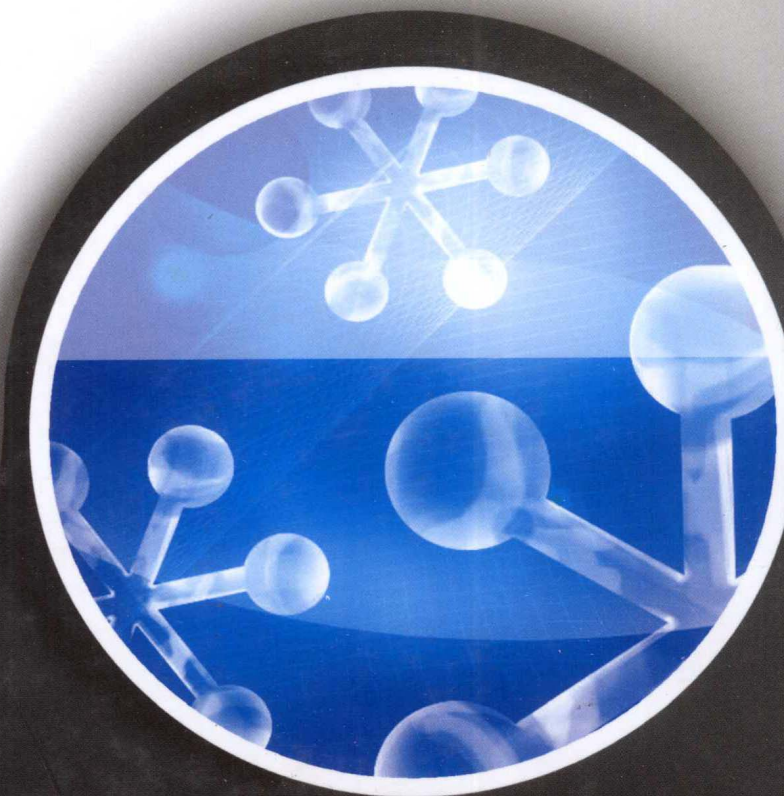


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纳米制造手册

Handbook of Nanofabrication

Gary Wiederrecht



Handbook of Nanofabrication

纳米制造手册

Gary Wiederrecht

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by **Gary Wiederrecht**

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前 言

所有纳米科学的重要目标均有赖于用可靠的方法制造纳米结构。纳米制造面临很多挑战，首先是面向纳米结构的广泛应用、材料和几何构型等。应用包括纳米电子学、纳米光子学、纳米机械学、纳米催化、纳米天线、纳米传感器等。所需的材料具有广泛的性质：从金属至绝缘体，从硬的到软的，从惰性到反应性，从发光的到淬灭的，从晶体至玻璃体等。因此，大量的元素、化合物和合金都已经成为纳米结构和纳米制造的工具。此外，所需的纳米几何构型包括盘状、棒状、孔洞状、角锥状等，以及隔离的或偶联的纳米颗粒之间相互作用程度的可调性。纳米结构在一维、二维或三维方向上的随机或周期性的长程有序排列程度也是我们需要考虑的关键问题。显然纳米制造是一件艰难的任务。

针对这些结构的纳米制造方法如同下一代应用所需的材料、应用和几何构型一样，具有多样性。这些方法可分为“自上而下”和“自下而上”两种。自上而下制造方法指的是在宏观材料（例如薄膜）上形成纳米结构。因此，自上而下方法指的是电子束光刻（EBL）或聚焦离子束光刻（FIB）等方法。在这些方法中，聚焦的电子或离子被用在较大的构件上刻蚀纳米结构。相反，自下而上方法则是利用较小的单元组装纳米结构，例如胶体合成方法通过溶液中离子的化学中和形成中性原子，由于该原子的溶解度突然降低而发生团聚现象，进而组装形成胶体粒子。这种方法常用于制造等离子金属纳米颗粒或者半导体量子点。自下而上组装也涉及较大的层次结构的组装，例如，胶体自组装形成较大的结构以用于特定的目的。它们可应用于各种各样的场合，如构建三维周期光子能隙结构或周期结构，用于研究纳米尺度上的电荷输运过程。

