Surface Functionalization in the Nanoscale Domain

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Abstract

This chapter discusses the modification of surfaces using thin layers of organic molecules to control or modify the properties of the surface. Methods for placing monomolecular adlayer films on various surfaces are outlined, as are methods that result in nanoscopic multilayered films. First, the general properties of surfaces are discussed in the context of how a thin organic film can be used to change their properties and behaviour. Then, an overview of methods for coating various surfaces with nanoscopic organic films (i.e., less than 10 nm thick) is given. Finally, methods for generating thicker films are discussed. Throughout this chapter, illustrative examples are given to show the structure of the film in question or to show how the properties of the modified surface can be dictated by the choice of the specific chemical composition of the adlayer.

7.1   Introduction and Scope

It is a well known consequence of geometry that the surface/volume ratio of an object increases as the object becomes smaller. The progression of many aspects of science and technology into the nanoscale realm therefore inherently results in the greater importance of surfaces in determining the behaviour of nanoscale devices and phenomena. The relentless increase in device density in the microelectronics industry provides a very prominent example of the relative importance of surfaces to device fabrication and performance, as the feature size is currently a few tens of

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nanometers. If the "surface" is arbitrarily considered to encompass the typical escape depth of an excited electron (1–10 nm), then the progression of microelectronic feature sizes from 65 to 32 nm and below is rapidly approaching the point where the finished device is "all surface". In addition to occupying a greater fraction of device volume for smaller devices, surfaces also provide the opportunity to create unusual arrangements of atoms and molecules. The bulk structure of a given material is interrupted at its surface, and it is often possible to orient and/or bond materials with quite different properties at an interface between dissimilar materials.

Nanofabrication involves a wide range of surface modification procedures that are important in many different areas of nanotechnology. This chapter will emphasize mainly chemical methods for surface modification at the monolayer and near-monolayer level (generally, we consider here films that are less than 10 nm thick), with particular attention to the interactions between the bulk substrate material and the surface modifier occurring at their interface. Spin-coating and vapour deposition are commonly used for surface films substantially thicker than a monolayer, and will not be discussed in this chapter. Atomic Layer Deposition is a monolayer deposition method that is discussed in Chap. 6. Certain self-assembly techniques such as block co-polymer deposition and ordering have structure at the monolayer level, and are discussed Chap. 6. Here, we will focus on methods for orienting and bonding surface layers on solid substrates such as silicon, metals, carbon, and oxides. Such interactions are often classified into two categories: "physisorption" involving relatively weak attractions between the substrate and surface modifier (e.g., electrostatic attraction), and "chemisorption" involving strong surface bonds, often covalent. Of particular interest will be the orientation and structure of the interfacial region resulting from various surface modification procedures. The introduction of order at the substrate/modifier interface often distinguishes the methods described in this chapter from the comparatively disordered interfaces resulting from spin coating and vapour deposition.

It is common to classify surface modification techniques according to their surface chemistry. For example, Au/thiolate self assembled monolayers (SAMs) are considered as one class, while silanes on SiOx represent another. In this chapter, we will instead focus on *function* rather than *chemistry*, since usually the function of the nanostructure is more important to potential applications than its chemical structure and bonding. Overall, we intend the chapter to provide a "toolbox" of surface modification methods to aid nanofabrication and produce particular behaviours, be they electronic, improved environmental tolerance, chemical reactivity, etc.

7.2   A Functional View of Surface Modification

Before considering specific surface modification techniques, it is useful to summarize common objectives underlying the approach. The list below is illustrative rather than comprehensive, but it does cover many of the end results important in

nanofabrication. It will become apparent that many of these objectives are controlled by the strength of the interaction between the modifier and the substrate surface, which is in turn controlled by the surface bonding chemistry.

7.2.1 Wettability

A very familiar and readily observed surface property is controlled by the interaction of a liquid, often water, with the surface. Water spreads out evenly on a "hydrophilic" surface, since the interaction between the surface and water is stronger than the intermolecular interactions in bulk water. "Hydrophobic" surfaces, on the other hand, weakly attract or even repel water to produce droplets or "beads" of water on the surface due to much weaker surface interactions. Thus, the wettability of a material can be quantified by measuring the contact angle of a water droplet on the surface of the material. The range of values for this angle from 0° (completely wetted) to above 150° (a "superhydrophobic" surface) can also be related to the surface-free energy [1], as discussed in more detail below. An example of how the surface chemistry of a single molecular layer can dramatically alter wettability is shown in Fig. 7.1, which shows a gold surface coated with two different monolayers: one presenting a hydrophilic –OH end group (left side) at the surface and one having a hydrophobic –CH$_3$ end group (right side) [2]. The relative concentration of the two layers varied from left (−OH groups only) to right (enriched in –CH$_3$ groups) across the figure. This figure illustrates that the surface chemistry will have a significant effect on any nanofabrication process involving water or that depend on the interfacial surface free energy.

The concept of wettability may also be applied to many materials other than water and can be used to describe the tendency for a material to coat a surface. For example, vapour deposited metals may form quite uniform films on a substrate in which the metal-surface interaction is attractive, but will form beads if the attraction is weak relative to the metal-metal interatomic forces. Since solvents themselves can be either hydrophobic or hydrophilic, the wettability of a particular solvent on a surface can vary significantly with the nature of the surface. The basic principle underpinning wetting applies to water as well as all other cases: the
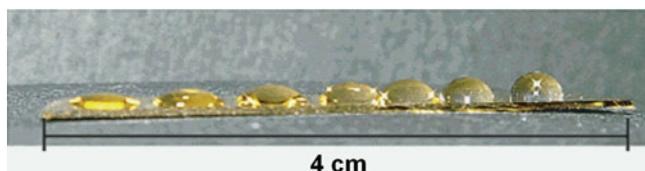
Fig. 7.1 Drops of water on the surface of a gold sample coated with pure ω-hydroxyundecanethiolate (*left*-most drop showing a small contact angle and therefore a high surface energy) and an increasing concentration of methyl-terminated dodecanethiolate (moving to the *right*, where the contact angle increases, indicating lower surface energy) [2]. This figure illustrates that surface energy, as measured using contact angle, is highly sensitive to the chemical groups present at the surface (Reproduced with permission from Ref. [2])

balance of *adhesion* (the attraction of modifier to the surface) and *cohesion* (the attraction between modifier atoms or molecules) acts to determine the wetting characteristics for a particular solid–liquid pair. This balance is the basis of "surface energy", which indicates the propensity of a material to form a surface rather than a particle. Materials with a high surface energy favor particle formation, as the energetic cost of breaking bonds in the bulk materials is large. The contact angle is measured between a line that lies in the plane of the solid surface and the line on the droplet that meets the solid near its edge (usually measured through the liquid). Thus, a contact angle approaching 0° occurs on a wettable surface, while a contact angle above 90° indicates a hydrophobic surface with a weakly interacting surface.

