid substrate.

In order to deposit a multilayer LB film, the substrate continuously moves up and down through the monolayer with a moving barrier mechanism while the surface pressure is kept constant. For the production of high quality LB films, a clean environment is required. Thus, the whole LB trough system is placed in a semiconductor clean room with temperature and humidity control. A number of parameters can affect the LB film, such as the surface pressure during deposition, deposition speed, nature of the solid substrate, subphase composition, pH value and temperature of the subphase. There are three types of LB film structures, *i.e.* X-type, Y-type and Z-type (see Fig. 7).

In this figure, amphiphilic molecules are shown with a hydrophilic head and a hydrophobic tail. In the X-type structure, the hydrophobic groups of the amphiphile are directed toward the substrate, and in the Z-type structure, the hydrophilic groups are directed toward the substrate. Meanwhile, in the Y-type structure, both the hydrophilic and hydrophobic groups alternatively change their direction layer by layer.

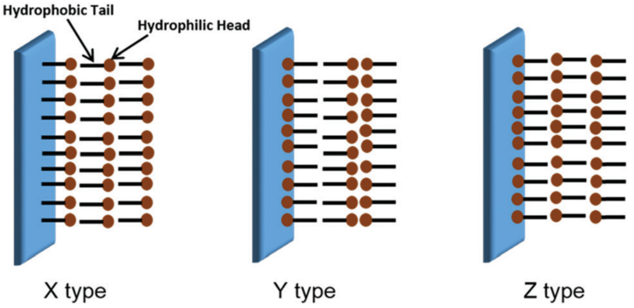

Fig. 7 The three types of Langmuir–Blodgett film structures.

4.2 Self-assembled monolayer from solution (dipping technique)

In this technique, a well-cleaned solid substrate is dipped into the SAM solution. Different types of solvents, such as ethanol and toluene, have been used to form SAMs. However, the selection of solvent depends on the solubility of the SAM in it and the nature of the substrate used. This selection is more critical when instead of a bare substrate, the substrate contains a thin film, nanostructures, *etc.* After the solution is made in a container such as a vial, the substrate is dipped into it (Fig. 8).

To grow an ordered monolayer, the whole system is generally maintained inside the incubator under stirring and, in a few cases, the temperature is also maintained. The growth of the monolayer depends on many factors, such as the molarity of the solution, size of the substrate, temperature, and growth time. The interaction of the substrate and SAM molecules during formation of the SAM layer can be physical adsorption, van der Waals, electrostatic, *etc.*, depending upon their nature. This method is very simple and inexpensive because no large laboratory equipment is required.

4.3 Self-assembled monolayer from vapours (vapour method)

In this method, the solid substrate is maintained under the influence of the SAM vapor for a sufficiently prolonged time. Sometimes the process is carried out in ultra-high vacuum conditions; however, it can also be carried out in a simplistic way. One simple way is to perform this process in a Petri dish. Specifically, the SAM solution is dispersed in a Petri dish and the substrate is attached to the cap. The whole system is maintained in a humid environment so that the solvent does not evaporate too rapidly. The molarity of the solution, type of solvent, time given for the formation of the SAM layer, distance between the solution and substrate and other physical conditions,

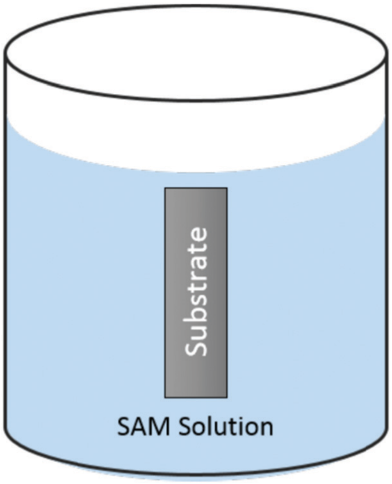

Fig. 8 SAM formation by dipping the solid substrate in the SAM solution.

such as temperature, humidity, and cleanliness, should be adjusted and selected very carefully. Before reaching the final stage, full optimization of all the abovementioned factors is required. Otherwise, the process can lead to the formation of a disordered and loosely bound monolayer. During the process, the SAM molecules evaporate and interact with the substrate surface. This interaction can occur by physical adsorption, van der Waals interactions, *etc.* depending on the nature of the surface and the SAM monolayer. Regarding control of the SAM formation, the concentration and stability are important; this process is as useful as the previously discussed method. However, due to its simplicity and the fact that no expensive instruments are necessary, this method can be useful for preliminary work.

5. Post-deposition processing of SAMs

Post-deposition processes, *i.e.* rinsing of the SAM-functionalized surface and, sometimes, heat treatment, are very important. After removing the substrate from the SAM solution or vapors, loosely bound SAM molecules remain present on the surface.[36] To remove these entities, rinsing with the solvent used in the SAM process is a crucial task. The process of SAM functionalization is not complete without this step. Without rinsing, one cannot obtain the desired results. Furthermore, the solvents used for the SAM process sometimes do not quickly evaporate and remain on the surface even after drying with nitrogen or synthetic air. To remove these solvents, SAM-functionalized substrates are also annealed above the solvent boiling point.[37]

6. Roles of SAMs in different electronic devices and their use for patterning

Having discussed the fundamental concept of monolayers and techniques for their deposition on solid substrates, we will now discuss their applications in electronic devices. In this review, we have reviewed the roles of SAMs in three types of electronic devices, *i.e.* chemical sensors, biosensors, and thin film transistors. The following sections are designed in such a way that authors can easily access information about the SAMs used in the reported articles and their process of SAM functionalization. Specific information about the solvents, molarity of the SAM solution, SAM processing technique and processing time is clearly provided. Moreover, the use of SAMs for pattering and the techniques used for this purpose are presented.

6.1 Self-assembled monolayers in chemical sensors

Self-assembled monolayers with outer functional groups, which can be electron donors or acceptors, can be used to detect different chemical analytes.[38] Moreover, the end groups of SAMs can serve as selective binding agents of biomolecules and can also determine the wettability of the surface. In this section, we reference interesting articles involving SAMs in chemical sensors that were reported over a year. This section is divided into two sections based on the types of surface used for the formation of the SAMs.

6.1.1 Self-assembled monolayers on gold surfaces. The use of SAM in chemical sensors began decades ago. In 1992, Larry J. Kepley *et al.*[39] reported a highly selective and durable self-assembled composite monolayer-based surface acoustic wave (SAW) chemical sensor. For SAM functionalization, the Au-coated substrate was immersed in a 0.1 M solution of 11-mercaptoundecanoic acid in ethanol for 8 to 12 hours. The functionalized SAW sensors were used to detect diisopropyl methylphosphonate (DIMP) analyte. In 1996, Rickert *et al.*[40] functionalized Au(111) with dialkylsulfide-substituted resorcin[4]arene SAMs for the detection of gas analytes such as tetrachloroethene, chloroform, and toluene. SAM formation was performed by immersion of the Au(111) substrate in a 1 mM solution of dialkylsulfide-substituted resorcin[4]arenes in ethanol/chloroform (7 : 3) at 60 °C for 18 hours. Moreover, highly sensitive and selective sensors for acetic acid and alcohols were fabricated by functionalizing the Au electrode of a quartz crystal microbalance (QCM) with alkanethiols (6-benzyloxyhexane-1-thiol and 6-hydroxyhexane-1-thiol).[41] The functionalization was performed by immersing the cleaned crystal in a 1 mM solution of alkanethiol in chloroform for 5 hours. In another interesting approach, ion sensors based on peptide nanotubes supported with a 1-dodecanethiol SAM were prepared.[42] Herein, for SAM functionalization, the gold-coated silicon wafers were immersed in 10 mM solutions of 1-dodecanethiol in ethanol for 12 hours. Finally, the SAM-supported peptide nanotube sensing platform was synthesized by immersing the functionalized Au substrate in a 0.1 mM solution of cyclic peptide for 12 hours.

