Hybrid molecule-on-silicon nanoelectronics: Electrochemical processes for grafting and printing of monolayers

D.K. Aswal a,b,*, S.P. Koiry b, B. Jousselme a, S.K. Gupta b, S. Palacin a, J.V. Yakhmi b

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ABSTRACT

The hybrid nanoelectronics, i.e., organic molecules deposited on Si exhibiting electronic functionalities is expected to extend the scaling limits of Si microelectronics down to few nanometers. In this review, first we make an overview of the organic molecules exhibiting various functionalities, such as, dielectric, diode, memory and transistor. We then review the literature on electrochemical grafting of organic molecules to Si, which have been carried out using terminal vinyl (C=CH), ethynyl (C≡C), halide (Cl, Br, I), tetraalkylammonium salt, diazonium salt and silane as reactant. It has been demonstrated that electrochemistry not only allows grafting of molecules on Si but also provides very useful information on the characteristics of the grafted layers. The electronic functionalities of various electrografted molecules are discussed. An additional advantage of the electrochemical process is that monolayer patterns with spatial resolution in a wide range, i.e. from nanometer to millimeter, can be easily prepared. The recent advances made in the spatial patterning of monolayers using electrochemical lithography are briefly reviewed.

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* Corresponding author.
E-mail address: dkaswal@yahoo.com (D.K. Aswal).

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1. Introduction

Silicon microelectronics has undergone relentless miniaturization during the last three decades or so, leading to dramatic improvements in computational capacity and speed. This miniaturization is characterized by Moore’s Law, which predicted an increase of the bit density by a factor of 2 every 18 months for memories or every 24 months for microprocessors in integrated circuits (ICs) [1]. Now it is being anticipated that the Si technology will face the scaling limits in very near future [2]. This is because, as the projected size of the transistors goes down to 20 nm or below, the physics of the transistors leads to unacceptable power dissipation. In addition, technological and economic factors impose severe limits on the integration process. Therefore, scientists and engineers have been investigating another promising avenue: using individual molecules as functional electronic devices, and this branch of research is popularly termed molecular electronics [3]. Simple molecular electronic test devices usually consist of organic molecules sandwiched between conducting electrodes. In fact, the foundation of the molecular electronics was laid in early seventies with the following two major works: (i) first experimental demonstration of tunneling transport through monolayer of alkyl-chains, i.e. \( CH_2(CH_2)_n-COOH \) sandwiched between two metal electrodes, indicating their dielectric character [4], and (ii) theoretical concept of a molecular rectifying diode in an acceptor–bridge–donor (A–b–D) molecule [5]. In an A–b–D molecule, the electron donor (D) having low ionization energy is separated from a high electron affinity acceptor (A) by an insulating alkyl-chain (b). Under forward bias, the electrons can tunnel from the donor to the acceptor through the spacer. However, for the reverse bias conduction is not as easy. According to this seminal theoretical work, such a junction should give current–voltage (J–V) characteristics similar to the rectifying behavior observed in the semiconducting p–n junction or diode.

An intense research carried worldwide during last couple of years has demonstrated that molecules indeed exhibit different electronic functions, e.g. rectification, negative differential resistance, memory, etc., and many more new molecules with desired electronic functionalities are being synthesized by the chemists around the world [2,6,7]. Physicists and engineers, on the other hand, devised several new methods to measure the electronic transport of a single molecule or monolayer. These include break-junction [8–10], cross-wire [11], metal nano-particle [12], conductive-probe atomic force microscopy (CP-AFM) and scanning tunneling microscopy (STM) [13–15], nano-pore [16–18] and planar sandwich geometry [19]. However, till date building electronics solely using molecules appears to be a science fiction and it might take several decades for development. At present, we are only at the materials stage of the molecular electronics, that is, working to understand fundamentally the electronic transport in molecules. Development of electronics using molecules would be the next step, where one can actually interconnect all of the molecular devices. Transforming discrete molecular devices into practical circuits, i.e. making billions of molecular devices electrically accessible, is not an easy task. Thus, a medium term solution, say for next 10–15 years, is to make molecules compatible to silicon, so that the nanoscale electronic functionality of molecules can be utilized in silicon-based microelectronics, and this research field is termed as hybrid nanoelectronics [2,20,21]. The advantage of the molecule-on-Si hybrid concept is that the inputs available from an already existing powerful Si-based integrated circuit industry can be used effectively for the development of integrated hybrid devices. This hybrid approach in a way will not require a complete rethinking of the circuit, as it would be an extension of microelectronics into nanoelectronics, i.e. functional molecular components are assembled on a micro-electronic frame. The hybrid nanoelectronics, therefore, will be complementary to the traditional electronic devices.

The molecule-on-Si hybrid approach attracts the following obvious questions. (i) Which molecules exhibit electronic functionalities? (ii) How functional molecules are grafted on Si? (iii) How the molecular devices will be interconnected? In fact, at present it is not easy to answer these questions as the research in this field is at infancy. This review mainly aims at answering the second question. Self-assembly has customarily been used as the most appropriate approach to deposit organic molecules to Si and there are several reviews on this aspect [2,22,23]. Some of the self-assembly routes for depositing monolayers on Si are: (i) the condensation of molecules containing alcoholic groups at H-terminated Si surfaces [24]; (ii) the silanization of hydroxyl-terminated Si surfaces via reaction with chlorosilane-terminated molecules [25–29]; (iii) the hydrosilylation of alkenes at H-terminated Si surfaces [30–34] and (iv) the arylation of H-terminated Si via its reaction with diazonium salts and elimination of HBF4 and N2 [35]. Self-assembly process allows preparation of high-quality monolayers on large area of Si substrates; however, in the absence of an adequate mechanism of external control, there is no feasible way by which spontaneous self-assembly processes alone would lead to molecular devices spatially patterned to resolutions down to nanometers. Therefore, external intervention, such as, an electric bias, is unavoidable if self-assembly is ultimately to become a viable approach to nanofabrication.

In fact, electrochemical deposition has traditionally been used for coating conducting surface with metals. Electroplating is being extensively used in coating surfaces for different applications, such as, automotive, petrochemical and aerospace industries; propulsion, combustion and microwave applications; printed circuit boards and copper interconnect for microelectronics; and decorative applications [36]. Electrodeposition of organics was initially employed for the deposition of conducting polymers, where a potential supply is required throughout the deposition to fuel the redox process. Electrografting is relatively a new technique that allows deposition of very thin organic films (typically between one monolayer and 50 nm). Electrografting essentially is an electro-initiated process and takes place by the formation of covalent bonds between the substrate atoms and the molecules. Electrografting requires a charged electrode (e.g. doped Si), which could be anodic (positive potential) or cathodic (negative potential). However, cathodic electrografting has a distinct advantage: since a negative potential is applied to the Si substrate, the oxidation and/or hydrolysis of Si surface is out of question during the grafting process, which results in a clean molecule/Si interface. Moreover, the applied negative potential becomes a controlling parameter for driving the molecules to the Si surface and, therefore, one can generate the monolayer patterns using a suitable mask. In fact, cathodic electrografting was originally used by Lecayon et al. [37] to deposit adherent polymers on conducting surfaces using anhydrous solutions of vinyl monomers, such as, acryonitrile, etc. In recent years, it has been demonstrated that any cleavable electroactive molecules, e.g. vinyl (C=CH), ethynyl (C≡CH), halide (Cl, Br, I), tetraalkylammonium salt, diazonium salt, silane etc., can be electrografted to H-terminated Si surfaces. In this article we review electrografting of such organic molecules to Si surfaces.

This article is organized as follows. The concepts of various possible molecular architectures for hybrid devices and efforts made so far in their realizations are discussed in Section 2. One of the basic requirements for electrochemical grafting is the preparation of high-quality H-terminated silicon surfaces. The procedures for making H-terminated Si(111) and Si(100) are
presented in Section 3. A brief overview of electrochemical deposition processes and various routes employed for electrografting organic molecules on Si substrates are reviewed in Section 4. The characterization and electronic transport studies on the electrografted molecules are also discussed in this Section. In Section 5, recent developments on the electrochemical printing of monolayers are described. Finally, a summary is presented in Section 6.