7.2.2 Uniformity and Pinholes

Surface coverage and thickness uniformity are obviously major concerns when coating any surface with an overlayer, and become significantly more demanding when the film thicknesses decreases below 50 nm. This issue is well illustrated by considering the "aspect ratio", i.e., the dimension of the surface film parallel to the surface divided by its thickness. Spin coating a 1 μm thick film on a 100×100 μm surface yields an aspect ratio of 100, while a monolayer film of a 1 nm length molecule on the same surface has an aspect ratio of 10^5. Thus, ensuring high coverage and uniformity essentially requires the monolayer film to be 1,000 times more exacting in its spreading over the surface, clearly indicating that successfully fabricating a high coverage, uniform monolayer over even relatively small areas is demanding. For example, significant problems have been encountered when attempting to make molecular electronic devices from single molecular layers due to the presence of a minute population of pinholes in the monolayer that can allow direct electrical contact between the substrate and any top electrical conductors used to complete the circuit [3–7]. Furthermore, techniques such as profilometry, ellipsometry, and interference microscopy are commonly used to determine the uniformity of films with thicknesses greater than ~10 nm, but such methods are generally unsuitable for molecular monolayers. Uniformity for nanoscale surface modifications is largely a function of the relative kinetics of surface bonding, intermolecular interactions, and the reversibility of the surface bond [7, 8]. If adhesion and cohesion are used to describe the energetics of the modifier-surface interaction, the uniformity of the layer and pinhole formation can be directly related to the kinetics of the interactions. For example, consider the commonly used "parylene-N" coating which is applied by polymerization of xylene radicals thermally desorbed from a precursor solid [9, 10]. The reactive xylene radicals can bond to many surfaces, but also to themselves to generate a highly cross-linked and hydrophobic protective film. If the surface bond forms rapidly compared to dimerization reactions, the nucleation rate will be high and the initial adlayer will resemble a "wheat field". Unmodified surface areas will be rapidly coated with additional modifier such that the density of pinholes will be small. On the
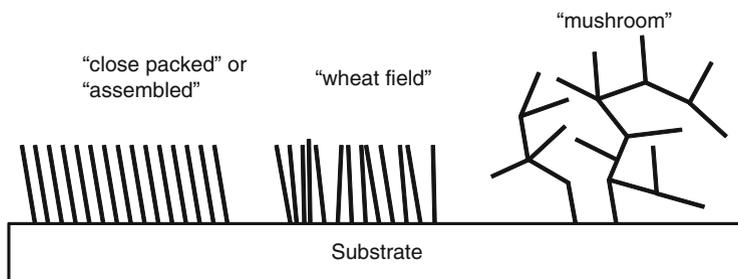
Fig. 7.2 Examples of surface modifying layers that self-assemble to form a close packed structure with highly ordered domains (*left*), less ordered structures that remain oriented and resemble wheat fields (*center*), and disordered layers that result from uncontrolled growth to produce mushroom-like clusters of molecules (*right*)

other hand, if the dimerization (and eventually polymerization) rate is fast compared to the surface reaction, "mushrooms" will result, shown schematically in Fig. 7.2 [8, 11]. Many readers will recognize this issue as an example of "nucleation and growth" kinetics, and it affects a wide range of surface modifications. In the case of parylene, the coatings are usually thick enough (>100 nm) that pinholes are encapsulated by the subsequent layers of the film. But for films of <10 nm thickness, particularly monolayers, the eradication of pinholes is often difficult [3, 12].

A related issue is the process of "self-assembly," which refers to the formation of an ordered layer of molecules by equilibration to a structure of minimum free energy. The Au/thiol SAM and Langmuir-Blodgett films are the most prominent examples, and are discussed in more detail below. In order to "assemble", the surface-modifier bond must be at least partially labile, so it can break and form again to reach the highly ordered structure. In contrast, modification methods which form irreversible surface bonds are unable to "assemble", but have the attraction of relatively high thermal stability. As always, the choice of surface modification procedures is governed by the eventual application, and the relative importance of stability vs. order.

7.2.3   Chemical Reactivity

Wettability, as discussed in Sect. 7.2.1 is an example of the broader description of a surface in terms of chemical reactivity. There are many examples in the literature of a surface modification designed to enable a subsequent interaction between the surface and additional modification, analogous to a "primer" between a coating and a solid surface. For example, a monolayer of an organic compound bonded to a metal may completely change the chemical characteristics of the surface, depending on the identity of the terminal group of the organic modifier. The molecule can be terminated by a functional group that is hydrophilic, acidic, chelating, or that has
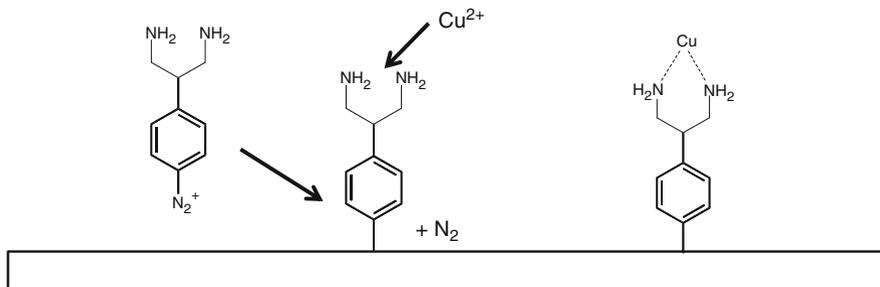
Fig. 7.3 Hypothetical example of a "seed layer" deposited onto a surface using a chelating molecule that is grafted to a surface. The chelating agent acts to bind Cu^{2+} ions from solution to result in a seed layer that promotes uniform plating of copper. Note that this is an illustrative example only; actual molecular structures are generally proprietary

other chemical properties which are quite different from those of the original metal. A solution or gas in contact with the modified metal surface will "see" the layer of organic molecules terminated by a range of possible functional groups first, and the properties of the metal (such as possible high reactivity) may become irrelevant (or at least secondary to the properties of the adlayer).

A prominent example from the semiconductor industry is the "seed layer" for the Damascene copper plating process. Effective electroplating of Cu requires nucleation sites on the surface to be plated, which typically consist of a sputtered layer of Cu applied in a vacuum. More recently, "primers" made from organic molecules with binding sites for Cu^{+2} ions have been used to provide seed layers in regions not accessible by sputtering, as shown schematically in Fig. 7.3. The reactive diazonium reagent bonds to the surface to be plated irreversibly, and contains a functional group that attracts Cu^{+2} ions from the electroplating solution. The diazonium surface modification is aggressive, and forms a high density of nucleation sites on the surface for the Damascene process. Primer layers based on organic modification of conducting and non-conducting surfaces are available commercially for use in semiconductor manufacturing (e.g., www.alchimer.com/technology/index2; www.zettacore.com/molecularinterface.html)

As already noted, "primers" are possible for a variety of additional surface modifications with many more end uses than copper plating. Examples include silane bonding of thiophene precursors for electropolymerization on tin oxide [13], surface epoxy groups on carbon fibers to initiate epoxy curing [14], surface-bound ligands for metal complexes [15] and binding of biomolecules to a silicon surface modified with aromatic amines [16]. There is an extensive literature on surface modification by a variety of methods to impart particular reactivity on electrodes for electrochemistry [17–22]. Adhesion between two materials is a special case of surface reactivity, and is governed by some of the same principles as wettability. Strong adhesion generally involves strong bonds between the two materials, with covalent bonds generally much stronger than typical physisorption governed by electrostatic or dipole–dipole interactions.

7.2.4 Protection

Prominent examples of surface modifications designed to stabilize surfaces toward environmental exposure and prevent corrosion include chemical modification of silicon and chromate conversion coatings on aluminum alloys. Such treatments can passivate a reactive native solid surface with more stable materials, often covalently bonded to the surface. These two example reactions are shown schematically in Fig. 7.4. The protection of aircraft alloys by reduction of chromate ions to an inert, insulating Cr^{III} oxide is essential to the aerospace industry to stabilize quite reactive aluminum/copper alloys [23–26]. The propensity of silicon to form surface oxides is well known, and bonding of a methyl group to the Si surface greatly enhances its resistance to photochemically induced corrosion [27–29].