In the field of sensors, microcantilevers have been widely used as sensing platforms due to their fast response, low cost, high sensitivity, low analyte requirement, and non-hazardous procedures.[43] In this direction, SAM-functionalized microcantilever-based ion sensors possessing high selectivity toward cesium ion have been reported.[44] In this report, a Au-coated microcantilever was functionalized with a 1,3-alternate 25,27-bis(11-mercapto-1-undecanoxy)-26,28-cal ix[4]benzocrown-6 SAM. Surface plasmon resonance (SPR) is another tool that has been used for chemical and biosensing applications.[45] Takashi Masadome *et al.*[46] reported an SPR sensor based on a stearylmercaptan (SM)-modified Au surface for nonionic surfactants. The Au-coated glass substrate was immersed for 2 days in a 10^{-2} M solution of SM in ethanol. Rui Yang *et al.*[47] reported an 11-mercaptoundecanoic acid (11-MUA) SAM-modified microcantilever sensor for the detection of trimethylamine (TMA) in gas and liquid phases. The MUA SAM was immobilized by rinsing the microcantilever with a 1 mM solution of MUA in ethanol for 2 hours.

6.1.2 Self-assembled monolayers on oxides and FET-based devices. For use in chemical sensors, oxides such as SiO_2, ZnO, and SnO_2 have also been functionalized with SAMs. In an interesting report, De Quan Li *et al.*[48] generated fullerene (C_{60}) multilayer supermolecular lattices using a (3-aminopropyl) trimethoxysilane (APTES) SAM as a linker on a passivating SiO_2 layer of a surface acoustic wave (SAW) microsensor. The ideal structure of the C_{60} multilayer superlattice is shown in Fig. 9. The sensors were used to detect different volatile organic compounds (VOCs). Furthermore, 4′-substituted 4-mercaptobiphenyl (MBP)-functionalized heterostructures of gallium arsenide (GaAs) and aluminum gallium arsenide (AlGaAs) were proposed for chemical sensor applications.[49] The functionalization of the GaAs/AlGaAs heterostructures with MBP was performed by immersing the substrate in 0.1 mM MBP solution in ethanol at 50 °C for 20 hours. In addition to using the SAM as a functionalized layer, SAMs were also used to create templates for micropatterning of tin oxide (SnO_2) for hydrogen gas sensing.[7] Optical images of a SnO_2 thin film on an n-octadecyltrimethoxysilane (ODS) template before and after rinsing in toluene are shown in Fig. 10. In 2007, Jung-Tang Huang *et al.*[50] used APTES on a SiO_2 substrate for the adhesion of a carbon nanotubes (CNTs)-based sensor for NH_3 and CO detection. The SAM was formed by immersing the oxidized Si chips in a 1 mM solution of APTES in acetone for 30 min. Indeed, the surface modification with APTES resulted in the formation of positively charged amine groups ($-NH_2$), which increased the adhesion properties of SiO_2 for the CNTs. For the past few years, field-effect transistor-based sensors have attracted a great deal of attention due to their ultra-sensitive detection, mass-production capability, and low cost of manufacturing.[51,52] In 2011, Michael Delalande *et al.*[53] modified the Au source–drain electrode of a single-walled carbon nanotube (SWCNT) field effect transistor (FET) (see Fig. 11) for the detection of gaseous nerve agents. In this case, Si/SiO_2 was used for the fabrication of the SWCNT-based FET device. The surface modification of the source–drain contacts decreased the Au-electrode work function, resulting in modification of the Schottky barrier of the gold/SWCNT interface. A reader can refer to this article for the full synthesis of the SAM monolayer compound. However, SAM functionalization of the Au surface was performed by immersing the sample in 0.7 mM SAM solution in ethanol overnight at room temperature under an argon gas flow. Argon gas was used to create the inert environment necessary for ordered and stable SAM formation on the Au surface.

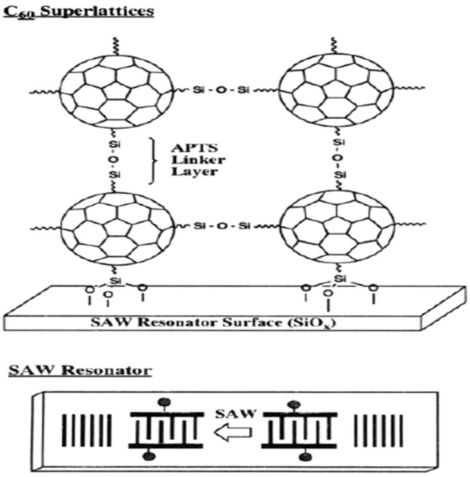

Fig. 9 Idealized schematic structure of a covalently bound, self-assembled fullerene (C_{60}) multilayer thin film (top). Schematic of a 200 MHz surface acoustic wave resonator (bottom). Reprinted (adapted) with permission from ref. 48. Copyright (1993) American Chemical Society.

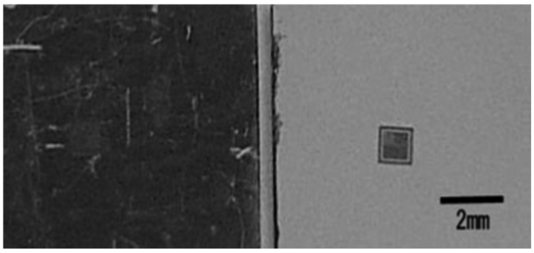

Fig. 10 Optical image of a tin oxide (SnO_2) thin film deposited on an octadecyltrimethoxysilane (ODS) SAM template (a) before and (b) after ultrasonic rinsing in anhydrous toluene for 30 min. Reprinted with permission from ref. 7. Copyright (2004) John Wiley and Sons.

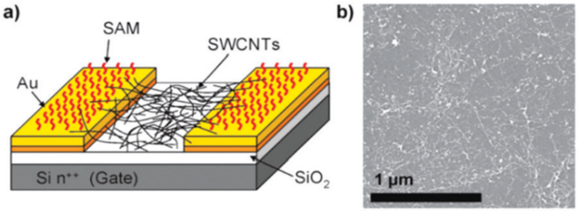

Fig. 11 (a) Schematic structure of a carbon nanotube field effect transistor (FET) with SAM-functionalized Au electrodes. (b) SEM image of a single-walled carbon nanotube (SWCNT) network. Reprinted with permission from ref. 53. Copyright (2011) Royal Society of Chemistry.