2. Organic molecules exhibiting electronic functionalities

Apart from the theoretically predicted A–b–D molecular rectifiers [5], there are no other predicted molecules exhibiting active electronic functionalities. However, due to different types of chemical bonding in molecules, one can envisage some of the molecular architectures exhibiting electronic functionalities. In molecules, two different chemical bonds, namely, $\sigma$- and $\pi$-bonds can form, as shown schematically in Fig. 1. A molecule orbital that is symmetric along the axis connecting two atomic nuclei is called $\sigma$-bond, which is formed from overlapping s or overlapping p orbital. $\pi$-bonds are formed when p orbitals overlap side-by-side. Alkane molecules are singly bounded molecules like C–C or C–H and contain only $\sigma$-bonds. The positive charge of the nuclei prevents electron to travel along the axis of the molecule and, therefore, alkyl-chains cannot easily transport electrons. The separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in alkyl-chains is very large (~8 eV) [19], and thus, can be utilized as insulators in molecular circuits. On the other hand, conjugated molecule consists of alternating single and double bonds that link the subsequent atoms. There is an extended series of overlapping p orbital, which makes the $\pi$-bond. In conjugated oligomers, electrons from $\pi$-bonds are delocalized over the entire molecule. The HOMO/LUMO separation in $\pi$-conjugated molecules depends strongly on the overlapping of neighbouring $\pi$ orbitals, which is in turn related to the planarity of the molecule and to side groups. In many cases, the HOMO/LUMO energy gap is relatively small (~3 eV) and the molecules can be doped to assume an n- or p-type character. Thus, the $\pi$-conjugated molecules can act as semiconducting channels in molecular devices.

Using a combination of alkyl-chains and conjugated moieties, conceptual design of various molecular components, such as, dielectric, rectifiers, memory, resonant tunnel diodes (RTD), transistors etc., are schematically shown in Fig. 2. In these devices, highly doped Si (resistivity < 0.001 $\Omega$cm) is used so that it also acts as an electrode. For counter-electrodes, one can use liquid Hg-drop, thermally evaporated gold/aluminum pads, CP-AFM/STM tip or carbon nanotubes. It may be noted that the conduction through a molecule depends on the quality of the molecule–electrode interface. Often the metal atoms, particularly when the counter-electrode is prepared using thermal evaporation, diffuse through the monolayers and create an electrical short-circuit. Thus, in order to avoid the metal diffusion, it is essential that the metal atoms and surface group of the monolayer form a chemical bond, e.g. Al with COOH or OH groups, Ti with COOH$_2$, OH or CN groups, Au with SH group, etc. [38–45]. The overlayer formed due to the reaction between metal and surface group prevents the diffusion of metal atoms into the organic monolayer [45].

The concepts of various molecular test devices and the progress made so far in their realizations are briefly summarized below.

Fig. 1. Schematic depicting the formation of $\sigma$-bonds using s and p orbitals, and $\pi$-bond using p orbitals.

Fig. 2. Schematic representation of the concepts of various hybrid molecule/Si(n ++) test devices: (a) molecular dielectric using alkyl-chains, (b) molecular diodes using $\sigma$–$\pi$ molecules, (c) $\sigma$–$\pi$–$\sigma$ resonant tunnel diode and (d) molecular transistors. The $\sigma$ components are alkyl-chains of different lengths, and $\pi$ components are conjugated molecules.
2.1. Molecular dielectrics and wires

The dielectric property of the alkyl-chain monolayers has been well established [4]. The electrical measurements of the ordered alkyl-chains sandwiched between two electrodes, as shown in Fig. 2(a), have revealed that the current through alkyl-chains follows the usual distance-dependent exponential law predicted by the tunneling law: \( I = I_0 \exp(-qd) \), where \( d \) is the monolayer thickness and \( \beta \) is the distance decay rate. However, the reported value of \( \beta \) lies in a wide range 0.5–1 Å\(^{-1}\) [20]. The \( \beta \) value is related to the tunneling barrier height (\( \phi \)) at the molecule/ electrode interface and to the effective mass (\( m' \)) of carriers in the monolayer using the expression: \( \beta = \pi(\hbar m_0)^{1/2} \phi^{1/2} \), where \( m_0 \) is the rest mass of the electron and \( \phi = 4\pi(2m_{e0})^{1/2}/h \) (\( e \) is the electron charge and \( h \) is the Planck's constant) [44,46]. Thus, a wide variation in the \( \beta \) value is associated to different \( \phi \) values (2.5–4.5 eV), which arise due to variations in the quality of Si/molecule and molecule/counter-electrode interfaces. High values (4–4.5 eV) are generally reported when at least one interface is weak e.g. for physisorbed LB monolayers [47,48], monolayer mechanically contacted by conducting atomic force microscope tip [49,50] or counter-electrode (Al or Au) weakly coupled to monolayer [51,52]. Lower barrier heights (2.2–2.5 eV) have been obtained when both the interfaces are strong e.g. Au counter-electrode on SH-terminated monolayer of alkyl-chains grafted on native oxide of Si [44,53]. Similarly, the reported values of \( m' \) have been found to vary in a wide range 0.16 \( m_e \)–1 \( m_e \) (\( m_e \) is the mass of free electron). In order to understand the wide variation in \( m' \), investigations on the electron–molecule vibration coupling need to be carried out. Other effects that might influence the transport in an ordered monolayer include current-induced local heating in a molecular junction [54], dynamical charge fluctuations [55] and spin-polarized transport [56,57]. If the monolayer is disordered or contains defects, the electronic conductance through the monolayer can take place by other mechanisms, such as, tunneling, thermionic emission, Poole–Frankel emission and/or hopping conduction. One can identify the responsible mechanism by carrying out the temperature and bias dependences of the current density through monolayers, and the details of these mechanisms can be found in Ref. [2].

While alkyl-chains are proven to act as a dielectric, short oligomers of \( \pi \)-conjugated molecules, such as, di(phenylene-ethynylene)benzenethiolate [58,59], terthiophene [59], short conjugated oligomers [8–10,60,61], organometallic [62], porphyrin–oligomer [63], etc. are considered as the prototype molecular semiconducting wires. The \( J-V \) curves of such molecular wires are in general non-linear with steps (i.e. peaks in the first derivative), corresponding to resonant charge carrier transfer through the molecular orbitals of the molecules [64]. The measured conductance corresponds to the conductance through the molecules and the conductance of the molecule/electrode contact. Thus, the influence of the chemical link between the molecules and the electrode is of prime importance and requires further investigations using different sets of molecule/electrode combinations.

2.2. Molecular diodes

Based on Aviram–Ratner (AR) A–b–D concepts of molecular diode (as discussed in the introduction), several molecular rectifying diodes have been synthesized, e.g. hexacycloxyli- nium tricyanoquinodimethanide molecule (C\(_{15}\)H\(_{33}\)-Q–3CNQ) with donor and acceptor moieties linked by \( \sigma \)– or \( \pi \)-bridge [65–70]. Also, the molecule is \( \sigma \)-substituted by an alkyl-chain, which is essential to allow a monolayer formation by the Langmuir–Blodgett (LB) method. These molecular diodes exhibited rectification ratio (a ratio of current density at \(-1 \)V (in absolute value) and the current density at \(+1 \)V) up to \( 2 \times 10^4 \). However, in the case of C\(_{15}\)H\(_{33}\)-Q–3CNQ the AR model may not be applicable as it is a D–\( \pi \)-\( \pi \)-A molecule [68], and due to the \( \pi \)-bridge, the HOMO and LUMO may be more delocalized than expected in the AR model. Theoretical calculations show that the direction of easy current flow (i.e. rectification current) depends on: (i) the placement of the HOMO and LUMO relative to the Fermi levels of the metal electrodes before bias is applied and (ii) a shift induced in HOMO/LUMO by the applied bias. This situation is more complex than the AR mechanism and the electrical rectification can result from the asymmetric profile of the electrostatic potential across the molecule [71]. Thus, the rectification in the C\(_{15}\)H\(_{33}\)-Q–3CNQ molecule can be attributed to the asymmetry profile due to alkyl tail. Prediction of a symmetric \( J-V \) curve in this molecule without an alkyl-chain also suggests that asymmetric electrostatic potential is the cause for rectification in C\(_{15}\)H\(_{33}\)-Q–3CNQ molecule [72–75]. Based on the rectification due to asymmetric electrostatic potential profile in a molecular system, experimentally a simple molecular rectifier with only one donor group and an alkyl spacer chain [76], as schematically shown in Fig. 2(b), has been demonstrated. Such \( \sigma \)–\( \pi \) molecular rectifiers with \( \pi \)-groups, such as, phenyl, pyrene, thiophene, anthracene, quaterthiophene (4T), etc. coupled to alkyl-chains of different lengths have indeed been deposited on Si using a sequential self-assembly process. These \( \sigma \)–\( \pi \) rectifiers have exhibited rectification ratio up to 37. It has been further demonstrated that the rectification in such \( \sigma \)–\( \pi \) molecular diodes occurs due to resonance through the HOMO of the \( \pi \)-group [76]. More emphasis is thus required to design \( \sigma \)–\( \pi \) molecular diodes with different \( \pi \)-groups so that high rectification ratios are obtained.