7.2.5 Electronic Interactions

Of the many known electronic phenomena in solid state structures and in solutions, several of direct relevance to surface modification deserve special note. Rather than considering "bulk" properties such as dielectric constant, conductivity, and mobility, we will focus on electronic effects present at surfaces, many of which are strongly affected by the structure and orientation of surface layers. A relatively simple example is the effect of surface dipoles on the apparent work function of a solid substrate. Bonding of a molecule containing a finite dipole to a surface by a
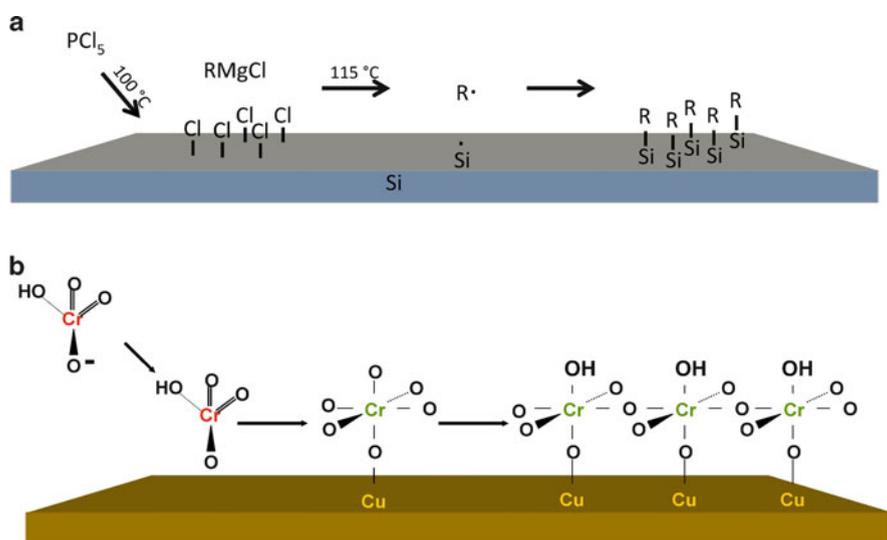
Fig. 7.4 (**a**) Passivation of a silicon surface by chlorination followed by reaction with a Grignard reagent to bind R groups at the surface [29]. (**b**) Passivation of a Cu surface by a chromate conversion coating
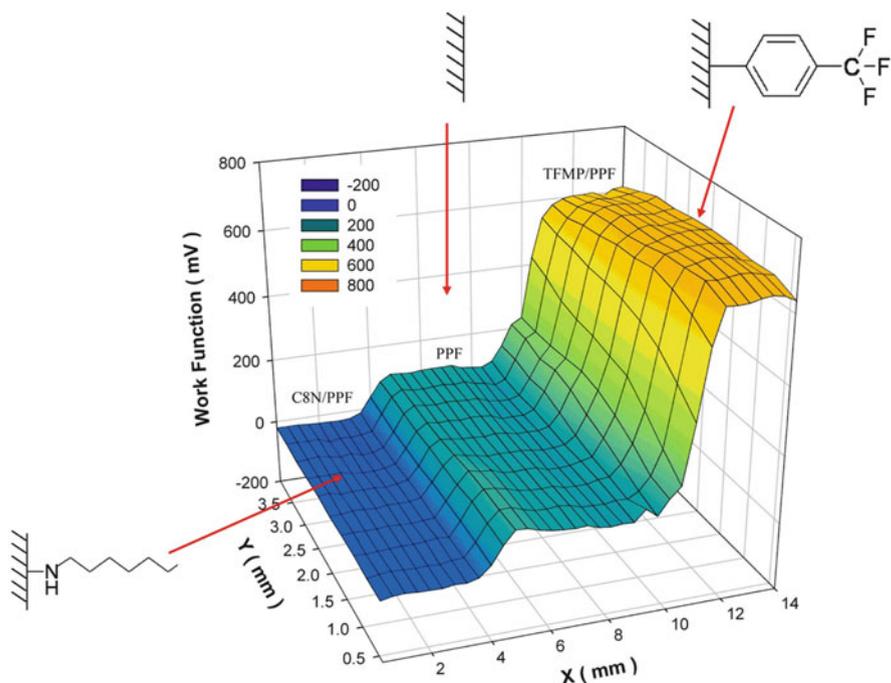
Fig. 7.5 Modification of the work function of a carbon surface (PPF, or pyrolyzed photoresist film, *center* region) by molecular layers with different dipole orientations. The alkylamine dipole is oriented toward the surface, causing the decrease in work function to the left of the bare carbon. To the right of the unmodified carbon film, an increase in work function results for a trifluoromethylphenyl layer that has its dipole oriented away from the surface (Reproduced with permission from Ref. [34])

method which orients the dipoles relative to the surface produces a shift in the work function of substrate/monolayer combination, as judged from Kelvin probe or Ultraviolet Photoelectron Spectroscopy (UPS) [30]. This effect has been used to alter injection barriers and promote tunneling in both molecular junctions [31–35] and organic thin film electronics [36, 37]. An example is shown in Fig. 7.5, for the case of molecular layers on flat, graphitic carbon [34]. A scanning Kelvin probe was used to map the work function of the surface, with the sample divided into three regions. The middle "stripe" was unmodified, while the remaining "stripes" had covalently bonded $C_8H_{17}N$ or trifluoromethylphenyl (TFMP) monolayers on the carbon surface. The alkylamine dipole is oriented toward the surface, while that for the TFMP is oriented in the opposite direction. Note that the apparent work function varies by >600 mV due to the surface modifier, with the electron withdrawing TFMP decreasing the interfacial energy relative to the unmodified surface.

It is generally recognized that bonding a molecule to a surface can change the electronic properties of both components in more respects than the surface work function. Strictly speaking, a covalently bonded molecule on a conducting surface

is a new "molecule" with some degree of electronic coupling between the orbitals of the molecule and those of the surface. There is strong theoretical and experimental support for the conclusion that the modified surface should be considered a "system" with possibly quite distinct properties from the component parts [38, 39]. The energies and appearances of the molecular orbitals of the surface bound molecule change upon surface bonding, but the molecular orbitals may also mix with those of the graphite support [40].

An interesting consequence of orienting molecules by bonding to surfaces is the effect on the dielectric constant and polarizability of the molecular layer [41–43]. Although dielectric constants are often considered for bulk materials to be isotropic, they are in fact tensors which depend on molecular orientation. For example, the delocalized electrons in anthracene cause the polarizability along the longer Z axis of the molecule to be higher than that along either the X or Y axes. Furthermore, the polarizability and resulting dielectric constant can increase as the length of a conjugated molecule increases [42]. A related phenomenon relevant to electron transport is the electronic coupling between the surface layer and the substrate. In the limit of strong electronic coupling, the electrons can be considered to be delocalized over a region including both substrate and molecule orbitals, with the combination behaving as one electronic system [41].

Electron transport in thin films has been studied extensively, of course, due to its importance in the behavior of microelectronic devices. Tunneling and field emission of electrons through thin films of SiO_2 are major considerations in widely used devices such as field effect transistors and floating-gate "flash" memory. The investigation of electron transport through single molecules and molecular monolayers has been stimulated in the past decade by "molecular electronics", in which molecules become circuit components. Since the great majority of non-polymeric molecules have dimensions of less than a few nm, transport by quantum mechanical tunneling can contribute significantly, or completely control charge transport through surface modification layers.

It is useful to consider electron transport in surface layers as a function of thickness and transport mechanism. Classical transport in bulk conductors occurs by a series of scattering events, in which the electron travels a short distance, usually a few tens of nm, then scatters and changes direction. Progress through the conductor is diffusive, with the net motion of charge carriers along the conductor driven by the applied electric field. For thick films on surfaces, i.e., >100 nm thick, transport across the layer is also by a series of small steps, either by scattering or "hopping". "Hopping" is a rather general term, which usually involves "sites" where an electron (or hole) can reside temporarily during its progress through the material [44–47]. For organic semiconductors, such sites are cation or anion radicals, for hole or electron transport, respectively. The low mobility and temperature dependence of most organic semiconductors are due to the energy required to form and eliminate these radical sites during transport, as well as the usually limited delocalization of electrons or holes in the materials. Another term for transport between radical sites is "redox exchange" with the associated activation barrier equal to the "reorganization energy" [48–50]. In conducting polymers, the "doped"

forms contain delocalized radical sites, often referred to as "polarons", which exhibit band-like transport over distances of up to ~10 nm. Unless the polymer is heavily doped, electrons still must hop between polarons, leading to a positive dependence of conductivity on temperature.