As can be clearly observed, in most published research articles, SAMs are generally employed as a functionalized layer on active sensing materials. However, in 2010, Anne-Marije Andringa *et al.*[54] reported a SAM-based field effect transistor (FET) for gas sensing applications. In this report, chloro[11(5-ethyle-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethien-5-yl)undecyl] dimethylsilane was used as a semiconducting layer for an FET sensor in order to detect nitric oxide. Prior to SAM formation, the SiO_2 surface was activated using oxygen plasma followed by acid hydrolysis. The SAM was formed by immersing the activated Si/SiO_2 substrate in a 1% solution of SAM in dry toluene at 85 °C under argon flow.

Concerning gas/chemical sensors, much research interest has been devoted to the detection of VOC compounds. Bin Wang *et al.*[55] used APTES SAMs with different end groups to functionalize silicon nanowire-based FETs for VOC detection. The interactions between the SAMs and VOCs were classified into three types: (a) dipole–dipole interactions between the molecular layer and polar VOCs; (b) induced dipole–dipole interactions between the molecular layer and nonpolar VOCs; and (c) molecule tilting as a result of diffusion of the VOCs between the chains of the molecular layer.

Along with VOCs, detection of toxic gases such as nitrogen dioxide (NO_2) is always a challenge; thus, it interests many researchers worldwide. An ultra-selective NO_2 resistive sensor based on *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (en-APTAS)-functionalized SnO_2 nanowires has been reported.[56] For functionalization, the SnO_2 nanowire samples were immersed in 1% ethanol solution of en-APTAS for 6 hours. After this, the samples were rinsed with ethanol to remove the residual SAMs and dried in a vacuum oven for 1 hour at 60 °C.

Moreover, rapid-response resistive sensors for H_2 gas were developed by depositing Pd@Pt core–shell nanocrystal on a trimethylchlorosilane (TMCS) SAM.[57] For SAM immobilization, drops of TMCS solution were degassed on SiO_2/Si in a vacuum desiccator. Nasima Afsharimani *et al.*[58] functionalized a graphene FET device with 1-octadecanethiol and 1-dodecanethiol for heavy ion sensing. Surface functionalization was performed by drop-casting the SAM solution of these two thiols on the surface of CVD-grown graphene.

A humidity sensor based on chitosan SAM-modified ZnO nanorod-patterned piezo-resistive silicon MEMS microcantilevers was reported by Jiushuai Xu *et al.*[59] The functionalization with chitosan was performed by dipping the microcantilever in 1% chitosan solution for 10 seconds.

Recently, in 2019, Yuxiang Qin *et al.*[60] reported an octadecyltrichlorosilane (OTS)-functionalized porous silicon nanowires (SiNWs)-based resistive sensor for detection of NO_2 gas. The conjugation of OTS with SiNWs was performed by treating the nanowire samples with 1 vol% OTS in toluene for 1 min at room temperature. OTS functionalization was found to increase the immunity of the SiNWs sensors to humidity.

6.2 Self-assembled monolayers in biosensors

A biosensor is a device that detects biomolecules such as enzymes, proteins, DNA, cells, or other biological molecules.[61] Basically, a biological or chemical reaction occurs between the analyte and the active sensing material and is detected by means of electrical, optical, *etc.* signals. For example, in FET-based biosensors, a change in drain current with respect to gate voltage has been detected when this type of reaction takes place.[62] Typically, a biosensor consists of three parts: biorecognition elements, *i.e.* bioreceptors, a transducer and a signal reader. Out of these three, the bioreceptor element is the most important because the biological reaction occurs on it. The selection of the bioreceptor depends upon the biological analyte to be detected and *vice versa*. For example, in order to detect an antigen, the active sensing material is biofunctionalized with antibodies.[63] The functionalization process of the active sensing material with biological entities is crucial and delicate. When the surface of a material such as zinc oxide comes into contact with biological environments, biological or chemical reactions take place at the interface (cell adhesion, protein adsorption and displacement, *etc.*).[1] In most cases, nonspecific adsorption processes occur between the biomolecules and solid surface, resulting in loss of interface functionalities. To avoid this problem, SAMs play an important role. Because of their characteristic functional end groups, SAMs allow the attachment of different biomolecules on the surface of the active sensing material and simultaneously protect the surface from biofouling.[1] This section is divided into two subsections based upon the surface used for the SAM formation.

6.2.1 Self-assembled monolayers on gold surfaces. From the beginning, SAM-modified gold electrodes have been immensely employed to fabricate biosensing devices such as amperometric[64] and electrochemical[65] devices. With advancements in research on biosensors, various other biosensing platforms, such as electrolyte-gated thin film transistors (EG-TFTs),[66] have emerged. In this part, we will present literature related to all types of biosensing devices involving SAM monolayers.

In 1993, Itamar Willner *et al.*[67] reported an amperometric biosensor based on a SAM-modified Au electrode on which glucose oxidase (GOD) was immobilized. Prior to GOD immobilization, the Au electrode was functionalized with a cystearnine SAM (incubation for 2 hours in H_2O). Moreover, Jie Horeek *et al.*[68] reported a label-free piezoelectric immunosensor. In this interesting work, Au electrode was functionalized with different SAMs, such as dithio-bis(succinimidylpropionate) (DSP), 4-aminothiophenol (ATPh), cysteamine, cystamine, and APTES. After the SAM functionalization, the amine groups of the SAMs were activated by treating the SAM-modified Au electrodes with a 2.5% solution of glutaraldehyde (GA) in phosphate buffered silane (PBS) for 1 hour. In order to detect DNA hybridization, a capacitive biosensor has been reported.[69] In this report, prior to the immobilization of the 5′-phosphorylated oligonucleotide probe on the gold surface, the Au electrode was modified with 2% (w/w) cysteamine solution in ethanol for 16 hours. An attomolar detection limit for DNA fragments was achieved with this biosensor platform.

A SAM-based piezoelectric immunosensor functionalized with an anti-human Immunoglobulin E (IgE) layer was used to detect the total human IgE in serum samples.[70] The Au electrode was treated overnight with 0.1% cysteamine in water, followed by GA activation of the amine groups; finally, the immobilization of anti-human IgE was performed. In other interesting work, Sami Ameur *et al.*[71] achieved a pictogram/millilitre detection limit for antigen by direct binding of 2-mercaptoethylamine (2-MEA) (cysteamine) on a gold surface.[72] Furthermore, H. Aoki *et al.*[73] reported an Au electrode functionalized with mixed SAMs of peptide nucleic acid (PNA) and 6-mercapto-1-hexanol for the detection of oligonucleotides at a micromolar level with the ion-channel sensor technique. For mixed SAM formation on the Au surface, the electrode was immersed in 1 mM aqueous solution of 6-mercapto-1-hexanol and 100 μM of PNA for 30 min at room temperature. With this strategy, the authors were able to distinguish complementary and one-base mismatch oligonucleotides.