2.3. Molecular memories

Molecular memories have been designed employing three different properties of the molecules, as discussed below

(i) Resistive memory: the resistive memory or switch is based on the electrical bistability (i.e. two different conduction states for same bias voltage) exhibited by the organic molecules. Electrical bistability has been reported in a number of molecules, such as, rotaxanes [77,78], catenates [79], stearic acid [80], eicosanoid acid [81] and phenylene-ethynylene oligomers [82–85]. In order to explain the observed switching behavior various proposals have been put forward. These include electrical charge transfer [86,87], molecular conformational change [83,85] and bond fluctuations between the molecule and their electrical contacts [88]. While these efforts have demonstrated the basic functionality of a resistive molecular switch, there are several open questions that need to be answered. (i) Can the structure of molecules exhibiting electrical bistability generalized? (ii) Will the current controversy on the origin of molecular switching be resolved? (iii) Can molecular switches be made compatible with the technologically important silicon substrates? Clearly, in-depth experiments would be needed in future to answer these questions.

(ii) Capacitive memory: in this case, one utilizes the different redox states of a molecule. The capacitive memory works on the principle of charging and discharging of the molecules into different chemically reduced or oxidized (redox) states [89–92]. Redox-active molecules, such as metalloocene, porphyrin and triple-decker sandwich coordination compounds attached on a silicon substrate have been found to act as charge storage molecular devices [90–92]. It has been demonstrated that porphyrins: (i) offer the possibility of multibit storage at relatively low potentials (below 1.6V); (ii)
can undergo trillions of write/read/erase cycles; (iii) exhibit charge retention times that are long enough (minutes) compared with those of semiconductor DRAM (tens of ms); and (iv) are extremely stable under harsh conditions (400°C-30 min) and therefore meet the processing and operating conditions required for the use in hybrid molecule/silicon devices [92].

(iii) Resonant tunnel diodes (RTD): RTD memory utilizes the negative differential resistance (NDR) behavior of molecules in their \( J-V \) characteristics. The architecture of the molecular RTD device, as shown in Fig. 2(c), is analogous to its solid-state counterpart [93]: a potential well separated from the electrodes by two tunnel barriers. Here alkyl-chains can act as tunnel barriers, while a π-moiety acts as the potential well. The advantages of RTD molecular memory compared to ‘resistive’ and ‘capacitive’ molecular memories are fast switching times and possible long-retention times. However, till date no success has been made in the \( \sigma-\pi-\sigma \) types of molecular RTDs. In literature, NDR behavior has been reported using STM measurements carried on a single molecule attached to Si [94] and this effect has been attributed to resonance through the molecular orbitals [95]. However, this interpretation subsequently has been ruled out both experimentally [96] and theoretically [97], indicating that RTD molecular device has not yet been demonstrated unambiguously. Thus, synthesis of new types of \( \sigma-\pi-\sigma \) molecules, suitable for grafting to Si, is required.

2.4. Molecular transistors

The concept of molecular transistor, as shown in Fig. 2(d), is analogous to the solid-state counterpart of the field-effect transistor, which is a three-terminal device [93]. The source (S) and drain (D) electrodes, separated by a distance \( L \), are deposited on semiconducting channel made from π-moieties. The alkyl-chains of length \( t \) act as gate dielectric (G). FETs are based on a gate field modulating the conductance of the semiconducting channel to turn the device “off” and “on.” Kagan et al. [98] have investigated the chemical and physical requirements necessary for a successful design and fabrication of molecular FETs. A theoretical analysis using electron tunnelling and device electrostatics place \( L > 2.5–3 \) nm and minimum gate dielectric thickness \( t = 1–15 \) for such devices [98]. However, till date no molecular-FET has been experimentally demonstrated. However, it has been independently demonstrated that (i) alkyl-chains work as good dielectric materials in FETs made using sexithiophene- or pentacene-based organic thin film transistors (OTFTs) [99,101] and (ii) OH-functionalized tetracene self-assembled monolayer indeed works as an active channel of the transistor [101]. However, in this case, a layer of aluminium oxide (\( \sim 5 \) nm) was utilized to act both as a dielectric layer and also as a primer for the assembly of the monolayer. Probably it is just a matter of time when true molecular transistors will be fabricated. One of the critical requirements for making molecular transistors is availability of π-molecules with exceptionally small (\( <0.5 \) eV) HOMO–LUMO gaps, which have now become synthetically achievable targets [102].

3. Hydrogen-terminated silicon surfaces

For electrochemical grafting, highly doped Si wafers (n-type on doping with P or As, and p-type doping with B) of resistivity \( <0.001 \) \( \Omega \) cm are used as working electrodes. Since Si wafers are always covered with native oxide, it is essential that this oxide layer is removed and a clean hydrogen-terminated surface is created. The hydrogen termination of Si surfaces is prepared either by reaction of a clean surface with hydrogen atoms in UHV or by chemical etching in aqueous fluoride. For electrochemical grafting experiments the chemical etching process is adopted. In literature, Si(111) and Si(100) are the two surfaces on which essentially all of the grafting has been carried out.

A simple wet chemical method for the preparation of atomically flat hydrogen-terminated Si(111) has been described by Chabal and his co-workers [103,104]. They found that the HF etching of Si(111) at pH 8–9 or 40% ammonium fluoride results in the formation of hydrogen-terminated Si(111) surfaces in which the Si–H bond is oriented normal to the surface as shown in Fig. 3. The observation of a single narrow line at 2083.7 cm\(^{-1}\) (the Si–H stretch) with p-polarized infrared light (i.e. the electric field component is perpendicular to the surface) and the absence of this vibration with s-polarized infrared light (i.e. the electric field component is in the plane of the surface) provided unambiguous proof of the orientation of the Si–H bond. STM image showed formation of atomically flat Si(111) surfaces: a 3-fold symmetric arrangement of silicon atoms, separated by 0.384 nm, each capped with a hydrogen atom [105,106].

Because of the anisotropic nature of the ammonium fluoride etching of silicon, it is not possible to produce atomically flat H–Si(100) surfaces by chemical etching. In fact, chemical etching of Si(100) surfaces tends to roughen the surface by exposing Si(111) facets leading ultimately to the formation of porous silicon [107]. Using 2% HF it is possible to produce relatively flat surfaces with small atomically resolved domains but the structure of hydrogenated surfaces produced in this way are not uniform and contain some SiH and SiH\(_3\) groups but are predominantly SiH\(_2\) [108]. Under UHV conditions it is possible to produce uniform H–Si(100) surfaces. For this the Si (100) surface is first heated in UHV to obtain a clean surface (i.e. the surface atoms are not chemically terminated but have so-called dangling bonds protruding into space) followed by exposure to hydrogen atoms. The hydrogen-terminated silicon surfaces are actually quite stable and can be handled in air for several minutes without oxidation [109].

4. Electrochemical grafting of organic molecules

The electrografting of organic molecules to Si surface is carried out using a three-electrode electrochemical setup, as schematically shown in Fig. 4. The current \( I \) flows between the working electrode (WE) and the counter-electrode (CE). The working electrode is the electrode on which the molecules are grafted, that is, H-terminated Si. The counter-electrode is usually a Pt wire. The potential \( V \) is measured between the reference electrode (RE) and the working electrode. No current passes through the reference electrode. Reference electrode is an electrode which has a stable and well-known electrode potential. The high stability of the electrode potential is usually reached by employing a redox system with constant (buffered or saturated) concentrations of each participants of the redox reaction. Commonly used reference electrode is standard hydrogen electrode (SHE), which is also known as “normal hydrogen electrode” (NHE). Other used reference electrodes are saturated calomel electrode (SCE) \( (E = 0.242 \) V with respect to the SHE), copper-copper(II) sulfate electrode \( (E = 0.314 \) V) and silver chloride electrode \( (E = 0.225 \) V saturated) [110,111]. The commonly used supporting electrolytes include tetrabutylammonium perchlorate (TBAP) or tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)) prepared in dry and deoxygenated dichloromethane (CH\(_2\)Cl\(_2\)) or acetonitrile (CH\(_3\)CN). To avoid oxidation of the H-terminated Si surface, the electrografting process is generally carried under...
inert ambient. The electrografting is usually carried out using either cyclic voltammetry (CV) (i.e. the working electrode potential is ramped linearly versus time) or constant applied potential mode.

Once the electrografting reaction has been achieved, it is essential to ascertain the presence of the organic layer on the Si surface. For this purpose, the electrografted Si is thoroughly rinsed ultrasonically, so that all physisorbed molecules are removed from the surface and only chemically bonded molecules remain on the surface. In order to prove the presence of the attached monolayer, a number of electrochemical and spectroscopic techniques are used. The characterization of organic monolayers typically involves a combination of multiple techniques, such as, ellipsometry, water contact angle measurement, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy, etc. For chemical analysis, FTIR is commonly used. The frequencies and intensities of the vibrational modes observed in FTIR provide detailed information about the nature of the chemical functional groups. The XPS technique provides excellent information about the elements and their oxidation states present in the monolayer. In addition, XPS allows determination of thickness of the grafted organic layers. Thickness of the organic layers can also be determined using ellipsometry. Contact angle measurements provide information on the surface group of the grafted organic layer [2]. The ordering of the monolayer can be assessed by imaging the morphology of the organic layers using AFM and STM. In order to measure the electronic transport of the grafted organic layers, counter-electrodes, such as, liquid Hg-drop, thermally evaporated gold pads, CP-AFM or STM tip or carbon nanotube, as shown in Fig. 2, are used to fabricate a metal/monolayer/Si(n++) structure.