与上述图案化方法同等重要的是沉积方法。在很多情况下，自上而下或自下而上的方法产生的图案不符要求。在这种情况下，这种图案化的材料仅用作模板，以通过沉积来产生人们感兴趣的真正纳米结构，对于光子晶体尤其如此，例如，自组装的胶体作为模板在其间隙区域沉积高折射率材料。另一个例子是等离子纳米结构，在这种结构中金属沉积在聚合物膜内由电子束光刻所形成的图案化孔洞中。

在很多情况下，这些纳米制造的进展已经产生了令人惊异的物理和化学发现及现象，而这是那些较宏观的结构所不能比拟的。例如一个新现象就是半导体材料中的电子态的限域而产生量子化的电子跃迁，而不是体相半导体中典型的能带结构行为。与体相材料相比，这些纳米结构材料具有全新的光学和电子性质，例如窄的发射线宽、产生多激子可用于太阳能转换、纳米光源等。其他的新现象包括利用纳米结构制造在可见光波长范围内具有负折射率的材料（虽然目前仅针对可见光谱内波长最长的光波，并且该材料具有很大的吸收损失）。由于负折射率材料不以其他方式存在，因此这些超颖材料根本没有类似物。

在基础科学进展之外，纳米制造也为解决具有重要意义的技术难题提供方法。例如，由于硅晶体管的尺寸减少至依赖于单个电子的传输，因此电子集成电路将很快需要

一种全新的构筑方式。此外，这种尺寸具有大量的工程难题，因为高密度的晶体管形成了巨大的热负荷，并且需要更复杂和昂贵的制造工具进行光刻。当晶体管的大小降低至10nm的尺度，纳米制造的进展已使完全不同的材料能被应用于下一代晶体管。这些晶体管包括基于碳纳米管或石墨烯的晶体管，甚至是单分子晶体管。纳米制造对于下一代能量转换和储存器件也非常关键，例如纳米结构锂电池可改善再充电和功率输出性能。相对于体相材料而言，纳米颗粒巨大的比表面积对于新的高效催化过程也是很重要的。

本书描述了在纳米制造领域真正领导者的最近工作。这里，描述的工作覆盖了自上而下和自下而上的光刻方法。在自上而下的方法中，Tennant 和 Bleier 阐述了电子束光刻的前沿进展，电子束光刻可能是自上而下制造纳米结构的最常用方法。Sreenivasan 等在纳米压印光刻的章节中阐述了大面积可靠地制备纳米结构图案的新方法。Siringhaus 等在另一章描述了在制造中具有很大应用潜力的方法，如喷墨印刻。在自下而上的方法中，本书描述了制备优美的长程有序纳米结构的方法，包括定向组装（Rosei and Macleod）、生物调控组装（Luo 等）和图案化的分子键联（Reinhoudt 等）方法等。本书也介绍了针对下一代纳米应用和器件的重要纳米制造方法，包括应用于催化领域的光学活性结构的制备方法（Baddeley and Held）和纳米结构分子马达（Credi）。

可以确信，随着纳米技术的兴起，纳米制备方法的重要性和数量将会急剧增长。显然，不同领域的科学家和工程师从生物、化学和物理方面获得的启发使他们在纳米制造领域做出了巨大的贡献。因此，我们相信不同领域的读者们将会在这一跨学科的主题中发现自己感兴趣的材料，甚至可能获得发明下一代纳米制造方法和工具的新灵感。

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Preface

All of the grand goals for nanoscience are dependent upon reliable ways to fabricate nanostructures. The challenges to nanofabrication are many, beginning with the incredibly broad range of applications, materials, and geometries that have been proposed for nanoscale structures. Applications include nanoelectronics, nanophotonics, nanomechanics, nanocatalysis, nanoantennae, and nanosensors, to name only a few. Materials are needed that possess almost every conceivable range of properties: metallic to insulating, hard to soft, inert to reactive, luminescent to quenched, crystalline to glassy – the list goes on. As a result, an immeasurable number of elements, compounds, and alloys have been subject to nanostructuring and nanofabrication tools. Add to this the range of geometrical nanostructures required: disks, rods, holes, pyramids, etc., and a range of tunability in the degree of interaction between nanoparticles to be isolated or closely coupled. The degree of long range ordering, either random or periodic, can also be a critical consideration, as well as whether that ordering extends in one, two, or three dimensions. It is clear that nanofabrication is a daunting task.