The mixed SAM strategy was further followed by A. Gasper *et al.*[74] in order to establish direct electron transfer between enzymes and Au. In this work, Au electrode was immersed in a solution consisting of a mixture of 3-carboxypropyl disulfide or hexamethyl cystamine and 3,3′-dithiodipropionic acid di-(N-succinimidyl ester) for 90 min at room temperature.

In an interesting report, Fung *et al.*[75] detected salmonella in aqueous solution using 3-mercaptopro-pionic acid (MPA)-modified quartz piezoelectric crystal. The gold electrode of quartz crystal was immersed in a 1 mM solution of MPA in ethanol for approximately 15 to 24 hours, followed by activation with EDC-NHS for immobilization of the antibody.

Furthermore, Casero *et al.*[76] used thiol-based SAMs on an Au surface to induce order at the nanometer level in a membrane-bound fructose dehydrogenase layer. For functionalization with the decylmercaptan (DM) SAM, the Au electrode was immersed in a 2 mM solution in ethanol for 3 hours at room temperature. Meanwhile, for 5-(octyldithio)-2-nitrobenzoic acid (ODTNB) SAM

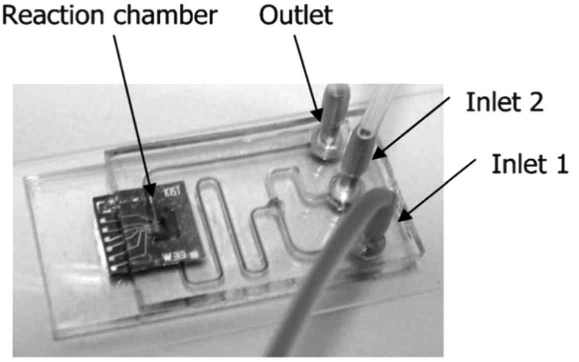

Fig. 12 Liquid test cell made using poly(dimethylsiloxane) (PDMS). Reprinted with permission from ref. 16. Copyright (2004) Royal Society of Chemistry.

formation, the Au electrode was immersed in 20 μM solution in ethanol for 3 hours at room temperature. The SAM was selected on the basis of the structure of the protein used for immobilization. On the other hand, an optical fiber biosensor based on anomalous reflection of a SAM-modified gold electrode was reported by Mitsuaki Watanabe *et al.*[77] Prior to immobilization of biotin, the Au surface was immersed in 0.1 mM solution of 1-amino-11-undecanethiol (AUT) in ethanol for 2 hours. In 2004, Hwang *et al.*[16] performed *in situ* quantitative analysis of a prostate-specific antigen (PSA) using a SiO_2/Ta/Pt/PZT/Pt/SiO_2 cantilever. For immobilization of the PSA antibody, an Au layer was deposited on the cantilever and then functionalized with calixcrown SAMs (the AU-coated cantilever was immersed in a solution of calixcrown in $CHCl_3$ for 3 hours at room temperature). The dynamic measurement in a liquid environment was performed by fabricating a liquid test cell using poly(dimethylsiloxane) (PDMS), as shown in Fig. 12.

Based on electrochemical impedance spectroscopy (EIS), an immunosensor for the measurement of 2,4-dichlorophenoxyacetic acid was reported by Iva *et al.*[78] For immobilization of anti-HAS monoclonal antibody (MAb), Au electrodes were treated with cystamine, ATPh, 3,3*V*-dithiopropionic acid di-(*N*-succinimidyl ester) (DTSP) and 11-mercaptoundecanoic acid (MUA) SAMs. The three different types of sensors fabricated in this work are shown in Fig. 13. A magnetoelastic bioaffinity sensor for the detection of avidin was developed by modifying the Au surface with 10 mM solution of 2-aminoethanethiol hydrochloride in ethanol.[79] After SAM modification, the samples were immersed in 20 mg ml^{-1} biotin-PEG-NHS solution for 2 hours at room temperature. With this sensor, a detection limit of 200 ng ml^{-1} for avidin was achieved. Moreover, label-free detection of DNA oligonucleotide sequences was performed by using ac impedance measurements.[80] In this work, a working Au electrode was functionalized with a mixture of two SAMs, *i.e.* 2-mercaptoethanol (2-ME) and 11-mercaptoundecanoic acid (11-MUA), to achieve the goal. Indeed, the SAM was formed by immersion of the Au electrodes in solutions of 2-ME, 11-MUA, or mixtures of these two in methanol for 24 hours. For the development of an odorant biosensor, Yanxia Hou *et al.*[81] transferred Langmuir and LB films of odorant-binding protein/amphiphile onto Au substrates. Prior to the LB process, the Au substrate was modified with 1-octadecanethiol (ODT) SAM in order to obtain a hydrophobic surface. 1 mM ODT ethanol solution was prepared, and the Au substrate was immersed in it for 21 hours at room temperature. In 2006, rhodopsin (G protein-coupled receptor (GPCR), which mediates the sense of vision) was successfully immobilized on Au substrate by LB and SAM techniques.[36] In the SAM process, the Au surface was functionalized with a mixed solution of 16-mercaptohexadecanoic acid and biotinyl-PE in absolute ethanol at concentrations of 1 and 0.1 mM, respectively, for 21 hours.

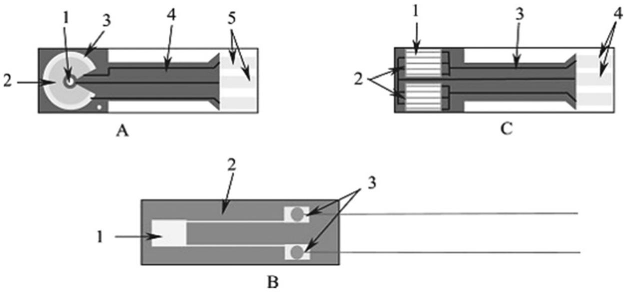

Fig. 13 Schemes of electrodes: (A) strip sensor: 1 – working electrode, 2 – reference electrode, 3 – auxiliary electrode, 4 – alumina support, 5 – contacts. (B) Interdigitated array electrode: 1 – Pt (platinum) working interdigitated electrode, 2 – connection (interdigitated array contacts), 3 – contact. Reprinted with permission from ref. 78. Copyright (2004) Elsevier B.V.

Due to their unique ability to immobilize different biomolecules, a large number of reports in which SAMs play an integral role in building biosensor devices were published between 2006 and 2010. For the reader, here, we reference a few very important studies.[17,18,82–91]

Moreover, an enzyme-based electrochemical biosensor for the detection of ethanolamine was reported by B. Sikarwar *et al.*[6] Before the immobilization of monoamineoxidase A (MAO-A), the Au electrode was modified with a 4-mercaptobenzoic acid (4-MBA) monolayer followed by modification with EDC-NHS. The 0.01 M solution of 4-MBA was prepared in methanol and the Au electrode was dipped in it for 2 hours.