4.1. Terminal vinyl (C≡C) as reactant

Alkene-1 and vinyl-terminated derivatives of molecules, for example, 5-(4-undecenyloxyphenyl)-10,15,20-triphenylporphyrin (TPP-C11), have been deposited on doped n-Si substrates by an electrochemical process via formation of Si–C bonds [112]. The molecular structure of TPP-C11 molecule is shown in Fig. 5(a). It consists of a vinyl (C≡C)-terminated 11-carbon atom alkyl-chain attached to the conjugated porphyrin ring. The monolayers of 1-undecene (C11) and TPP-C11 were deposited on H-terminated Si (111) by CV using a solution containing 1:1 (v/v) of 0.1 M TBAP supporting electrolyte and 1 mM C11 or TPP-C11 in dry CH2Cl2.

Typical CV scans recorded using TPP-C11+TBAP and, 1-undecene (C11)+TBAP solutions are shown in Fig. 5(b), which are nearly identical. It is seen that the presence of an irreversible oxidation peak at \(-0.3\) V, observed for the first scan, disappears rapidly as the number of scans increased and, eventually vanishes for 50th scan. However, no peak at \(-0.3\) V appeared when the CV was run using the TBAP solution alone. The fact that the voltammetric peak is irreversible, indicates that an irreversible reaction (i.e. the cleavage of vinyl-group) is associated with the electron transfer. Disappearing of the peak with increased cycles is indicative of the blocking of the surface by the molecules (TPP-C11 or C11), which become attached to the H-terminated Si surface.

The proposed electrochemical reaction of the grafting of molecules is shown in Fig. 6, which takes place in several steps. In the first step, application of a negative potential to the working electrode (H-terminated Si) makes Si radical atoms at the surface by releasing hydrogen hydride (Fig. 6(a)). These anions on transferring from electrode to the electrolyte solution generate
the current. The Si-radicals, in the second step, react with vinyl-group (C=C) of the TPP-C11 or C11 molecules to form Si–C bond and a new carbon radical is formed. The carbon radical then reacts with hydrogen of the surface, leading to the formation of Si radical (Fig. 6(b)). This mechanism is similar to that described for the thermal grafting of alkene monolayers on silicon [30–34]. The irreversible oxidation peak at −0.3 V could be attributed to the oxidation of the hydride obtained in the first step (Fig. 6(c)). As the numbers of CV scans are increased, this peak is diminished owing to the non-availability of the silicon radicals at the surface. A very low current at 50th scan indicates that the TPP-C11 or C11 monolayer has fully covered the Si substrate. Here, it may be noted that on application of negative potential to H-terminated Si, alternatively, can lead to the formation of Si-anion and hydrogen radical. However, this may not have any major influence on the electrografting process presented in Fig. 6, instead Si-radicals Si-anions will react with vinyl-group (C=C) to form Si–C bond.

The thickness determined from the ellipsometry for grafted TPP-C11 and C11 layers were, respectively, 2.3 and 1.1 nm. These values are smaller than the theoretical lengths of the TPP-C11 (2.84 nm) and C11 molecules (1.34 nm), indicating that the grafted molecules are tilted from the substrate normal by ∼30°. The FTIR spectra recorded for the TPP-C11 and C11 monolayers are shown in Fig. 7. It is seen that TPP-C11 monolayer exhibits a clear N–H stretching frequency at 3305 cm⁻¹ [113], confirming the presence of porphyrin group in the monolayer. For both the monolayers, observation of symmetric (νₛ) and asymmetric (νₐ) stretching modes of CH₂ group at 2881 and 2935 cm⁻¹ indicate presence of disordered alkyl-chains [2].

As electrochemistry is used to graft organic molecules to the Si surface, it can also be used to characterize the grafted monolayer if the molecules are electroactive. In this respect, porphyrin group is a good electroactive group. The recorded CV using monolayer (surface area = 0.025 cm²) as working electrode and 0.1 M TBAP prepared in dry CH₂Cl₂ as electrolyte is shown in Fig. 8. The CV was recorded at a fast scan, i.e. 100 V/s. The presence of reversible oxidation (Eox) peak at +0.6 V indicates presence of the porphyrin moiety. This peak however is faint on a large background current, which could be due to the charging effect as the C11 chain is insulating in nature. It may be noted that cathodic and anodic peaks are located nearly at the same potential, indicating that the species undergoing the redox process do not diffuse to and from the electrode, and are, therefore, chemically bonded to the surface.

From the oxidation peak, it is possible to estimate the number of molecules grafted on the surface [114]. The enlarged plot of the oxidation peak, after the background current subtraction and potential scale converted to time scale, is shown in the inset of Fig. 8. The net charge transferred during the oxidation process, calculated from the area under the curve, is 4.2 × 10⁸ C, which corresponds to a surface coverage of 1.05 × 10¹⁴ molecules/cm². This indicates that the surface covered by the porphyrin ring is 95 Å². It has been shown that in a monolayer, the area covered by porphyrin rings arranged in face-on and edge-on orientations are 160 and 70 Å², respectively [115]. Thus, a surface area of 95 Å² indicates that the porphyrin rings are tilted, which is due to the

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**Fig. 6.** Schematic depicting the two-step electrografting process of C11 or TPP-C11 monolayer on Si via formation of Si–C bonds [112].

**Fig. 7.** FTIR spectra recorded in the range of N–H and CH₂ modes for 1-undecene (C11) and TPP-C11 monolayers [112].

**Fig. 8.** Fast scan CV recorded for the electrografted TPP-C11 monolayer at a scan rate of 100 V/s. The inset shows the enlarged plot of the oxidation peak with potential scale converted to time scale [112].
fact that alkyl-chains are tilted by 30° from the substrate normal. A densely packed monolayer, as shown in Fig. 9, has also been observed by atomic force microscopy.

To measure $J-V$ characteristics of the monolayers, a metal/monolayer/Si(n+) structure was completed by using a very small drop of liquid mercury as a counter-electrode. Typical $J-V$ plots recorded for TPP-C11 and C11 monolayers are shown in Fig. 10. $J-V$'s are slightly asymmetric, which is attributed to the different work functions of the electrodes, i.e. Si (4.1 eV) and Hg (4.5 eV) [42]. It may be noted that the $J-V$'s of C11 monolayer do not exhibit any hysteresis; whereas for TPP-C11 monolayer a pronounced hysteresis is observed, indicating a predominant role played by porphyrin ring. In the positive bias scan, i.e. from 0 to +0.8 V, current jumps by an order of magnitude at +0.6 V. However, on the reverse scan (+0.8–0 V) the current does not retrace the curve, and remains at higher values. Thus, the $J-V$ in the voltage range −0.6 V to +0.6 V exhibits two conduction states: one with low current (OFF) and other with higher current (ON).

The electrical bistable behavior of TPP-C11 molecules has also been demonstrated for molecular memory effects. The memory phenomenon in electrically bistable devices is best demonstrated under ‘write–read–erase–read’ operations. In such a sequence of cycles, the low-conducting (‘write’) and high-conducting (‘erase’) states are induced repeatedly and the states are monitored (‘read’) in between. In the present case, 0 and +0.8 V pulses for 10 s were applied, respectively, to ‘write’ the low-conducting state and ‘erase’ the high-conducting one. These states were continuously monitored (‘read’) by measuring the device current (at 0.5 V), for more than 50 reading operations, and a section of ‘write–read–erase–read’ operation recorded for such a device is shown in Fig. 11. The magnitude of the device current under the ‘read’ voltage pulse is ~130% higher for high-conducting state (‘erase’) as compared to that for low-conducting state (‘write’). The observed change in current for these devices is far superior than that reported recently (~30%) for memory devices fabricated using oligo(phenylene–ethynylene) molecules [80].

Electrografting of other vinyl-group-terminated molecules, such as, $N$-succinimidyl acrylate (NSA), on Si substrates has also been demonstrated in literature [116]. The NSA-modified Si electrodes were immersed in isopropylamine in order to transform the grafted chains to the thermoresponsive poly($N$-isopropyl acrylamide), which are promising for microfluidics application. However, the electronic transport properties of NSA layers have not been investigated.