The range of nanofabrication routes towards these structures is almost as diverse as the materials, applications, and geometries needed for next-generation applications. The approaches can begin to be compartmentalized by separation into either a “top-down” or “bottom-up” approach. Top-down fabrication refers to methods where one begins with a macroscopically dimensioned material, such as a thin film, into which is placed nanostructured defects. Top-down thus refers to approaches such as electron beam lithography (EBL) or focused ion beam lithography (FIB). In these cases, either focused electrons or ions are used to carve nanostructures out of larger structures. Alternatively, in the bottom-up approach, one begins to assemble nanostructures from smaller units. Examples include colloidal synthesis, where frequently the colloids are literally assembled from single ions in solution that are chemically neutralized so as to produce an aggregation process resulting from a sudden lack of solubility of the now neutral atom. Such processes are frequently used for the creation of plasmonic metal nanoparticles or semiconductor quantum dots. Bottom-up assembly also refers to the assembly of larger hierarchical structures, where, for example, colloids self-assemble into larger structures for a particular purpose. These can be for diverse applications such as the creation of three dimensionally periodic photonic bandgap structures or periodic structures for the study of charge transport processes at the nanoscale.

Equally important to the patterning steps described above are the deposition methods. In many cases it is not enough to produce a pattern from top-down or bottom-up methods. In these cases, the patterned material simply serves as a template for the deposition of the true nanostructured material of interest. This is frequently the case for photonic crystals where, for example, the self-assembled colloids serve only as a template for the high refractive index material that is deposited in the interstitial regions of the template. Another example is plasmonic nanostructures, where metal is deposited into the EBL patterned holes in polymer films.

In many cases, these nanofabrication advances have produced stunning physical and chemical discoveries and phenomena that have no analog in larger scale structures. One example of new phenomena is the confinement of electronic states in semiconductor materials to produce quantized electronic transitions rather than band structure behavior that typifies bulk semiconductors. Entirely new optical and electronic behavior is produced in such materials compared to their bulk counterparts, such as narrow linewidths for emission, multiexciton generation for solar energy conversion, nanoscale light sources, etc. Other examples of new phenomena include the use of nanostructuring to produce materials with a negative index of refraction at

visible wavelengths (although, at this date, for the longest wavelengths in the visible spectrum and for materials with significant absorption loss). These metamaterials have no analogs in nature as negative index materials do not exist otherwise.

In addition to basic science advances, nanofabrication is leading the way towards solving technological challenges of great importance. For example, entirely new architectures in electronic integrated circuitry will likely be needed soon, simply because silicon transistors are approaching sizes that will rely on the transport of a single electron. Furthermore, enormous engineering challenges are present at this length scale, as the high density of transistors create tremendous heat loads and the lithography requires ever more complex and costly fabrication tools. As transistors scale down to the 10 nm length scale, nanofabrication advances have enabled totally different materials to be explored as next generation transistors. These include carbon nanotube or graphene-based transistors, or even single molecule transistors. Nanofabrication is also proving critical for next generation energy conversion and storage devices, such as nanostructured lithium in batteries for improved recharging and power delivery properties. The high surface-to-volume ratio of nanoparticles relative to bulk materials is also proving important for new, efficient catalytic processes.

This book describes the recent work of true leaders in the field of nanofabrication. The work described herein covers both the bottom-up and top-down lithography approaches. In the top-down category, Tennant and Bleier describe the state-of-the-art in electron beam lithography, perhaps the most used means to create nanostructures from the top-down. Novel approaches to patterning nanostructures reliably and over large areas is described in the chapter on nanoimprint lithography by Sreenivasan et al. Routes that have great potential in manufacturing, such as inkjet printing, are described in the chapter by Sirringhaus et al. In the bottom-up category, methods that produce nanostructures with elegant long range order are described. These include directed assembly (Rosei and Macleod), bio-mediated assembly (Luo et al.) and patterned molecular binding (Reinholdt et al.) methods. Important nanofabrication methods towards next generation nanoscale applications and devices are also described. These include routes towards optically active structures with applications in catalysis (Baddeley and Held) and nanoscale molecular motors (Credi).