As one can observe from our discussion, generally, thiol-based SAMs are used for modification of Au. However, Zhijun Li *et al.*[92] presented an alternative SAM for Au modification, *i.e.* N-heterocyclic carbene (NHC), to fabricate an SPR biosensor. In this report, two precursors of NHC, namely 5-(dodecyloxy)-1,3-diisopropyl-1*H*-benzo[d]imidazol-3-ium hydrogen carbonate and 5-((11-hydroxyundecyl)oxy)-1,3-diisopropyl-1*H* benzo[d]imidazol-3-iumhydrogen carbonate, were used. The Au surface was immersed in a 10 mM solution of NHC precursor in dry methanol for 48 hours at room temperature. In their concluding remarks, the authors stated that the NHC SAM presents several advantages in SPR biosensing compared to thiol SAMs, such as lower non-specific binding ability, better chemical stability and significantly superior thermal stability, higher reproducibility, shorter equilibration time, and longer lifespan. Recently, in 2019, interesting reports were published in which SAMs were used to fabricate biosensing devices.[93–95] In one of these, a toll-like receptor (TLR)-based impedance biosensor[96] was reported; to immobilize the TLR-4 receptor, the Au electrode was modified with a mixture of three different SAMs to achieve carboxylic, hydroxyl and ferrocene terminations. Specifically, the Au electrode was treated with a mixture of 11-mercaptoundecanoic acid (MUA), 11-mercaptoundecanol (MUO) and 10-mercaptodecyl-ferrocenylcarboxamide (MFc). In another report, a label-free electrochemical DNA sensor was reported based on carbon dots (CD) stabilized with silver–lipid nanohybrids.[97] To anchor the lipid-carbon dots-capped silver nanoparticles on the Au electrode, a 3-mercaptopropionic acid (MPA) monolayer was used in order to avoid the vesicle rupture and bilayer formation that occurs during direct contact. For SAM formation, the Au electrode was immersed in 1 mM MPA solution in PBS for 1 hour.

6.2.2 Self-assembled monolayers on oxides, nitrides and FET-based devices. An immunosensor based on silicon nitride was prepared in the form of an electrolyte-insulator-semiconductor (EIS) structure.[98] Silicon nitride was prepared on an Al/n-Si/SiO wafer and was functionalized with aminopropyl-triethoxysilane before the immobilization of a cross-linker (glutaraldehyde) and anti-rabbit IgG. To obtain amino groups, the substrates were immersed in 10% aminopropyl-triethoxysilane in distilled water for 4 hours at 80 °C. The pH value of the solution was adjusted to 4 with hydrochloric acid. An innovative report was published by H. Kawarada *et al.*[99] in which a field effect transistor (FET) gated with diamond electrolyte solution was used to detect DNA and proteins. In order to immobilize different biomolecules, a variety of terminations, such as amine (NH_2) termination and carboxylic termination, was achieved by using SAMs. In electrolyte-gated FET (EG-FET) devices, electrolyte solutions such as water[100] and ionic liquids[101] have served as gate dielectrics instead of conventional SiO_2. The major advantage of these devices is their low voltage operation and the possibility to use biological fluid as a gate dielectric.[100] In the EG-FET top-gate, a bottom-contact configuration has been used. Using this unique concept, S. Casalini *et al.*[102] fabricated organic semiconductor-based EG-FET devices (see Fig. 14) for dopamine sensing. Poly(3-hexylthiophene) was used as a semiconductor and was deposited on the interdigitated patterned source/drain contacts using a spin coating technique. The top Au gate electrode was functionalized with cystamine (CA) SAMs by placing the electrode in 1 mM solution CA in ethanol for 4 hours at room temperature.

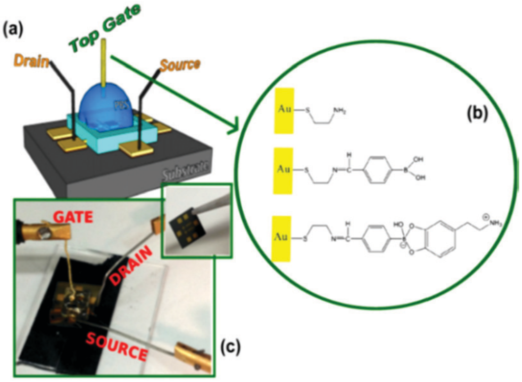

Fig. 14 (a) Schematic of our test pattern integrated with a poly(dimethylsiloxane) pool for confining a droplet of phosphate buffer solution (PBS). (b) The SAM steps are (1) cysteamine, (2) 4-formylphenyl boronic acid and (3) dopamine. (c) Photograph of the system. Reprinted with permission from ref. 102. Copyright (2013) Elsevier B.V.

Furthermore, M. Singh *et al.*[103] proposed a water-gated ZnO-based TFT for protein sensing. In this work, a sol–gel-prepared ZnO thin film was functionalized with an APTES SAM. Specifically, the ZnO thin film was incubated in a 10 mM solution of APTES in toluene for 18 hours at room temperature. A novel electrochemical biosensor based on silicon nitride (Si_3N_4) for the detection of ochratoxin A (OTA) was reported in 2016.[104] The surface of Si_3N_4 with a structure of Si_3N_4/SiO_2/Si-p/Al was modified with an APTES SAM and magnetic nanoparticles before the immobilization of OTA antibody. In this work, the Si_3N_4 layer was deposited using chemical vapor deposition (CVD) and aluminum contact was realized on the backside of the wafer. For SAM formation, Si_3N_4 was treated with 1% APTES in ethanol overnight at room temperature. The whole functionalization process is depicted in Fig. 15. In order to obtain the hydroxyl (OH) groups for the formation of the APTES monolayer, Si_3N_4 was treated with piranha solution for 30 minutes. A disposable indium tin oxide (ITO)-based electrochemical immunosensor for label-free detection of MAGE-1 (where MAGE stands for melanoma antigen) was reported by B. Demirbakan *et al.*[105] For the immobilization of MAGE-1 antibody, the ITO electrode was immersed in a 1.5% solution of 3-glycidoxypropyltrimethoxysilane (3-GOPS) in toluene for 16 hours. Fast detection of a tumor marker (CA 19-9) was achieved using aluminum gallium nitride (AlGaN) and gallium nitride (GaN) high electron mobility transistors (HEMT).[106]

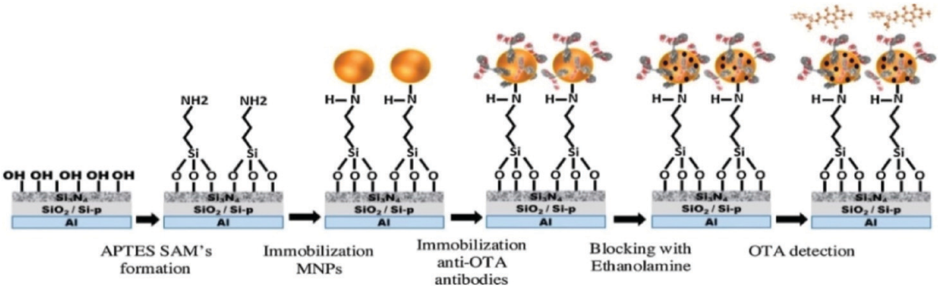

Fig. 15 Schematic of the functionalization procedure based on magnetic nanoparticles (golden dots) and anti-ochratoxin A antibodies. Ethanolamine (black dots) was used after immobilization of the antibodies to avoid nonspecific adsorption. Reprinted with permission from ref. 104. Copyright (2016) Elsevier B.V.