When the thickness of a surface layer is in the range of $<$1–10 nm, electron tunneling becomes possible, and transport behavior may change dramatically. Tunneling through such layers has been studied in electrochemistry, in which the electron tunnels through the layer to react with a molecule in solution, and in molecular electronics, where a 1–10 nm thick molecular film separates two solid conductors. The quantitative dependence of tunneling rate on film structure and thickness is often complex, but some useful generalizations are possible in the context of the early "Simmons" model [41, 51, 52] (7.1).

$$J = \frac{q}{2\pi h d^2}\left(\bar{\phi}e^{-A\sqrt{\bar{\phi}}} - (\bar{\phi} + qV)e^{-A\sqrt{\bar{\phi}+qV}}\right) \qquad (7.1)$$

$$A = \left(\frac{4\pi d}{h}\right)\sqrt{2m_{\mathrm{e}}}$$

where m_{e} is the electron mass, d is the film thickness, ϕ is the tunneling barrier height, q the electron charge, and V the voltage applied across the film.

First, the tunneling rate and therefore conduction through thin films is exponentially dependent on film thickness, d. For ohmic (diffusive) conduction and hopping mechanisms, the current usually scales with d^{-1}. The exponential dependence of the tunnel current leads to vanishingly small conduction by tunneling when $d > {\sim}5$–6 nm (at which point the hopping current becomes dominant [53, 54]). Second, the tunneling rate is also exponentially dependent on the barrier height, ϕ, usually taken as the offset between the surface Fermi level and a single orbital energy in the film. Usually, a good approximation of the barrier height can be obtained by using the Lowest Unoccupied Molecular Orbital (LUMO) for electron tunneling or the Highest Occupied Molecular Orbital (HOMO) for hole transport, since these lie closest to the Fermi level in energy. The actual barrier is usually more realistically visualized by using a spectrum of orbital energies [55, 56] rather than a single orbital, but this requires significantly more complex methods to determine the barrier. To illustrate how the barrier height correlates with molecular properties, it is known that the molecular frontier orbital energies for conjugated, aromatic molecules are generally closer to the Fermi energy of most contact materials compared to alkanes, indicating that tunneling through aromatic layers is more efficient and will lead to higher tunneling currents. The Simmons model has a variety of enhancements to account for the electric field strength, the effective carrier mass, the tunneling barrier shape, etc., so correlation of theory and experiment is often quite involved [41, 57]. A useful empirical parameter is the attenuation factor, β, with units of nm^{-1}, which is the absolute value of the slope of a plot of $\ln(J)$ vs. d, where J is the tunneling current density and d is the layer thickness. For example, $\beta = 1.0~\mathrm{nm}^{-1}$ indicates that each nm of layer thickness decreases the
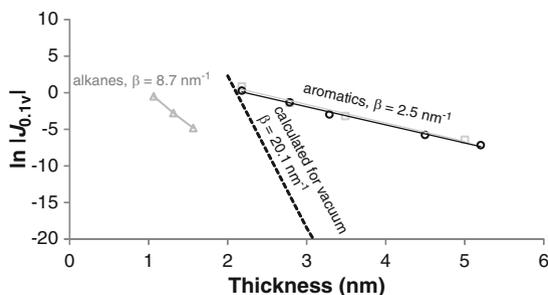
Fig. 7.6 Attenuation plots given as the tunnel current density at 0.1 V as a function of thickness for different molecular structures and a vacuum gap. The alkane series (*triangles* [58]) yielded a value for β of 8.7 nm^{-1}, while two different aromatic layers (*squares* = azobenzene, circles = nitroazobenzene) give a much lower β of 2.5 nm^{-1}. Finally, the dashed line shows an attenuation plot calculated using the Simmons model with image charge effects included [41, 51] for a vacuum gap with a 4 eV barrier height (with dielectric constant and effective mass equal to 1) that gives β = 20.1 nm^{-1}

tunneling rate by a factor of 1/e. Although the Simmons relation predicts that β is proportional to $\phi^{1/2}$, there are often other factors included in the experimental value, notably the effective carrier mass. Figure 7.6 compares experimental and predicted plots of ln(*J*) vs. *d* for several cases, to illustrate the large range of β possible for thin film materials [41, 58].

It is obvious from (7.1) and Fig. 7.6 that tunneling is a strong function of thickness and layer structure, but is usually exponential with layer thickness and weakly dependent on temperature. It should also be noted that this discussion applies to "off resonant" tunneling, in which there is a barrier between a molecular orbital and the substrate Fermi level. "Resonant tunneling" can occur when orbital energies are with *kT* of the Fermi level, and such transport is expected to a lead to a β close to zero [59–61].

7.2.6 Thermal Stability

The thermal stability of chemically modified surfaces is a function both of the bond between the surface and the modification layer, and of the inherent stability of the molecules comprising the layer. While the molecular stability may vary over a wide range for the many possible surface modifications, some generalizations about the surface bond are useful for predicting thermal stability. As noted in Sect. 7.2.2, self-assembly techniques based on Langmuir-Blodgett and Au/thiol chemistry require a relatively weak surface bond to permit the modification layer to "assemble" into an ordered, low energy configuration. The commonly studied Au-S bond for thiols adsorbed to Au surfaces has a bond energy of ~1.6 eV (~40 kcal/mol), while the typical forces that hold L-B structures on a surface are significantly weaker (< 0.5 eV).
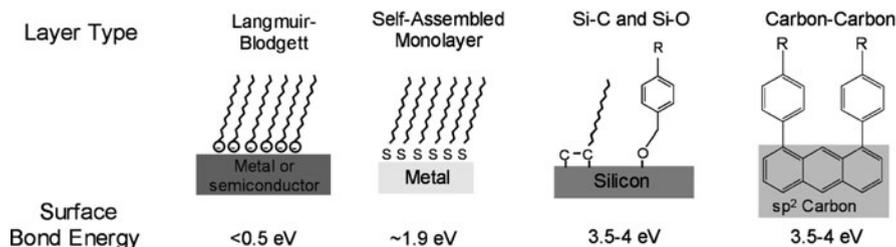
Fig. 7.7 Examples of different modification chemistries that show varying surface-molecule bond strengths, illustrating that the surface chemistry impacts layer stability (Reproduced with permission from Ref. [8])

Irreversible adsorption through C-C, Si-C, and Si-O bonds is mediated by much stronger bonds, as indicated schematically in Fig. 7.7.

Thermal stability of modified surfaces deserves attention in at least two applications. First, subsequent processing of the modified surface in order to incorporate it into a finished product may involve temperature excursions of possibly hundreds of °C, with the possibility of damage or disordering of the modification layer. Second, the end-use of the device may require operation over a much wider temperature range than that of the laboratory or fabrication line. Examples of thermal stability issues in molecular electronics are the failure of Au/thiol surface modifications at 50–100°C which resulted in device failure [62, 63]. Similar molecular junctions based on C-C surface bonds survived 40 h at 150°C [64] or brief exposure to 250°C in vacuum.

7.3   Nanomolecular Layers

As noted above, derivatizing a surface with a nanoscopic layer of organic molecules can alter the properties of the interface in a controllable fashion. The modifying layer can impart some chemical or physical property that is required in order to meet the demands of the end-application, or it can be used to study fundamental phenomenon. For example, the surface of a medical device may need to be rendered bio-compatible, or a systematic study of electronic and/or optical interactions of a solution phase molecule with a particular substrate can be carried out as a function of modifier hydrophobicity, length, etc. As described in this Section, there are many different ways to modify the surface of a substrate material, and the choice of the method that is used usually depends on more than the desired properties of the interface imparted by the modifier. For example, if a hydrophobic surface is desired for the application of a hydrophilic metal, there are methods available to achieve a hydrophobic adlayer. However, one method may require a complicated, time-consuming procedure but result in a highly stable layer, while another may provide a suitable hydrophobic layer with ease that is less robust. Thus, the application should be considered and balanced against these other factors when choosing a modification method.

The thicknesses of the films discussed in this Section generally reside in the nanoscale domain, having a total thickness of less than 10 nm, with thicker films discussed in Sect. 7.4. The reason for this distinction lies partially in how the properties of a material vary with length, and is somewhat arbitrary. As noted in the introduction, the surface of a material becomes increasingly important as the size of an object is reduced. Partially a consequence of this phenomenon, the properties of a material often undergo significant changes as the size approaches the nanoscale. Thus, a sample of bulk material has the same properties when divided into two separate pieces. However, if this division is continued until at least one dimension approaches the nanoscale (roughly defined as less than 100 nm), the properties begin to depend quite sensitively on thickness. That is, a 20 nm slice of the material can have vastly different properties than a 5 nm slice, and both of these slices can have different properties than the bulk material even for identical molecular structures. Since these effects underlie the emerging field of nanoscience and nanotechnology, we refer to modifying layers with thicknesses less than 10 nm as *nanomolecular* layers.