Fig. 9. 500 nm x 500 nm AFM image and height profile of the TPP-C11 monolayer electrografted on Si(111). The average surface roughness is <1 nm.
4.2. Terminal ethynyl (C≡C) as reactant

Buriak et al. [117] have reported a cathodic electrografting process that directly attaches alkynes to the porous Si surface. The electrografting was carried out using a solution of alkylene mixed with 0.1 M tetrabutylammoniumhexafluorophosphate electrolyte in CH$_2$Cl$_2$. A current of 10 mA is then applied typically for 120 s. Later, the sample is gently washed with CH$_2$Cl$_2$/pentane and dried under a nitrogen stream. FTIR analysis of electrografted phenylacetylene reveals Si–H$_x$ stretches, which are broadened and decreased in integrated intensity compared to unmodified porous silicon. The absence of a ν (≡CH) mode around 3300 cm$^{-1}$ and an observed sharp silylated alkylene ν(C≡C) at 2159 cm$^{-1}$ is consistent with a Si–alkynyl surface and not simple physisorption. It has been proposed that the cathodic electrografting reaction of alkynes proceeds via a silyl anion intermediate formed by reduction of surface Si–H bonds in a space charge layer [118,119], as shown in Fig. 12. The subsequent in situ generation of a carbanion from deprotonation of the weakly acidic alkylene leads directly to nucleophilic Si–Si bond attack [120,121].

Cathodic electrografting of hexynoic acid, CH≡C(CH$_2$)$_3$COOH, to silicon nanowire surfaces has also been reported [122]. The electrografting mechanism in this case is expected to be similar to that presented in Fig. 12. Carboxylic acid-terminated (–COOH) alkane monolayers have also been covalently anchored on Si by cathodic electrografting with a terminal alkynyl as reactant [123,124]. For comparison, monolayers have also been grafted using heat- or light-promoted chemical reactions. It has been demonstrated that cathodic electrografting produces the best-quality monolayers. Moreover, it is worth to recall that during cathodic electrografting silicon is normally protected against oxide (SiO$_2$) growth, which is instead enhanced in photochemical and mostly in thermal processes.

Covalent bonding of alkynes to Si using anodic electrografting has also been reported [117]. The anodic electrografted surfaces show a complete reduction of all unsaturated bonds. The results of FTIR revealed that a surface-initiated cationic hydrosilylation reaction is responsible for the Si–C bond formation in anodic electrografting. Positive charges are stabilized in the depletion layer at the semiconductor–electrolyte interface, which are attacked by alkynyl monomers. This can then be the starting point for a successive hydrosilylation or cationic polymerization reaction. It may be noted here that anodisation of silicon in the presence of water unavoidably leads to the formation of a layer of silicon dioxide, or, in the case of fluoride electrolytes, to the dissolution of silicon [125]. If an organic modification of Si is desired by anodic electrografting, it is essential that the process must be carried out under rigorously anhydrous and oxygen-free conditions. Thus, due to potential risk of the oxidation of Si, anodic electrografting is not a very suitable process for making monolayers for hybrid nanoelectronics.

4.3. Terminal halide as reactant

The electrochemical grafting of molecules on H-terminated Si surfaces has also been reported using reductive electrolysis of alkyl halides mainly iodides [126]. The reductions have been performed in 0.2–0.4 M solutions of the organo halides in dry, deoxygenated acetonitrile or mixtures of acetonitrile and tetrahydrofuran containing 0.2 M LiBF$_4$. Alkyl/benzyl bromides, which do not graft, were converted into the iodides in situ by replacing LiBF$_4$ with Lil as the electrolyte. Passing a cathodic current (2 ± 10 mA cm$^{-2}$) for short periods of time (30 ± 120 s) resulted in a high coverage of the silicon surface with organic species, as determined by FTIR i.e. appearance of the Si–C stretching mode in the infrared spectrum at 766 cm$^{-1}$ [127]. Also, the integrated intensity of the Si–H stretching vibrations, located at approximately 2120 cm$^{-1}$, decrease substantially with increasing alkyl coverage. This suggests that the reduction produces alkyl or benzyl radical species that then react with the hydrogen-terminated surface to form radical silicon. The electrografting process may occur by two different routes as schematically shown in Fig. 13. In the first route, the reduction process produces alkyl radical, which then directly reacts to the surface silicon radical, Fig. 13(a). The second route would be through the reduction of the silicon radical to the anion followed by nucleophilic attack on the organohalide, Fig. 13(b). The grafted alkyl layers were found to be stable in boiling chloroform, aqueous ethanolic HF and 0.1 M KOH as demonstrated by the difference between contact angles measured on grafted and nongrafted surfaces, respectively.

Monolayers of 2,2′-bipyridines have been prepared by cathodic electrografting on H-terminated n- and p-Si (10 0) surfaces using a solution of 5-bromomethyl-2,2′-bipyridine [128]. The monolayers of 2,2′-bipyridines were also prepared by two other methods namely, photochemical reaction of 5-vinyl-2,2′-
4.4. Tetraalkylammonium salts

The cathodic alkylation of H-terminated silicon surfaces has been reported using 0.1 M ammonium (or phosphonium/pyridinium) salt solution in dichloromethane by passing a cathodic current (typically 10 mA cm\(^{-2}\)) [129]. AFM scribing of covalently modified surfaces has been used to provide measurements of the thickness of the graft layer [130]. First, the surface was imaged at contact mode with minimized force (less than 5 nN). Then, the AFM tip was pushed to scratch the surface with a force of 200 nN in a zoomed area. The corresponding control experiment on an H-terminated Si surface is also carried out to ensure that this force does not significantly damage the underlying silicon. Finally, the area was imaged with minimized force, and from the height of the trench thickness of the grafted layer is estimated. It has been shown that the trench was 1.4 nm deep, which corresponds to the approximate length of the dodecyl group indicating the grafting of the molecule. The two mechanistic pathways by which the alkylation reaction could proceed are shown in Fig. 14. The mechanism starts with the reduction of the tetraalkylammonium NR4 cation, which decomposes into R radical and NR3. Subsequently, the R radicals lead to radical-based surface alkylation. In a first pathway the silicon radical reacts with another R radical, Fig. 14(a). In the second possible route, formation of silyl anions under the cathodic conditions on the surface could be followed by nucleophilic attack on the trialkylammonium cation, Fig. 14(b), which is similar to the halides reaction (see Fig. 13).

![Fig. 14. The two possible mechanistic pathways for alkylation of Si surfaces (after Ref. [129]).](image)

4.5. Diazonium and iodonium salts

The grafting of organic molecules to Si surface using electrochemical reduction of diazonium is a very simple process [131–133]. A diazonium salt (BF\(_4^-\)N\(_2\)ArR, where Ar and R represent benzene ring and a functional group, respectively) of typical concentration 1–10 mM is dissolved in an aprotic medium with a supporting electrolyte (ACN+0.1 M NBu\(_4\)BF\(_4\)) or in acidic aqueous medium (for example H\(_2\)SO\(_4\) 0.1 M). The diazonium salt is then reduced using H-terminated Si as a cathode, which results in the grafting of ArR molecules to Si surface. The grafting can be carried out in CV mode or by applying a constant potential (determined from the voltammetric reduction peak of the diazonium) for a variable period of time, typically few tens of seconds. The H-terminated Si is then rinsed in an ultrasonic bath in order to remove physisorbed molecules. This approach, apart from Si, has been used to graft molecules on different substrates, such as, carbon (GC, HOPG, pyrolized photoresists, pyrolized Teflon, carbon fibers, carbon blacks, carbon nanotubes, diamond, etc.) [134–142], semiconductors (GaAs) [143] and metals (Au, Cu, Fe, Ni, Pt, Pd, etc.) [144–146].

Here, we describe the electrografting of a specially synthesized \(\sigma-\pi-\sigma\) molecule, that is, \(N-(2-(4-diazoniophenyl)ethyl)-N'-'-hexylnaphthalene-1,8:4,5-tetracarboxydiimide tetrafluoroborate\) (DHTT) to the Si using its diazonium salt. The molecular structure of this molecule is shown in Fig. 15 and the length of this molecule is 2.06 nm. Typical cyclic voltammogram of this diazonium salt recorded using H-terminated Si(111) as working electrode and ACN+0.1 M TBAPF\(_6\) as electrolyte is shown in Fig. 16. The CV shows an irreversible peak at \(-0.66 V/Ag,Ag^+\), which shifts continuously to higher values with increasing cycles (e.g. \(-0.69 V\) for fourth cycle). The presence of an irreversible reaction indicates cleavage of dinitrogen, and hence a covalent reaction between H-terminated Si and the molecule through an electron transfer mechanism. If there would have been formation of only a dense and impervious monolayer then one had expected the disappearance of the diazonium reduction peak during second cycle, as has been reported for 4-nitrobenzene diazonium tetrafluoroborate [132]. Disappearing of the diazonium reduction peak during second cycle is indicative of the blocking of the H-terminated Si surface with covalently grafted monolayer. However, in the present case, the diazonium reduction peak does not vanish with successive cycles and, in fact, shifts to higher potentials. This indicates that the density of grafted molecules is not high enough in the first cycle (i.e. making free H–Si surface available), which during subsequent cycles allows further electron transfer even if the diazonium salt reduces on the already grafted molecules. This process, therefore, results in the formation of highly branched or reticulated multilayer.