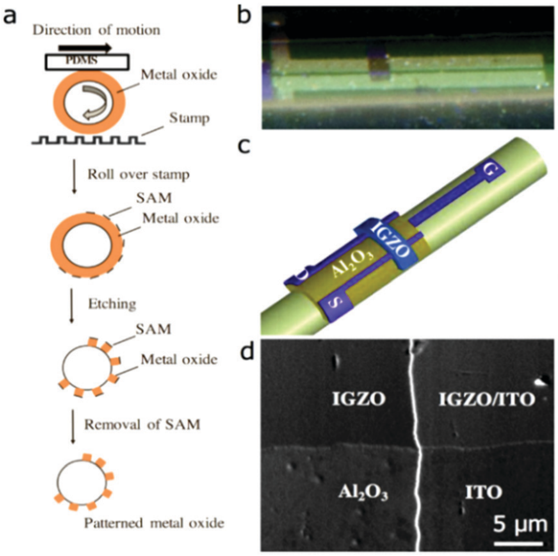

Fig. 16 (a) Schematic of micro contact printing (μCP) on a curved substrate. (b) Optical image and (c) schematic of the structure of an amorphous indium gallium zinc oxide (a-IGZO) field effect transistor on a curved substrate (width/length ratio of 100 μm/20 μm). (d) SEM image of the step edges between indium tin oxide (ITO) and aluminium oxide (Al_2O_3) and between IGZO/ITO and a-IGZO. Reprinted with permission from ref. 5. Copyright (2018) Elsevier B.V.

In order to immobilize the antibody, the surface of the HEMT was functionalized by immersing the device in a 10% solution of APTES in ethanol for 1 hour. In another interesting report, transparent indium gallium zinc oxide (IGZO) thin film transistor (TFT) devices were fabricated on a highly curved substrate (see Fig. 16) and used for glucose sensing.[5] For immobilization of glucose oxidase (GOx), IGZO TFT was functionalized with an aminopropyltrimethoxysilane (APTMS) SAM. 1% APTMS solution was prepared in ethanol and IGZO TFT was immersed in it for 2 hours. On the other hand, Su *et al.*[107] used a mixture of trimethoxysilyl chloride (DMOAP) and APTES SAMs for label-free detection of HBD-2 (human β-defensin-2). In this work, glass slides were immersed in solution of 3% (v/v) APTES and 1% (v/v) DMOAP in ethanol at 80 °C for 2 hours. It is interesting to point out here that in FET biosensors, the immobilization of biomolecules on the semiconductor surface can degrade the device performance. In an interesting report, E. Macchia *et al.*[35] immobilized biomolecules on an Au gate electrode instead of on the semiconductor surface in an EG-FET device. In this work, the detection of C-reactive protein (CRP) in saliva was achieved. For immobilization of anti-CRP, the Au electrode was functionalized with a mixture of 3-MPA and 11-MUA SAMs. In particular, the AU electrode was immersed in a 10 mM solution with a 10 : 1 M ratio of 3-MPA and 11-MUA in ethanol. The Au electrode was maintained in this solution for 18 hours at 22 °C under N_2 gas flow.

6.3 Self-assembled monolayers in organic field-effect transistors (OFETs)

In addition to using the SAM approach for biomolecule immobilization, SAMs have been used in thin film transistors (TFTs). In particular, the performance of organic thin film transistors (OTFTs) has been greatly improved by using SAMs on dielectric and source–drain (S/D) electrodes and semiconductors. SAM-modified S/D electrodes have been used to control the contact resistance of the electrode/semiconductor interface. The structure of a thin film transistor in the top-gate, bottom-contact configuration is shown in Fig. 17. The S/D electrodes are in direct contact with the semiconductor; hence, the electrode/semiconductor interface controls the charge injection. Typically, in OTFT devices, the noble metal gold (Au) is used to fabricate the S/D electrodes, whose work-function rarely matches the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) levels of organic semiconductors (OS). Indeed, for efficient injection of charges, ohmic contact is highly desirable; however, this is difficult to achieve due to the selection of semiconductors/electrodes. However, the OS/electrode interface is generally regarded as a Schottky barrier due to the difference between the heights of the electrode work-function and the HOMO or LUMO of the OS. By inserting a SAM in this interface, the charge injection can be controlled and improved.

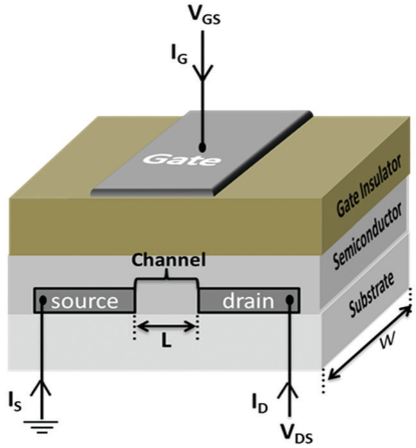

Fig. 17 Structure of a thin film transistor with channel length *L* and width *W*.

Pioneering work in this direction was presented by I. H. Campbell *et al.*[108] In this interesting work, the barrier between the silver (Ag) electrode and conjugated polymer poly[2-methoxy, 5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) was modified using three different SAMs. Thiol-based SAMs, *i.e.* $CH_3(CH_2)_9SH(CH_3)$, $NH_2(CH_2)_{10}SH(NH_2)$, and $CF_3(CF_2)_7(CH_2)_2SH(CF_3)$, were used, and the Ag electrode was immersed in the respective 10^{-3} M solutions for modification. The authors demonstrated that these SAMs act as a dipole layer that helps to tune the Schottky barrier.

In similar work, the hole-injection barrier of a Ag/(MEH-PPV) interface was tuned by modifying Ag electrode with alkanethiol SAMs.[109] The authors were able to tune the work-function of the Ag electrode from 3.8 to 5.5 eV using two different SAMs, namely $SC_{16}H_{33}$ and $SC_2H_4C_8F_{17}$. A number of reports related to this work are available in the literature.[110–113]

In TFT devices, another important interface is the semiconductor/gate dielectric interface. This interface is responsible for the accumulation of charge carriers on the surface of the semiconductor. The presence of defects on the dielectric surface or chemical species in the interface, such as moisture, can hinder the performance of the OFET. By modifying the gate dielectric, such as SiO_2, with SAMs, these entities can be addressed.[2] Modifying SiO_2 with a silane-based SAM eliminates electrostatic interactions such as hydrogen bonds and also renders the SiO_2 surface hydrophobic. Hydrophobization of the dielectric surface minimizes the electrochemical reactions between the accumulated charge carriers and the moisture layer at the surface.[2,114] In particular, in p-type OS-based OFET devices, the hydrophobic surface prevents the adsorption of water at the OS/gate dielectric interface. Z. Bao *et al.*[115] observed an increase in the charge carrier mobility of OFET by treating the SiO_2 surface with octadecyltrimethoxysilane (OTMS) and octadecyltrichlorosilane (OTCS) SAMs. These two SAMs were deposited on the SiO_2 surface using spin coating techniques. In a pentacene-based OFET, low-voltage operation was achieved using *n*-alkyl phosphonic acid (PA) SAM/hafnium oxide (HfO_2) hybrid dielectrics.[37] To obtain the PA layer, the HfO_2 substrate was immersed in a solution of PA in ethanol at 70 °C for 15 hours.