There are numerous methods for placing a thin layer of organic molecules on the surface of a material. In general, the substrate that is modified determines in large part the types of modification methods that can be used. There are specific methods that rely on interactions or bond formation between a substrate material and the modifying film and non-specific methods that can be generally applied. The former case is less versatile, but usually more stable. For each type of nanomolecular layer, a general description of the layer structure is given, along with commonly used preparation procedures and some brief example applications.

7.3.1   Langmuir-Blodgett Layers

Katherine Blodgett described the deposition of monolayer films on glass in 1934 [65] and provided a description of multiple layers of monomolecular films on solid surfaces in 1935 [66]. This remarkable feat of nanotechnology over 75 years ago laid the foundation for the application of Langmuir-Blodgett layers (L-B layers) [67] in numerous applications, although this did not happen for several decades following Blodgett's original papers. The technique relies on the interactions between amphiphilic molecules and water to create an ordered layer of molecules at the liquid–gas interface [68]. The oriented molecular layer is compacted by applying lateral pressure using a barrier, causing an increase in order and packing density to form a compact molecular layer at the air-water interface (a Langmuir film, Fig. 7.8a). To form an L-B layer, the Langmuir film is transferred to a solid support simply by passing the substrate slowly through the film, as shown in Fig. 7.8b, c. Repeatedly dipping the substrate can yield multilayer films, an example of which is shown in Fig. 7.8d. The details of layer orientation initially depend on the substrate surface chemistry, the type of molecule that is spread on the surface of the water, the orientation of the solid, and whether the support is lowered or raised through the interface (extending or receding deposition).

Fig. 7.8 Schematic of the process used to create an L-B layer. (**a**) First, a Langmuir film is formed at the air–water interface. (**b**) Next, a substrate is passed through the Langmuir film to create an L-B film at the surface of the substrate. (**c**) Additional steps can results in a multilayer film, shown in (**d**) (Reproduced from Ref. [67])
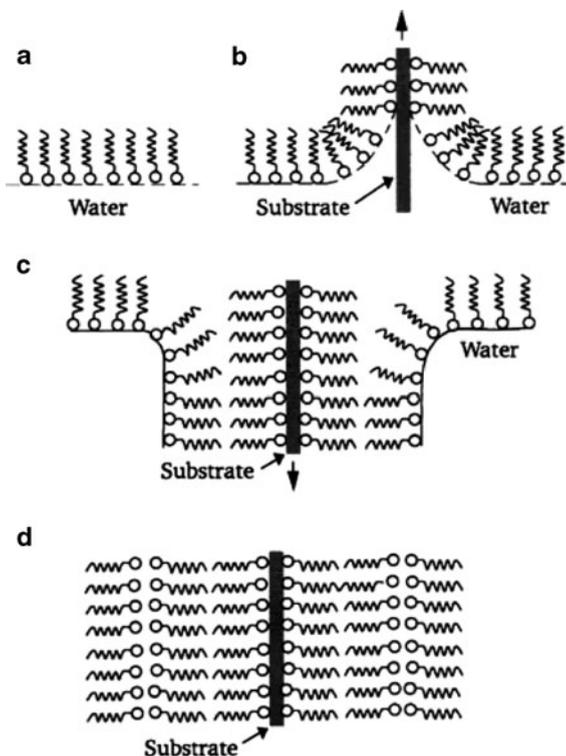
There are numerous molecules that can be used to create L-B films, with the only requirement being a dipole that imparts amphiphilicity. However, the ordering of the layer depends on intermolecular interactions between the molecules so that the most well-defined layers result from the use of regular repeating units (such as long-chain alkanes) with an appropriate functional group at one end to create a dipole. Thus, films formed using fatty acids have set the standard for quality and coverage [67].

L-B films have been extensively applied as nanomolecular layers in a large number of applications. The versatility of the structures that can be used and the flexibility in the number of layers makes them attractive for applications in which molecular scale precision is desired. Reported examples include molecular electronics [69, 70], biological sensing [71], scanning probe microscopy [72], organic electronics [73], and many other areas including electrochemistry and non-linear optics [74].

7.3.2 Self-Assembled Monolayers

Using specific chemical interactions, organic molecules can be spontaneously assembled onto many types of surfaces. Usually the organic molecule contains a

functional group at one end that has an affinity for the surface to be modified. This affinity leads to the formation of a chemical bond between the functionality and the surface such that the molecule is retained at the substrate surface and the terminus of the molecule is oriented outward from the surface. The fact that the adsorption is driven by a specific surface-molecule interaction limits the coverage to a single molecular layer, and the term *self-assembled monolayer* (SAM) has been widely adopted to describe these layers. In addition, the type of bond formed between the surface and modifier is usually labile: molecules have some mobility on the surface after adsorption. Although this limits the stability of the layer somewhat, it enables the formation of highly ordered structures with full monolayer coverage since adsorbed molecules can move to accommodate additional adsorbates. Thus, a SAM is stabilized by intermolecular interactions between molecules in the film, which serve to orient the layer. This driving force, combined with the surface mobility, enables molecules in low-coverage areas to migrate to more ordered domains, resulting in a well-ordered monomolecular film. The reversible nature of SAM-surface bonding is one element that distinguishes these types of layers from other methods that rely on permanent, irreversible bond formation, as will be discussed in more detail below.

Noble metals are a very common surface for SAMs [75] due to their ease of handling in laboratory ambient. In addition, many other surfaces serve as supports for SAMs [76], including a variety of semiconductors and metal oxides [77]. To illustrate the general features of a SAM, we will use the example of an alkanethiolate monolayer on gold, which has been studied in depth so that many of its structural and formation characteristics are well established [68, 75, 78–80].

A schematic of a self-assembled monolayer composed of alkanethiolate molecules at gold is shown in Fig. 7.9 [81]. As shown, a head group (in this case, the sulfur atom) acts to anchor the molecules onto the gold substrate by a specific interaction that leads to some form of bonding. Although this bond can be quite
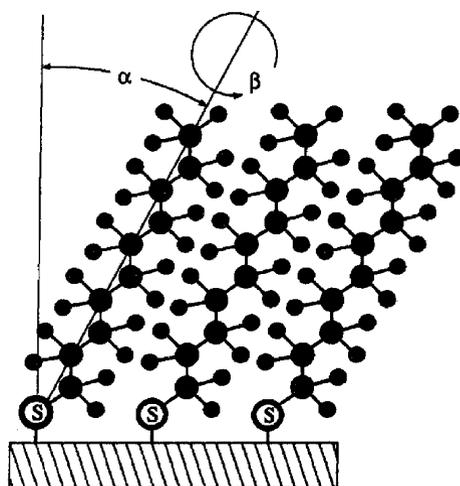
Fig. 7.9 Schematic of a SAM composed of alkanethiolates chemisorbed at Au [81]. The tilt (α) and twist (β) angles are shown here to define the precise orientation of the molecules on the surface (Reproduced with permission from Ref. [81])

strong, it is also reversible. The alkyl chains of the molecules pack into a low free-energy state characterized by van der Waals interactions between the chains. Finally, a tail group is present at the chain terminus. Often, the chemistry of the tail group can be used to control the properties of the interface. Note the that fine structure of the adlayer, including the orientation and packing density, evolve during the formation of the layer [82, 83]. However, very dense layers can be readily produced with a surface coverage that closely corresponds to the closest-packed value expected for a $(\sqrt{3} \times \sqrt{3})R30°$ overlayer at Au (111) $(7.7 \times 10^{-10} \text{ mol cm}^{-2})$ [79]. It is this relative ease of preparation of reasonably well-defined molecular monolayers that has made this method an extremely popular surface modification technique in the last few decades.