Let us now discuss possible reduction mechanisms of diazonium salts at silicon electrode that lead to the formation of the mono- or multilayers [135]. The monolayer formation process is schematically demonstrated in Fig. 17(a). The phenyl radical is produced directly “on the electrode” through an electron transfer...
concerted with the cleavage of dinitrogen to give the phenyl radical. The aryl radical then causes abstraction of the hydrogen from the Si surface and moves away from the surface. The silyl radical then reacts with a second aryl radical, which results in the formation of a $\equiv$Si–ArR bond, and hence formation of the first monolayer. However, other aryl radical might attack the grafted aromatic group of the monolayer, as schematically shown in Fig. 17(b), to form a bilayer. Repetition of this reaction would lead to the formation of the multilayers [147]. Since the attachment of subsequent molecules occurs randomly, the multilayers grown in this way are expected to be inhomogeneous in thickness.

In order to ascertain the presence of mono- or multilayer on the Si after the diazonium reduction process, the electrochemistry was carried out after thorough ultrasonic rinsing. Using grafted layer as the working electrode, the CV was recorded in a solution containing only the solvent and supporting electrolyte (CH$_2$Cl$_2$+0.1 M TBAFP$_6$). As shown in Fig. 18, CV exhibits two reversible peaks—which are the signature of the molecules—with cathodic and anodic peaks being nearly at the same potential, confirming grafting of the molecules to the Si surface. Similarly, other electrochemically active reporting groups, such as, 4-bromophenyl, 4-cyanophenyl, 4-phenylazophenyl, naphthyl, anthraquinone, 4-benzoxyphenyl, have been used to demonstrate the presence of the grafted organic layer [135]. The FTIR data too has confirmed the presence of the molecules on the surface. FTIR also allows the demonstration of the fact that the diazonium salts are not merely adsorbed on the surface through the absence of the $^+$N$_2$ stretching, which should be located in the 2300–2130 cm$^{-1}$.

Fig. 16. CV recorded using diazonium salt of $\sigma-\sigma-\sigma$ molecules using H-terminated Si (111) as working electrode. Note the shift in the irreversible peak to higher potentials with increasing number of scans.

Fig. 17. The possible formation mechanisms of (a) monolayer and (b) multilayers on H-terminated Si surfaces using the electrochemical reduction of the diazonium salts.

Fig. 18. CV recorded for the electrografted organic layers on Si grafted using the reduction of diazonium salt.
region [138,148]. Further evidence indicating the formation of a covalent bond between the substrate and the organic layer comes from the strength of this bond, which resists ultrasonic cleaning in a variety of solvents (ACN, dimethyformamide, dimethyl sulfoxide, benzene, benzonitrile, acetone, methanol, ethanol, dichloromethane and chloroform for 15 min each) [134]. On Si, 4-bromophenyl layers resisted 40% HF for 2 min and 10 M NH₄F for 1 min [131–133].

In order to measure, the electronic transport through the layers of the \( \sigma-\pi-\sigma \) molecules, an In–Ga eutectic liquid drop was kept on the top of the layer. Upon varying the potential between the In–Ga on top of the monolayer and Si at the bottom, the \( J-V \) s were recorded. It may be noted that the samples prepared using \( \leq 3 \) cycles exhibited electrical shorts, indicating the formation of inhomogeneous film. The layers prepared using 4 or more cycles were thick and many of them did not exhibit electrical shorts. However, as expected from the formation mechanism of the multilayer, these samples exhibited rough and non-uniform morphology. The average thickness of a sample prepared using 6 CV runs, as measured using ellipsometry, was \( \sim 12 \) nm, indicating more than 6 layers of the \( \sigma-\pi-\sigma \) molecules. Also, the measured water contact angle was \( \sim 80^\circ \), which indicated that the alkyl-chains are disordered and/or some of the \( \pi \)-moieties of the molecules are exposed to the surface. For CH₃-terminated surface of an ordered monolayer, the expected water contact angle is \( \sim 110^\circ \) [2]. Therefore, making monolayers of \( \sigma-\pi-\sigma \) molecules on Si using diazonium salts does not appear to be very easy. A typical \( J-V \) recorded for a 12 nm thick \( \sigma-\pi-\sigma \) multilayer is shown in Fig. 19. The \( J-V \) exhibits very small NDR effects in both positive and negative bias with peaks occurring at \( +1.2 \) and \( -1.6 \) V, respectively. Also the hysteresis is very little. The observation of a first attached molecule than far from this molecule. This could be due to stacking interactions of the aromatic molecules. Other groups obtained different morphologies and thickness of the samples prepared using reduction of diazonium salts. For example, 4-diethylaminophenyl groups grafted on HOPG surfaces revealed a continuous layer with protruding features having a height of nearly 8 nm [137]. Very thick layers (up to a thickness of 100 nm) of 4-nitrophenyl groups were obtained by scanning the potential for 20 cycles. Summing up, using diazonium salts, making monolayers is not very easy, as the multilayer formation takes place quickly. However, in a recent paper, it has been speculated that multilayer formation can be prevented if one hinders certain positions of the diazonium ion [149]. It has been demonstrated that if methyl group occupies 2- and 6-positions of diazonium salt then further grafting does not occur and results in the formation of a monolayer.

Electroreduction of diazonium salts has also been used as a mask-free technique to pattern homogeneous Si electrodes with local doping [150,151]. In this case, silicon substrate is locally doped in a desired pattern. It has been demonstrated that the underlying doping directs the electrografting of polymer film preferentially over the doped areas of the substrate. However, this patterning process is not suitable for hybrid nanoelectronics because of the following two reasons: (i) the grown film is usually quite thick and (ii) due to presence of intrinsic silicon (high resistivity), the measurement of the transport properties of the electrografted layer is not easy.

An electrografting method of forming covalent bonds directly to silicon hydride has also been demonstrated with the use of iodonium salt precursors [152]. Grafting on H-terminated Si surface has been accomplished by applying a negative bias of 2 V. Several molecules ranging from electron-deficient to electron-rich have been electrografted in this fashion. It has been shown that the electron-rich iodonium salts assemble as thicker films as compared to the electron-deficient iodonium salts. However, the understanding of this trend requires more experiments. The proposed mechanism of electrografting is analogous to the attachment of diazonium salts to hydride-terminated silicon surfaces, as discussed in Fig. 17. In the first step of the reaction mechanism, an electron is transferred from the surface of the silicon to the iodonium salt. A cleavage of the carbon iodine bond would result in a radical and iodobenzene. The radical can then be combined with the surface forming a Si-C bond.

4.6. Silanes

The electrochemical grafting of organic molecules on Si described in previous sections has been via the formation of Si–C bonds between Si and organic molecule. It has also been demonstrated that electrochemical process allows grafting of silane molecules on Si via formation of Si–Si bonds [153]. The octyltrichlorosilane (OTS) monolayer on H-terminated Si was
deposited in the CV mode under high-purity argon gas. CV was carried out using a solution containing 1:1 (v/v) of 0.1 M TBAP supporting electrolyte and 5 mM OTS in dry methanol. Control experiments were also carried out using TBAP solution alone.

Representative CV's recorded using OTS+TBAP and TBAP solutions alone are shown in Fig. 20. The variations in the value of current at −1 V (measured from data of Fig. 21) with number of scans are plotted in Fig. 21. It is seen that for TBAP solution the current is very small (∼10⁻⁶ A) and is nearly independent of the number of scans. On the other hand, for OTS+TBAP solution the current is very high (10⁻³ A) for scan 1, which decreases exponentially to ∼10⁻⁵ A for scan 30 (a decrease of nearly two orders in magnitude). Since TBAP is the supporting electrolyte, a very low current implies that there is no chemical reaction between the H-terminated Si working electrode and TBAP molecules, and, therefore, no electrochemical grafting of TBAP molecules takes place. On the other hand, a very high current for OTS+TBAP solution suggests that an electrochemical reaction takes place between H-terminated Si working electrode and OTS molecule. A possible electrochemical reaction, taking place in two steps, is shown in Fig. 22. In the first step, application of a negative potential to the working electrode makes “nucleophilic Si” atoms at the surface by releasing hydrogen-free radicals. These nucleophilic Si atoms, in the second step, then can react with “electrophilic Si” atoms of OTS molecule to form Si–Si bond, and in the process chloride ions are released [153].