Another important aspect of SAMs in FET-based devices is that they can be used as gate dielectrics. The pioneering work of using SAMs as gate dielectrics was performed by Vuillaume *et al.*[116–119] In a typical FET device, SiO_2 serves as the gate dielectric and is able to achieve a capacitance on the order of 10–20 nF cm^{-2}. By increasing this value, one can enhance the charge carrier density in the channel. High capacitance can be achieved either by using high dielectric constant materials or by decreasing the thickness of the dielectric.

In this direction, SAMs are ideal candidates because they can form monolayers with thicknesses in the nanometer range or lower. In one report, Vuillaume *et al.*[116] managed to obtain a 2.8 nm thick octadecyltrichlorosilane (OTS) insulating layer on a Si/SiO_2 substrate which was stable up to 450 °C.

6.4 Self-assembled monolayers for patterning

The typical structure of SAMs containing head and end groups was described in the introduction section. The end groups of SAMs play a particularly important role because they define the surface properties of the SAMs. SAMs with different end groups but identical anchor groups can form a monolayer on the same surface, giving rise to distinct surface properties. A random mixture of such monolayers with different end groups can be processed into defined patterns of two species.

The concept of using SAMs for patterning was introduced by G. M. Whiteside *et al.* in 1992.[120] In this work, long-chain alkanethiolate on an Au surface was used for patterning. In addition to their patterning ability, SAMs are used as ultra-thin organic resists in lithography. Indeed, the use of a SAM as a protective layer reduces the etching of metal surfaces when exposed to oxidizing solutions. Because the etching rates of the bare and SAM-covered metal surface are different, features can be patterned into the substrate that supports the SAM. The three main techniques that are used to achieve the patterning of SAMs will be discussed in this review.

6.4.1 Micro contact printing (μCP). μCP is a simple and low cost technique for obtaining a SAM pattern with a submicrometer lateral dimension. This method falls in the category of soft lithography. This technique is gaining popularity daily due to its large printing capacity, the ease of fabricating printing tools and its high spatial resolution.[8] It is a very useful technique for organized attachment of cells or biomolecules. In μCP, a flexible elastomeric stamp typically made of polydimethylsiloxane (PDMS) is used to transfer the SAM-forming molecules to the substrate.[121] Fig. 18 shows how the SAM pattern is achieved *via* the PDMS stamp.

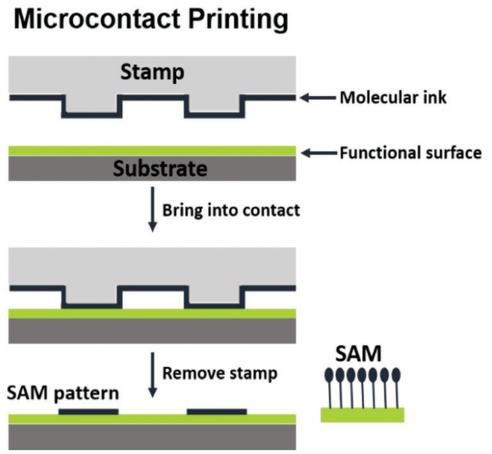

Fig. 18 Microcontact printing of a SAM using a polydimethylsiloxane (PDMS) stamp.

The PDMS stamp is fabricated by casting the liquid PDMS precursor on a lithographically patterned (photolithography or e-beam lithography) silicon wafer, followed by crosslinking of PDMS at elevated temperature. After this, the stamp is stripped off the substrate and dipped into a solution of SAM molecules, which is called the ink. After removal from the solution, the stamp is dried and pressed against the surface *via* mechanical contacts, resulting in transfer of the adsorbed molecules from the stamp to the surface area in contact. Thus, a pattern similar to the surface profile of the stamp is created. The resolution of the pattern formed *via* this technique largely depends upon the dimension of the PDMS stamp. Typically, patterns in the range of hundreds of nanometers to micrometers can be produced. In 2002, in the progress of their work, George M. Whiteside *et al.*[122] produced a pattern 30 nm in size using a PDMS stamp.

6.4.2 Scanning probe lithography. In scanning probe microscopy, such as atomic force microscopy (AFM), probe tips are usually used to examine the morphological information of the surface. However, in scanning probe lithography (SPL), the probe tips are used to manipulate atoms and molecules on surfaces. By using this method, high resolution patterns of SAMs have been obtained by scanning tunnelling microscopy (STM) and AFM; this also includes dip-pen nanolithography (DPN), nanoshaving and nanografting.

DPN was developed by Mirkin *et al.*[123] in 1999; they used an AFM tip to transfer the molecules to the substrate. Specifically, the capillary transport of molecules from the AFM tip to the solid substrate was used to directly write the pattern. In this work, 1-octadecanethiol (ODT) molecules were transferred to a gold surface. The AFM tip was coated with the ODT SAM, and

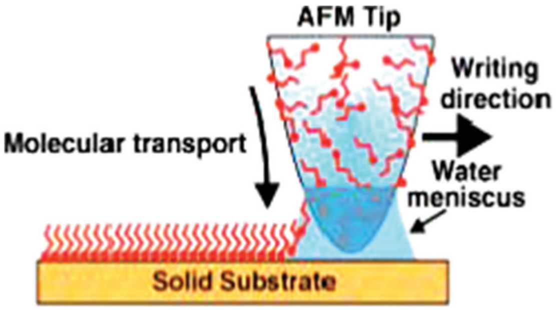

Fig. 19 Schematic of the dip pen nanolithography process. A water meniscus forms between the atomic force microscopy tip, which is coated with "ink" molecules, and the solid substrate. Reprinted with permission from ref. 124. Copyright (2004) John Wiley and Sons.

when this tip was brought in contact with the Au surface, the ODT molecules were transferred from the tip to the surface by capillary action. The whole process resembles a dip pen (see Fig. 19).[124]

In the nanoshaving technique, a nanopattern is formed by displacing the SAM adsorbates with the AFM tip. The AFM tip, in this case, operates with a load higher than the displacement threshold of the SAM molecules.[125] The pressure on the tip results in a high shear force during the scan, which causes the displacement of SAM adsorbates. If nanoshaving is performed on a surface that is immersed in a solution of different SAM molecules, the technique is called nanografting. Both processes are shown in Fig. 20.

Moreover, STM tips can be used to make nanopatterns of SAMs. If operated under certain conditions, it is possible to remove the surfactant from the SAM matrix *via* electrochemical and mechanical means. By performing the removal in solution, the cleared region can be backfilled with other SAM molecules.[121,126] Compared to the μCP technique, much smaller patterns in the range of tens of nanometers can be produced with the SPL technique; however, the process of pattering is slower that of μCP.