There are numerous examples of uses for self-assembled monolayer structures [75, 79, 80] including (but certainly not limited to) growth of nanoparticles, electron transfer studies, biological sensing, and uses as etch resists. An important point for many applications is the ease with which the chemistry and function of the surface can be controlled simply by variation of the tail group. Although SAMs can display good stability to some degree of ambient exposure, their stability is limited when subjected to more extreme conditions. Thus, surface modification procedures that utilize stronger covalent bonds have been developed, as described below.

7.3.3 Layers Anchored with Covalent Bonds

The use of irreversible chemical bonds to modify the surface of metals, semiconductors [28], carbon [84], and other surfaces produces stable modifying layers and has been growing in popularity in recent years. This demand is driven by the need for highly stable modified surfaces that can be exploited in an extensive range of chemical environments and physical conditions. Many of the methods used to modify a surface with covalent linkages stems from classical organic and inorganic chemistry. However, the reaction conditions often need to be adjusted to account for one of the reactants as a surface rather than a distinct chemical or functional group, and quite often the surface needs to be activated in order to obtain efficient modification. In addition, covalent chemical bonds can be formed between a pre-existing nanomolecular layer (e.g., SAM or L-B film) and a secondary layer. In this way, the intended functionality can be achieved using the covalent linkage, but with the advantages offered by self-assembly (high ordering, ease of preparation) available for the initial layer.

There are a large number of covalent modification schemes. Often, they rely on some external stimulus to initiate the chemical reaction that results in the formation of a new chemical bond between the modifier and the surface. Electrochemistry, light exposure, heat, or the addition of a chemical catalyst is often employed to activate the chemical reaction and increase efficiency. To illustrate the variety of modification schemes, we will give some specific examples for modification of metals, carbon, and silicon.

7.3.3.1 Covalent Modification of Metals

The covalent modification of metal surfaces generally follows two approaches: (1) treatment of the metal surface to contain a high density of surface groups such as oxides or hydroxyl groups that will serve to form a bond with the modifying layer [85, 86] or (2) direct reaction of the metal surface with a chemical agent. In the first case, conventional organic chemistry is used treating the surface as a hydroxyl moiety, while in the second case, the direct formation of a metal-modifier bond results. However, in either case, one reactant is confined to the surface of a material and steric hindrance and configurational limitations can pose significant restrictions on the yield and efficiency of the reaction. Thus, in order to obtain dense nanomolecular layers with high coverage, the more aggressive chemical reactions are often favoured.

For the purposes of this Section, we consider self-assembled monolayers to be a distinct class of nanomolecular layers due to the spontaneous nature of formation and the labile nature of the substrate-molecule bond. Instead, we focus here on targeted chemical reactions that result in the irreversible formation of a new covalent bond that anchors a nanomolecular layer on the metal. While some degree of modification can sometimes be achieved by the use of a spontaneous chemical reaction using these methods, most often they greatly benefit from some external assistance. For example, the desired reaction can be initiated by heat, light, an added reagent (such as a radical initiator), or an electron transfer step induced by controlling the substrate potential electrochemically. In the literature, the distinction between covalent modification and self-assembly is often not clear; spontaneity, the energy of the resulting anchoring bond, the number of steps required to prepare the surface, and other, more arbitrary criteria are often used to classify these films.

The modification of surfaces using diazonium chemistry involves the formation of the highly reactive $-N_2^+$ group on the molecular species to be anchored, and can generally begin from primary aromatic amine compounds. Diazotization can either be carried out during the modification (in-situ) [87–95] or separately by organic synthesis to yield an isolated diazonium compound [96]. Modification of a metal surface is then carried out by the reduction of the diazonium moiety, which leaves as N_2 gas and generates an aromatic radical species that can bond to the metal surface. The reduction of diazonium reagents is discussed below for carbon, noting that a similar reaction pathway has been shown for many different surfaces, including a wide variety of metals [97–105]. There may be significant differences, however, between the specific characteristics of diazonium-derived molecular layers on metals compared to those deposited on carbon.

7.3.3.2 Covalent Modification of Silicon

Modification of semiconducting surfaces has been gaining in popularity due to the well-defined nature of these surfaces and the excellent control of the surface structure and crystallinity that is available. While many semiconductors have been modified, the most prominent example is silicon [28] due to its ubiquitous use in the semiconductor industry. A variety of methods is available to form Si-C,

Fig. 7.10 Covalent
modification of Si: using
either an alkyne (*left*) or
alkene (*right*), a covalent
bond results between the Si
surface atoms and the
modifying layer. These
reactions can be activated
with heat, light, or an added
radical initiator (see text)
(Reproduced with permission
from Ref. [28])
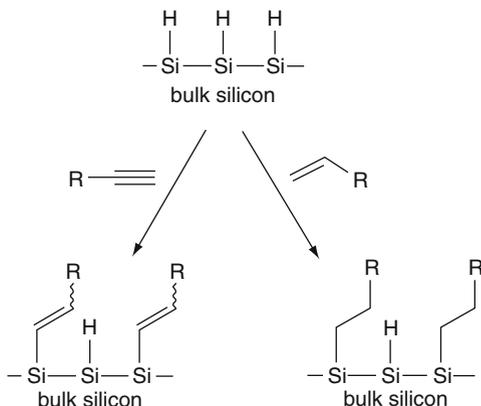
Si-O, and other covalent bonds between Si and a modifying molecule. While a full description of all available methods is beyond the scope of this chapter, we will give an example that illustrates covalent modification of silicon.

Figure 7.10 shows a popular covalent modification scheme that begins with a hydrogen-terminated silicon surface and uses an alkene, alkyne or alcohol functional group to bond the molecular layer [106–108]. Depending upon the specific surface and modifier involved, the reaction can be initiated in at least three ways, all of which involve a radical-mediated modification pathway: through the use of a chemical radical initiator, heat, or UV light. Diazonium reagents have also been demonstrated for forming surface bonds to silicon surfaces [109–112], as well as GaAs and semiconducting carbon nanotubes [113, 114]. The details of the reaction mechanisms and the resulting quality, packing density, surface termination, etc., of the nanomolecular layer are determined by the way the Si surface is prepared, the exact nature of the modifying molecule used, and the initiator. Thus, the choice of method depends on the demands of the application of the resulting modified surface and any limitations on the initial choice of the Si surface.

Many of the applications for modified Si surfaces are similar to that for other types of surfaces, including electronics [31] and biosensors [115].

7.3.3.3 Covalent Modification of Carbon

Carbon surfaces can be modified using a wide variety of chemical reactions. Classical organic chemistry can be carried out using a graphitic carbon surface as the reactant and reactions designed to target the edge plane or basal plane of the substrate. Furthermore, functional groups (such as oxygen containing –OH, –COOH, etc.) are often found at the surface of carbon materials, and these can be used to form chemical bonds. However, for methods that rely on a specific functional group, its concentration is usually increased through pre-treatment prior to modification procedures [11]. On the other hand, some methods do not require any additional specific functional groups to be present, but instead rely on a reactive solution phase molecule to modify the carbon surface in its native form.
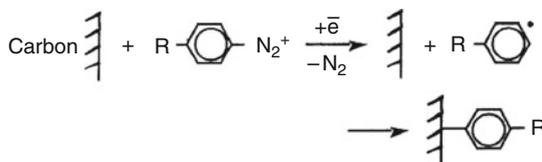
Fig. 7.11 Electrochemical reduction of aromatic diazonium reagents leading a covalently bonded layer, anchored by a carbon-carbon bond. This scheme can also be applied to modify many other surfaces, including metals and semiconductors (Reproduced with permission from Ref. [84])

A very common method for covalent attachment of nanomolecular layers to carbon makes use of diazonium chemistry [8, 11, 105]. The carbon surface to be modified is used as an electrode in a conventional three-electrode electrochemical cell containing a dilute solution of an aromatic diazonium reagent. The carbon electrode potential is controlled to induce reduction of the diazonium reagents, producing a carbon radical that attacks the surface and then bonds to the electrode (see Fig. 7.11). The use of electrochemistry is an advantage for several reasons. First, the electron transfer event that generates the radical species occurs selectively at the surface of the carbon electrode, which confines the reactive species to a thin diffusion layer adjacent to the surface being modified. Second, the number of radical species generated in a given time may be controlled by monitoring the electrolysis current. By carefully controlling the conditions during electrolysis, fine control of the layer thickness can be obtained [41, 116]. Finally, a wide variety of structures can be used, and the conditions during electrochemical depositions can be varied in order to obtain comparable layer characteristics (e.g., thickness) by accounting for the differences in reduction potentials of the diazonium reagents.