The OTS/Si interface was examined by recording the XPS spectra. The Si-2p spectrum, as shown in Fig. 23, exhibited the presence of a single peak at ∼99 eV (Si–Si bonding) [154]. From these data though it is difficult to distinguish the Si–Si bonding of Si/OTS from that of the Si substrate itself; the absence of a peak at 103 eV expected for oxide indicates that SiOₓ layer does not exist between Si and OTS monolayer. In addition, no peaks corresponding to the Cl (expected in the event of unreacted OTS molecules) were observed. Thus, XPS data support formation of Si–Si bonds between Si and OTS, as depicted in Fig. 22. As the OTS gets electrochemically grafted on the H-terminated Si surface, the substrate area to accomplish the reaction proposed in Fig. 22 becomes lesser, and hence the current decreases with increasing the number of scans. Thus, decrease in current gives the percentage of monolayer coverage, which is expressed by coverage (%) = 100(1–In/I₀), where I₀ and In are the current values at the beginning of the first scan and at the end of an nth scan. The coverage (%) as a function of the number of CV scans is shown in the inset of Fig. 21. It is found that the monolayer coverage increases exponentially with the number of scans and the coverage of ∼97% is attained at the end of the 30th scan. In order to see the actual coverage of the OTS monolayer, the AFM images and the line-height profiles were recorded as a function of CV steps, is shown in Fig. 22. In the first step, application of a negative potential to the working electrode makes “nucleophilic Si” atoms at the surface by releasing hydrogen-free radicals. These nucleophilic Si atoms, in the second step, then can react with “electrophilic Si” atoms of OTS molecule to form Si–Si bond, and in the process chloride ions are released [153].

![Fig. 20. Cyclic voltammograms recorded using TBAP+OTS electrolyte solution in the potential range between 0 and −1 V at a scan rate of 0.05 V s⁻¹ for different numbers of scans. H-terminated Si was used as a working electrode. Inset shows the CVs using TRAP solution [153].](image1)

![Fig. 21. Variation of current at −1 V as a function of the number of CV scans. Inset shows coverage (%) of the OTS monolayer on H-terminated Si as a function of the number of CV scans [153].](image2)

![Fig. 22. Schematic showing two-step electrografting process of OTS (R represents the CH₃ group) monolayer on Si via formation of Si–Si bonds [153].](image3)

![Fig. 23. Si-2p XPS spectrum recorded for the electrografted OTS monolayer on Si.](image4)
scan, the results are shown in Fig. 24. It is evident that the OTS monolayer gets grafted in the form of islands and the coverage increases with increasing the number of scans. Almost full coverage is obtained after scan 30, confirming the results obtained from the CV data. The average height of the islands, measured from the line-height profile of AFM images of a partially covered monolayer, was found to be \( \sim 1.3 \text{ nm} \). This height is nearly equal to the thickness (\( \sim 1.32 \text{ nm} \)) of a fully covered monolayer (as measured by ellipsometry) and is close to the theoretical length of the OTS molecule (i.e., 1.36 nm). After scan 30, the average roughness of the sample is \(<0.5 \text{ nm}\), which supports the electrochemical grafting of OTS monolayer and not that of a multilayer. Thus, the electrografting of monolayer in the present case takes place via 2-dimensional nucleation and growth mode.

The electrical properties of Al/OTS/Si\(^{(n^{++})}\) structures are presented in Fig. 25. Since Si\(^{(n^{++})}\) is heavily doped, Al/OTS/Si\(^{(n^{++})}\) structures can be considered as a metal/dielectric/metal capacitor. The leakage current through the OTS monolayer, as shown in Fig. 25 is \( \sim 10^{-4} \text{ A/cm}^2 \) at 1 V. This value is slightly lower than that of the OTS monolayer deposited on SiO\(_2\)/Si by silanization [2], despite the fact that the native oxide layer is absent in the present case.

Impedance spectroscopy is a powerful tool that can distinguish between different contributions to electrical conduction in

![Fig. 24. 1000 nm x 1000 nm AFM images and height profiles (across the white lines drawn in the AFM images) of electrochemically grafted OTS on H-terminated Si after different number of CV scans: (a) 1, (b) 10, (c) 20 and (d) 30.](image-url)
The physically insignificant values obtained for $Z$ measurement of real (exits at the interface or not. Impedance spectroscopy involves information on it, apart from the OTS monolayer a silicon oxide impedance spectroscopy it is possible to obtain an independent $k$. The solid line is a fit to data using a model of 600 Hz to 1 MHz with a bias of 1 V. The results have been plotted as points at high $Z$. The implicit parameter in this curve, and low frequency corresponds to points at high $Z$. The data have been analyzed using the equivalent circuit shown in the inset (see text) [153].

5. Electrochemical printing of monolayers

In the previous section, it has been demonstrated that the mono- and multilayers of various functional organic molecules can be grafted on Si substrates using electrochemical processes. However, to develop hybrid devices, it is essential that the grafted monolayers should be patterned in spatially defined features with a control down to the nanoscale so that molecular devices can be integrated with existing electronic structures. The issue of integration has been addressed in literature and various methods to pattern monolayers on the nanoscale, such as, nanoshaving and nanografting [156–159], dip pen nanolithography (DPN) [160–166], soft lithography [167–171], photolithography [172, 173] and electrochemical printing and lithography [174–179], have been invented. Here, we briefly review the efforts made on electrochemical nanowriting, nanolithography and microlithography of organic monolayers.

5.1. Nanowriting

Electrochemical nanowriting is very similar to the DPN. DPN is a scanning probe nanopatterning technique in which an AFM tip is used to deliver molecules to a surface via a solvent meniscus, which naturally forms in the ambient atmosphere [160–166]. This direct-write technique offers high-resolution patterning capabilities for a number of molecular and biomolecular ‘inks’ on a variety of substrates, such as, metals, semiconductors and monolayer functionalized surfaces. In order to create stable nanostructures, it is beneficial to use molecules that self-assemble to the substrate via chemisorption or electrostatic interactions. For example, when alkanethiols are patterned on a gold substrate, a monolayer is formed in which the thiol headgroups form relatively strong bonds to the gold and the alkane chains extend roughly perpendicular to the surface. Creating nanostructures using DPN is a single-step process and does not require the use of resists. Using DPN it is possible to achieve ultra-high resolution features with line-widths as small as 10–15 nm with a spatial resolution of 5 nm.

The concept of the electrochemical nanowriting is shown in Fig. 27. Here, under an applied potential, molecules can be directly interfaced with silicon through a covalent bond [174]. It has been demonstrated that alkyn electrografting reaction is mediated on the nanoscale by a CP-AFM. The alkyn molecules are loaded to the Pt-coated AFM tip by dipping it into liquid alkyn spread on the native oxide surface of Si (1 0 0) wafer. The Pt-coated AFM tip is biased (+) and the H-terminated Si surface is biased (−) to drive the cationic electrografting reaction under ambient conditions. As the tip moves across the Si surface, lines of the electrografted alkyn are drawn. Lines of monolayer having widths of 40 nm were produced reproducibly by this method [174]. The height of the drawn monolayer, as expected, was found to be nearly equal to the molecule length. The close proximity of the tip to the silicon surfaces enables the reaction to proceed in absence of electrolyte. In addition, application of a forward bias during the reaction renders the surface less sensitive to oxidation. The resulting patterned monolayers were very stable in air and basic aqueous solution. The proposed mechanisms of electrochemical nanowriting are as follows. The application of a negative bias to the silicon surface is expected to render the SiH groups more hydridic or progress further to silyl anions. Reaction of the forward-biased
SiH groups with the relatively acidic alkyne (pK_a ~ 25–26) could proceed via direct evolution of H_2 and formation of the alkyne termination in a concerted fashion. Alternatively, in situ generation of silyl anions could deprotonate the alkyne, leading to the alkynyl carbanion that then adds across weak silicon–silicon bonds to yield the final alkyne termination (similar to that presented in Fig. 12) [119]. It may be noted that so far only alkynes have been used for nanowriting, however other electrografting processes described in Section 4, can in principle be used for the nanowriting of organic molecules on Si substrates.

The advantages of electrochemical nanowriting are as follows. (i) The interfacial characteristics of the surfaces can be manipulated with extreme precision, allowing for exact and exquisite tailoring and hence writing of defined arrays. (ii) Because the same device is used to image and write a pattern, patterns of multiple molecular inks can be formed or aligned on the same substrate. (iii) The applied cathodic bias to the H-terminated surface during the electrografting reaction prevents oxidation of the Si surface. It has been shown that oxidation does not occur on HSi(100) with applied voltages of up to 10 V in ambient air, indicating that cathodic electrochemical nanowriting could be carried out in air [180].