6.4.3 Photo-induced pattering. Photolithography is a well-established technique used in the fabrication of semiconductor devices. In this process, the photoresist material is irradiated with UV light through a photomask to form the required pattern.[127] In a similar way, a SAM pattern can be formed on the substrate without using a photoresist material by irradiating the SAM layer though the photomask (see Fig. 21). On the uncovered areas of the SAM, photochemical modifications allow the surfactant to be either removed or equipped with different functionalities. The resolution of the formed SAM pattern depends on the dimensions of the shapes in the photomask and also on the limit of diffraction.[121] SAMs of alkanethiol and organosilane have been patterned with this technique.[128–130]

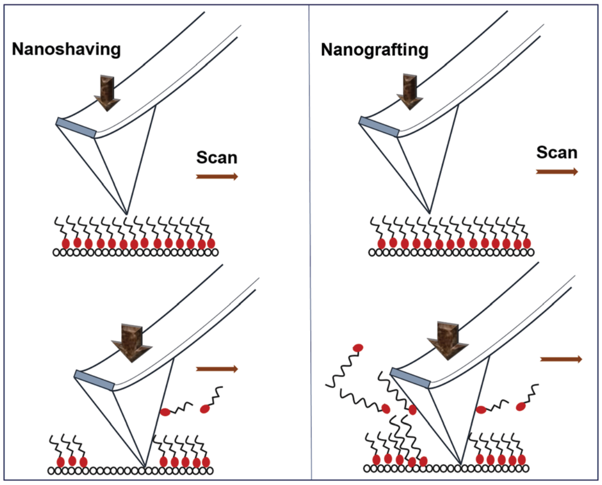

Fig. 20 Nanoshaving and nanografting.

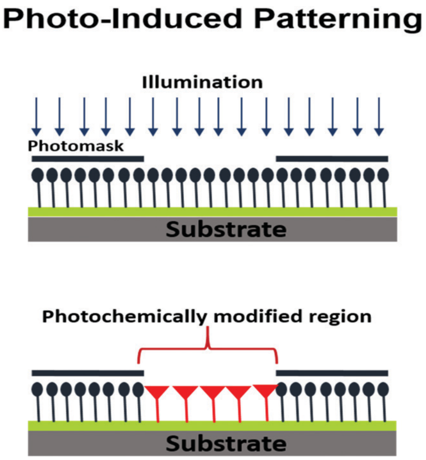

Fig. 21 Photo-induced patterning.

7. Some critical issues of self-assembled monolayers in their application context

There is no doubt that SAMs on particular surfaces, *e.g.* thiols on gold, can be used for various applications, such as biosensors, patterning, gas sensors, and immobilization of biomolecules. However, there are still some major issues that must be addressed before SAMs can be used for particular applications. In this section, we will briefly address all these issues; for more details, readers can refer to the review articles reported elsewhere.[25,131–133]

One major issue is the stability of SAM molecules, which can be affected by temperature, chemical environmental conditions, prolonged exposure to the ambient environment, ultra-violet (UV) irradiation, *etc.*[131] It has been found that when alkanethiolates on gold surfaces are exposed to ambient environmental conditions for prolonged times, they undergo oxidation of the sulfur head groups, which harms the functionality of the surface.[134–136] Further investigation showed that the reason for this oxidation is exposure of the SAM molecules to light.[137] Indeed, short chain alkanethiolates show immense instability under exposure to UV irradiation compared to long chain alkanethiolates.[138]

Another important issue is the reproducibility of the SAM formation process, which is difficult to achieve and control. As discussed earlier, many different parameters, such as temperature, concentration of the SAM solution, and content of water, should be chosen and adjusted carefully to obtain a highly ordered

SAM assembly. However, the natural spontaneity and self-organization of the molecules involved in SAM formation cannot be fully controlled, which influences the reproducibility of the process. For these reasons, *i.e.* instability and reproducibility, the industrial application of SAMs in the field of electronic devices such as biosensors and gas sensors is still questionable, and further work on these parameters is required.

Another issue with SAMs is the presence of defects, such as missing molecules on particular sites, that occur during SAM formation. These defects are found even when single crystalline surfaces such as Au(111) and optimal preparation conditions are used.[133,139,140] The presence of these defects limits the further application of SAMs in electronic devices.

Furthermore, for the selective immobilization of biomolecules, such as cell adhesion and protein adsorption, there is growing interest in the preparation of surfaces that possess mixed chemical functionalities.[1] In order to prepare these surfaces, a mixture of different SAMs can be used (see Section 3.1); recently, this procedure was used for the detection of C-reactive protein in saliva.[35] However, in these surfaces, spatial control of the SAMs, the exact state of the mixing components and the stability of their distribution are critical issues which are difficult to understand and control. The STM investigation of two similar alkanethiolates showed the presence of phase segregation. Further investigations showed that the phase segregation in these mixed functionality surfaces depends on both solvent and temperature. Despite recent advances in characterization techniques for the study of such complex systems, the mechanism of phase segregation in mixed SAMs is still not clear.[25]

Another area of SAM application is their use in patterning, as presented in Section 5.4. Based on their properties, techniques such as micro contact printing and photo-induced patterning have been developed. In all these methods, alkanethiolate-based SAMs on gold have been majorly adopted for patterning; this limits their use to certain applications because gold is not a technically useful substrate for fields such as microelectronics.[25]

8. Conclusions and future perspectives

In conclusion, we have reviewed a wide range of literature explaining the roles of SAMs in electronic devices such as chemical sensors, biosensors and organic field effect transistors. In particular, in all these devices, the processes of SAM formation on various surfaces and the physical/chemical conditions used have been presented. Mixing different SAMs and using them to fabricate ultrasensitive sensors has been found to be a very interesting approach. Thiols on Au surfaces are majorly employed to fabricate different sensing devices, such as electrochemical, aperometric, microcantilever, and SPR devices. Meanwhile, silane-based SAMs are generally used with oxide-based surfaces. We have also found that in most cases, the molarity of the SAM solution is on the millimolar order and ethanol is used as the solvent. In EG-FET devices, functionalization of Au gate electrodes with a mixture of 3-MPA and 11-MUA SAMs enabled label-free single molecule detection of C-reactive protein.

Furthermore, thiol-based SAMs on Au and Ag electrode surfaces improve the interface barrier in OFET, which improves the performance of the device. Meanwhile, modifying dielectric surfaces with SAMs prevents the adsorption of water at the OS/gate dielectric interface. Furthermore, the use of SAMs as a gate dielectric and active semiconducting layer in FET-based devices is an interesting approach that can be used to fabricate inexpensive molecular electronic devices. In particular, octadecyltrichlorosilane (OTS) is a potential gate dielectric which is also commercially available. In addition to this, many other SAM molecules are commercially available; thus, it is easy to perform more experiments in order to achieve highly efficient electronic devices.

We believe that with increased understanding of the fundamental concept of SAMs and the development of new SAM molecules, further major developments in electronic devices can be achieved. Particularly in FET devices, if high capacitance value SAMs can be obtained, low voltage operation can be achieved; this will be a great advance in the development of low energy consumption devices.

Conflicts of interest

The authors declare that they have no conflict of interest.

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