Diazonium chemistry is capable of producing highly stable nanomolecular layers that have very high coverage and excellent packing density. This is due, in part, to the aggressive nature of the radical-mediated bonding mechanism and the generation of the radicals at the surface of an electrode. This also, however, can lead to the formation of multilayers for certain molecules under certain conditions, as described in Sect. 7.4.1. Essentially, any site on the surface of the electrode that is capable of reducing the diazonium reagent will produce reactive radical molecules that will find a place to form a bond. This includes the terminus of the first monolayer of bonded molecules, as long as the rate of electrochemical reduction through the monolayer is sufficient to support further radical formation. In practice, some molecules are more prone to form multilayers than others. In addition, for those that do readily form multilayers, the electrolysis conditions can be adjusted to control thickness with excellent resolution (less than 1.0 nm). This can be used to advantage in studies of thickness dependent phenomenon [41]. Diazonium modification may also be used to form patterns on surfaces by micro-contact printing and scanning probe techniques [16, 102, 117–119].

In addition to diazonium chemistry, several other methods have been used to modify carbon surfaces with nanomolecular layers. The electrochemical oxidation of aliphatic amines [84, 120, 121], treatments with alkenes and alkynes (analogous

to that for Si surfaces described above) [122], and azide chemistry [123] are among the most prominent examples.

7.4   Multilayer Surface Modification

The approaches described in Sect. 7.3 for producing monolayers on surfaces are either self-limiting at one monolayer thick, or can be controlled to produce a nanomolecular layer. In all cases, the methods discussed excel at producing layers less than 10 nm thick. There are a variety of surface modification approaches which produce "multilayers" with thicknesses greater than one molecular unit, having total thicknesses from 1 nm to >100 nm. As noted in Sect. 7.1, we will exclude spin-coating and vapour deposition, but will consider "reactive" procedures involving chemical interactions between the substrate and modifying molecules. Examples include radical-based reactions which can form multilayers, "layer-by-layer" techniques which alternate electrostatically or covalently bonded layers, and "electropolymerization" in which the modification is driven electrochemically. Schematics and descriptions of these processes are provided in Sections 7.4.1–7.4.3.

7.4.1   Diazonium Reduction and Related Techniques

Although early reports on diazonium reduction to form covalent bonds on C, Si, and metals assumed that the resulting film was a monolayer, there are conditions where multilayers can form, and films up to >20 nm thick can be produced. As described in Sect. 7.3.3.3, reduction of a diazonium ion produces a phenyl radical which rapidly binds to many conducting surfaces to form the first monolayer. Since the monolayer is not a perfect insulator, additional electrons may transfer through the film to reduce more diazonium ions and the associated reactive radicals, as shown in Fig. 7.12, reactions 1 and 2. In the case of phenylacetic acid, nitrophenyl, and dimethylaminophenyl diazonium ions, the process can be continued to produce disordered, 15–20 nm thick multilayers, corresponding to >20 molecular layers [124]. It is likely that the film itself becomes conductive by partial reduction, since the thicknesses achieved are much greater than the tunnelling distance for electrons [116, 125]. In some cases, solvent molecules or ions may be incorporated into the multilayer, which may resemble a porous "sponge" permeable to species in solution [102, 126, 127].

   The degree of disorder in diazonium-derived multilayers varies significantly with the molecular structure, the substrate material [103, 105, 118, 129, 130], and the film-formation conditions. Atomic force microscopy shows that film growth can be quite uniform, with only minor increases in surface roughness as the film thickness increases [116]. FTIR and Raman spectroscopy of both mono- and multi-layers on flat carbon surfaces showed tilt angles of 31–44° relative to the surface normal, and this angle was similar for both mono- and multi-layer films
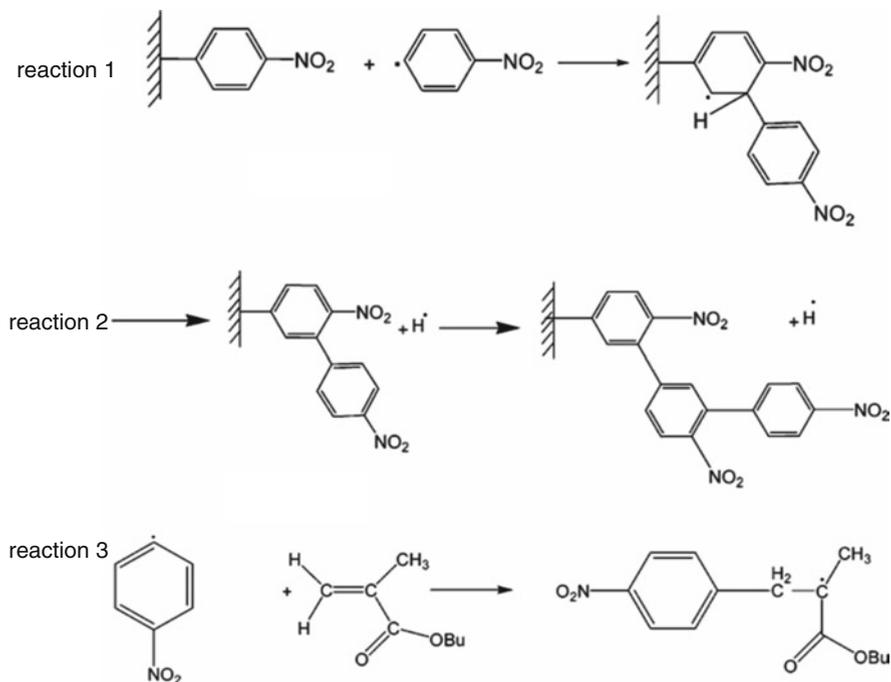
Fig. 7.12 Reactions 1 and 2 show the growth of multilayer films from diazonium precursors. Reaction 3 illustrates the SEEP process, in which olefin polymerization is induced by an electrogenerated diazonium radical. Alternatively, the SEEP process could be initiated from a surface radical (Reproduced with permission from Ref. [128])

[131]. The reader should be cautioned, however, that much of the available characterization data for diazonium-derived multilayers was obtained on carbon surfaces, and the behavior on metal or silicon surfaces may be quite different. Furthermore, the thickness and uniformity of diazonium-derived multilayers should be verified for the particular conditions employed for film formation, usually by AFM [116, 127, 132] and/or ellipsometry [114]. With suitable controls, the ability to grow molecular layers via diazonium reduction provides the benefit of forming films ranging from ~1 to >5 nm thick using similar reagents and procedures. This property of diazonium-derived multilayers was used to construct the attenuation plot of Fig. 7.6 for aromatic films with thicknesses in the range of 2.2–5.2 nm [41].

As noted in Sect. 7.3.3, radical reagents such as those generated by diazonium reduction are quite reactive, and usually form irreversible covalent bonds with the substrate, each other, or both. A beneficial result is high surface coverage, with the more reactive "bare spots" being sites for radical generation and irreversible absorption. A recent development exploits this reactivity in a different manner, by initiating a radical polymerization with a phenyl radical generated from a diazonium ion [128, 133], as shown in Fig. 7.12. Reaction 1 shows formation of a second nitrophenyl layer by reduction and bonding of nitrophenyldiazonium ion to

an initially formed monolayer. In this case, a radical center remains in the nitrophenyl film, but loss of an H atom may promote propagation past the bilayer (reaction 2). If an olefin is present, either the surface radical or an electrogenerated phenyl radical may initiate polymerization of the olefin (reaction 3). It is possible for the olefin to be contained in an emulsion, leading to the term "Surface Electroinitiated Emulsion Polymerization (SEEP)". The SEEP process has the advantage of covalent bonding of the polymer to the surface, and initiation of polymerization directly on the surface of interest.