5.2. Nanolithography

The lateral patterning of an organized monolayer deposited on Si by self-assembly or electrografting processes can be carried out using electrochemical or constructive nanolithography [175–179]. The various steps involved in this new approach of nanofabrication are schematically shown in Fig. 28. This constructive nanolithography works via site-selected nanoelectrochemical surface transformations carried out with the assistance of a properly biased CP-AFM tip that “inscribes” the desired lateral distribution of chemically active sites. This is schematically depicted in Fig. 28 by inscription of Y group (e.g. COOH) on the outer surface of a highly ordered monolayer terminated with X group (e.g. CH_3). This process thus creates a predefined monolayer template pattern with nanometer size features, which can guide the subsequent surface self-assembly of various organic monolayers e.g. silane (Fig. 28(c)) and inorganic species e.g. gold nanoparticles (Fig. 28(d)). The term “constructive” is used to emphasize the additive nature of the development process of the initial surface-composed chemical information, which is a characteristic of this bottom-up approach. This is in contrast to the usual downward transfer of the pattern produced in a resist layer, via destructive etching of the underlying substrate itself. In constructive nanolithography, the initial monolayer template is retained as part of the final fabricated structure, whereas the organic resist layer in top-down lithographic processes serves as a removable etching barrier.

The basic feasibility of the constructive nanolithography was demonstrated for the first time in the fabrication of spatially defined submicrometer lateral size monolayer structures of n-octadecyltrichlorosilane (ODTS, CH_3–(CH_2)_{17}–SiCl_3) [175]. For this purpose, first a densely packed, highly ordered 18-nondacetylchlorosilane (NTS, CH_2–CH–(CH_2)_{17}–SiCl_3)
monolayer template was self-assembled on a conducting p-type silicon wafer. The patterned monolayer template was then produced by tip-induced local electro-oxidation of the surface-exposed vinyl-group. Finally, this template was subjected to the self-assembly of OTDS, which takes place only at the oxidized vinyl-group sites leading to a patterned ODTS monolayer.

Several experiments have demonstrated that the constructive nanolithography is a generic approach to create defined patterns of diverse organic, metal, and semiconductor nanoentities [176, 177]. Starting with an inert CH₃-terminated silane monolayer on Si (ODTS/silicon), the CH₃ group is locally electrooxidized using an electrically biased AFM tip in the desired pattern. This is followed by the selective self-assembly of a vinyl-terminated silane (NTSox) overlayer. The vinyl-group then can be subjected to (i) photoreaction with H₂S in the gas phase to obtain a thiol-top-functionalized silane monolayer (TFSM) or (ii) chemical oxidation using aqueous (K₂MnO₄+KIO₄) to obtain a COOH-terminated (NTSox) bilayer template. Site-defined surface self-assembly of metallic silver, cadmium sulfide, or a third organic monolayer can, finally, be achieved using various template-controlled processes. The various possibilities include (i) binding of Ag⁺ ions to the thiol or the carboxylic acid surface functions of the TFSM and NTSox template, following by reduction with aqueous NaBH₄ or gaseous N₂H₄ and further development (if desired) of the silver nanoparticles so obtained with a silver enhancer (SE) solution, (ii) binding of a gold species to the TFSM surface, followed by gold-catalyzed silver metal deposition from the SE solution, (iii) binding of Cd²⁺ ions to the TFSM or the NTSox surface, followed by the formation of CdS upon exposure to H₂S and (iv) exposure of NTSox to a solution of a self-assembling silane, which would result in the formation of an organic trilayer at the tip-inscribed sites. These experiments suggest that organic and inorganic solid-supported nanostructures might be conveniently fabricated by direct surface self-assembly on a predesigned template. The template for this process is a highly stable, defect-free organic monolayer which by virtue of the chemical information inscribed on its outer surface, can control the site-defined chemical growth of various desired organic and inorganic nanocomponents. Constructive nanolithography differs conceptually from other lithographic techniques that make use of organic monolayers as passive ultrathin resists. In constructive nanolithography, the organic monolayer plays an active role as a template throughout the entire fabrication process; the initial lithographic pattern being imprinted non-destructively on its outer exposed surface, where all subsequent self-assembly events take place. By providing convenient access to a variety of post-patterning chemical manipulation and self-assembly routes, this synthetic build-up approach offers attractive new options for direct in situ fabrication of functional nanostructures that combine diverse useful materials and architectural motifs in a manner that may not be easily realized by other techniques. The selection of chemical routes allowed for post-patterning manipulation is subject to constraints posed by the need for site specificity, as only the tip-inscribed sites should be affected, leaving the rest of the treated surface unmodified. Although the previous successful demonstration of different modes of non-destructive monolayer patterning and development has already pointed to some of the attractive new options offered by constructive nanolithography, the use of base monolayer templates with chemically sensitive vinyl and silver thiolate top functions restricted considerably the choice of useful post-patterning fabrication routes. Ideally, one would, therefore, like to have a monolayer template with high chemical, thermal and mechanical stability, consisting of a pattern of chemically active surface sites embedded within an inert background that is compatible with a large variety of post-patterning modes of chemical manipulation.

Constructive nanolithography can offer, beyond extreme miniaturization, some rather unique advantages thanks to its remarkable chemical versatility and flexibility in the selection and handling of a large variety of different desirable components organic, inorganic and biological. Furthermore, whereas the lateral positioning accuracy routinely achievable in AFM patterning is in the order of several nanometers, combining this scanning probe technique with molecular self-assembly offers unmatched capabilities for subnanometric accuracy in the vertical positioning of such components on a nanometrically defined pattern. The main drawback of constructive nanolithography has to do with the inherently slow nature of any serial patterning method. It is, for example, impracticable to employ a scanning AFM tip for the fabrication of connector features bridging the micrometer/millimeter dimension gap, which are needed for communication with the macroscopic external world. Although such connector features may, in principle, be produced by suitable modifications of conventional top-down techniques, it would be highly desirable to avoid the expensive and inconvenient mixed use of different technologies in the development of a novel nanofabrication methodology.

5.3. Micropatterning

The concept of electrochemical nanolithography has been extended to the monolayer template patterns spanning the micrometer–millimeter dimension range [181–183]. The concept is very simple and is depicted in Fig. 29. The template pattern is created in one-step electrochemical printing of the entire desired pattern on the top surface of a high-quality CH₃-terminated ODTS monolayer self-assembled on silicon. The desired patterns are created using conducting metal stamps (e.g. copper grids of transmission electron microscope). The metal stamps are first exposed to a saturated water-vapor atmosphere (after being freshly cleaned to render them water wettable) and then immediately pressed against CH₃-terminated ODTS monolayer on silicon surface. A suitable electrical bias (~20 V) is then applied between the metal stamp and the silicon substrate. It is expected that under bias, top –CH₃ functions of the ODTS monolayer get converted to –COOH at locations where metal stamp is in contact with monolayer. In fact, the patterns, produced by the local oxidation (CH₃ converting to COOH) under the stamps, have been identified using lateral force microscopy. The high contrast in friction (lateral force) images appears because of the large difference between lateral forces exerted on the tip in polar (COOH) and nonpolar (CH₃) surface regions. The electrochemical

Fig. 29. Schematic depicting the electrochemical microprinting process (after Ref. [181–183]). The metal stamp exposed with water vapor is clamped against a self-assembled CH₃-terminated OTS monolayer on Si. A bias of ~20V is applied between the grid (negative) and the silicon substrate (positive). At the contact places CH₃ is converted to COOH, which is then used for the selective deposition of second OTS monolayer at the COOH sites.
oxidation is a non-destructive and therefore does not affect the surface topography significantly. Upon self-assembly at the surface-modified sites of a CH$_3$-terminated NTS monolayer, the homogeneous nonpolar character of the entire imaged surface was restored in the lateral force image. However, in the topographic image, step corresponding to the expected height of the NTS monolayer was clearly observed, indicating that the NTS monolayer self-assembles only at COOH sites.

It may be noted that experiments performed without exposure of the metal stamps to a saturated water-vapor atmosphere prior to contacting the monolayer surface, no definite patterns could be observed. This indicates that water layer also plays important role in the conversion of –CH$_3$ into –COOH. In order to achieve large-area molecular-scale contact between stamp and substrate it is essential that the stamp is made of a flexible soft material, like the elastomeric stamps currently employed in the many versions of soft lithography.

6. Summary

We have presented a brief overview of organic molecules exhibiting various electronic functionalities, such as, dielectric, diode, memory and transistor. We have also discussed various issues, such as, importance of molecule/Si interface, new molecular architectures for hybrid devices, etc. It has been demonstrated that functional organic molecules can be deposited on Si by the cathodic electrochemical process using terminal vinyl (C=C), ethynyl (C≡C), halide (Cl, Br, I), tetraalkylammonium salt, diazonium salt and silane as reactant. However, in some cases, particularly using diazonium salts, electrografting does not allow easy formation of monolayers, as the formation of reticulated multilayers is difficult to prevent. The electronic functionalities of some electrografted molecules, such as, di-electric behavior in OTS monolayers and resistive memory effect in TPP-C11 monolayers, have been demonstrated. A distinct advantage of cathodic electrografting over self-assembly is that the applied bias not only acts as a control to graft molecules on Si but also allows fabrication of monolayer patterns with spatial resolution in the nanometer scale for hybrid nanoelectronics.