7.4.2   Electropolymerization

There is a long history of the production of conducting polymers by electrochemical rather than chemical means, generally termed *electropolymerization*. Most conducting polymers start with a small monomeric unit such as pyrrole or thiophene, which are chemically oxidized in solution to produce radicals which then bond to nearby monomers. Free radical polymerization ensues, leading to a conducting polymer, often in a partially doped state. Alternatively, the initial radical may be generated electrochemically at a conducting or semiconducting surface, causing the polymer film to grow on the electrode surface. It is often the case that the polymer itself is readily oxidized at a potential close to that of the monomer, thus "doping" the polymer to a conductive state. The growing polymer surface then acts as its own electrode, permitting possibly thick films, readily >100 nm thick. Unlike chemical oxidation, the current and total charge used to oxidize the monomer may be controlled accurately, and initiation of the polymerization at the conducting or semiconducting surface assures a conformal and quite uniform film. Examples of the procedure for electrochemical formation of polypyrrole [134–137], polythiophene [138–140], and polyaniline [141, 142] show that the composition, morphology and thickness of the polymer film are strong functions of the formation conditions, notably the magnitude and form of the potential program used to oxidize the monomer. It is often advantageous to provide an "initiator" on the surface to act as a sight for initiating polymerization. For example, a chlorosilane derivative of thiophene bonded spontaneously to indium-tin oxide can serve as a nucleation layer for polymer growth [13], and "click" chemistry has been used to form a thiophene "termination" layer on conducting diamond [143].

In both cases, the resulting polymer film was more uniform than "random" nucleation on an unmodified surface. A scheme for providing a polyaniline seed layer using diazonium chemistry is shown in Fig. 7.13, in which diazonium surface modification was used to create a monolayer of diphenylamine on a carbon surface [144]. Subsequent oxidation of aniline produced a polyaniline film similar to that formed without the seed layer, and which was more chemically and thermally stable.

Electrochemical methods may also be used to form "redox polymers", in which the monomeric unit contains a redox center such a ferrocene [145, 146] or several Ru or Os complexes [147–149]. Electrochemistry may also be used to form patterns on
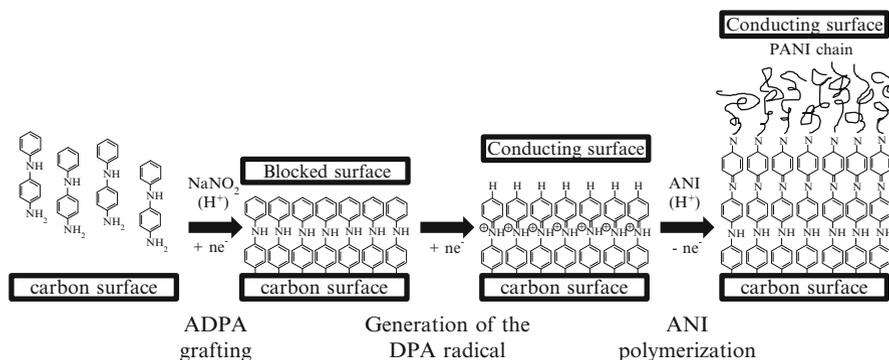
Fig. 7.13 Production of a stable polyaniline layer using a "seed" layer deposited using diazonium chemistry (step 1, resulting in a "blocked" surface) and activated by reduction (step 2) of the surface layer to produce a conductive surface upon which polyaniline can be grown (step 3) (Reproduced with permission from Ref. [144])

surfaces, on the monolayer level as noted in Sect. 7.3.3 above, but also of polymers [150], and to etch patterns on carbon surfaces [151, 152]. A review of electrochemical methods for micro- and nanopatterning has appeared recently [153].

7.4.3 Layer-by-Layer Deposition of Molecular and Atomic Multilayers

Thick films may be generated on surfaces by alternation of two materials, with the general term being "layer-by-layer deposition". A variety of chemical interactions between layers has been exploited to produce possibly thick multilayers, but generally each layer deposition is self-limiting. An example is shown in Fig. 7.14, based on a sequence of reactions between $C = C$ bonds and SH groups, commonly called the "thiol-ene" reaction [154]. A "diene" molecule containing $C = C$ bonds on both ends is initially bonded to silicon, to form a $C = C$ terminated monolayer. Then a "dithiol" with SH groups on both ends is bonded to the terminal $C = C$ bond with UV light and the thiol-ene reaction, resulting in an SH terminated layer. Then the thiol-ene reaction is repeated with alternating layers of diene and dithiol to build up a multilayer. Unlike spin coating or polymerization, the multilayer is formed one layer at a time, so that the total thickness is a linear function of the number of layer-by-layer cycles. In a different approach, formation of a covalent Si-O bond by reaction of a chlorosilane end group with an alcohol or ether can form the basis of a layer-by-layer structure of interest as a dielectric in organic thin-film transistors [155]. Alternating layers containing metal or metal oxide centers and organic molecules have been made, based either on electrostatic bonding or coordination bonds formed between metal ions and electron-rich ligands [156]. A non-vacuum analog to atomic layer deposition has been reported, which alternates electrochemical deposition of single atomic layers [157–160]. With proper conditions, single, epitaxial atomic layers of
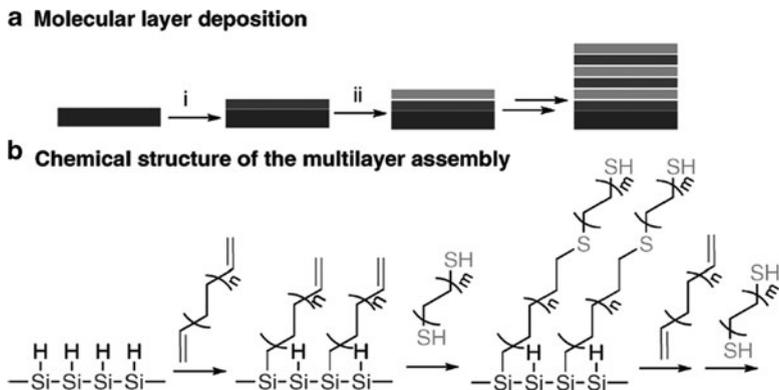
Fig. 7.14 Layer-by-layer growth utilizing the thiol-ene reaction scheme that links together C = C groups with SH groups (Reproduced with permission from Ref. [154])

Cu, Pt, Pb, Se, and other materials may be alternated to produce an ordered multilayer. The approach is a much lower cost alternative to vapor-phase atomic layer deposition (discussed in Chap. 6), and has been shown to produce multilayer structures with interesting electronic properties.

Electrostatic layer-by-layer formation is simpler and more common than "reactive" methods, and exploits the attractions between oppositely charged end groups to stabilize the multilayer [161–165]. Electrostatic interactions have been used to assemble the two components of organic photovoltaic cells, with reported increases in photoconversion efficiency [156, 166, 167].

7.5   Conclusion and Outlook

Although not intended to be comprehensive, this overview of surface modification techniques indicates the great variety of available methods, both in terms of surface chemistry and the properties imparted to the surface. It is noteworthy that many of these modification procedures were developed relatively recently, i.e. in the last two decades. The ability to form covalent bonds between a surface and a molecule with particular chemical properties is a significant advance over the time-tested approaches based on oxide formation, vapour deposition, and spin coating. The advent of molecular electronics was enabled by the ability to make oriented monolayers of molecules on surfaces, and it is now possible to make electronic devices with single-molecular layer active components [3, 8]. It is likely that the initial practical application of surface modification at the monolayer level will involve a process step for making conventional semiconductors, such as a "primer" for Damascene copper plating. However, the growing importance of surfaces to nanofabrication as the feature size continues to decrease provides a strong driving force for more widespread use of surface modification chemistry.

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