It is assured that the importance and number of nanofabrication approaches will grow dramatically in the coming years with the rise of nanotechnology. It is clear that scientists and engineers working from many different directions and finding their inspiration from biological, chemical, and physical sources, are all contributing greatly to the field of nanofabrication. Thus, it is our belief that readers from all fields will find material of interest in this multidisciplinary topic, and perhaps even find additional inspiration to invent the next-generation nanofabrication methods and tools.

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1 Directed Assembly of Nanostructures

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1.1 Introduction

The realization that nanoscale matter often behaves differently with respect to the same materials in the bulk form has prompted a wealth of research aimed at understanding, characterizing, describing, and predicting 'nano' [1,2]. However, while 'nanotechnology' has been a buzzword for almost two decades, it has delivered fairly little so far in terms of new technologies, that is, new products that are commercialized and used by the general public.

One of the great promises of nanotechnology is the ability to do more in the same space: to advance our current technologies through miniaturization, so that each crop of electronics is smaller, faster, and more powerful than the one before. This is the manifestation of Moore's law [3], the now-famous 1965 empirical prediction by Gordon Moore (who later went on to co-found Intel) that the number of transistors accommodated in a chip of given size doubles roughly every two years. The semiconductor industry has used this prediction as a roadmap over the last three decades. As the limits of this down-scaling approach the dimensions of single molecules and atoms, the discrepancy between nanoscale and bulk behavior has become evident. While this is detrimental in some situations, for example, in scaled-down versions of larger transistors that can exhibit problematic behaviors, such as unexpected leakiness, at nanoscale dimensions [4], it opens the door to opportunities for custom-designing new circuit architectures to exploit behaviors unique to the nanoscale. For example, quantum size effects [5,6], confinement of excitons [7,8], and high surface-to-volume ratios [9] can all impart new, unexpected, and potentially useful behavior to nanoscale systems.

To capitalize on the full potential of nanostructured materials and their properties, it is necessary to develop the ability to purpose-build nanoscale systems, a task which hinges on the precise placement of appropriate nanoscale building blocks in two and three dimensions (2D and 3D). This approach is generally referred to as 'bottom-up', implying the spontaneous formation of a desired architecture. This approach provides a diametric counterpoint to

the 'top-down' techniques (typically lithographic techniques, which are very precise but must adhere to Rayleigh's equation, and therefore cannot resolve fine nanoscale features [10]) used in the contemporary fabrication of semiconductor devices [11], and provides an intuitive mechanism for building architectures from countable numbers of atoms or molecules.

The use of molecules as the basic building blocks of nanoscale structures capitalizes on a wealth of knowledge that can be obtained from the study of biological systems [12–14]. Supramolecular chemistry [15], applied to nanoscale design [16–18], additionally benefits from the capabilities of synthetic chemists, since molecules can essentially be custom-designed for form and functionality salient to specific systems and devices [19,20].

The aim of this article is to provide an overview of the tools and techniques available for building nanoscale architectures from molecular building blocks, limiting ourselves primarily to a discussion of the geometry of molecular assemblies at surfaces, that is, structures confined to 2D. Outside of our focus will be atomic structures [21–24], clusters [25, 26], and quantum dots [27–29], all of which provide their own unique set of challenges and rewards. Our focus will be on the major experimental advances made via surface physics and chemistry over the past 25 years. The majority of the investigations that we describe have been performed with scanning probe microscopies (SPM), specifically, scanning tunneling microscopy (STM) [30–34]. The STM is a remarkably versatile instrument capable of imaging conducting and semiconducting surfaces [35], probing their electronic characteristics [36], investigating the vibrational characteristics of adsorbed molecules [37,38], interacting with the surface or adsorbates to produce new geometric and electronic configurations [39–41], or even to initiate chemical bond formation [42,43]. Many excellent books and reviews are available, describing various facets and uses of SPM [44–64].

After briefly discussing the fundamentals of directing nanoscale assembly of surfaces, as well as the most salient experimental techniques for probing these

systems, we will provide an overview of significant experiments grouped by the type of interaction used to pattern the molecules: strong bonding between the molecules and the underlying surface, molecular self-assembly driven by hydrogen bonding, and metal–organic coordination, using inclusion networks to position molecules, and, finally, surface-confined polymerization for producing robust, covalently bonded structures. An emerging area that we will unfortunately neglect due to space limitations is the formation of ordered multicomponent assemblies driven by curved surfaces. We refer interested readers to the relevant literature [65–77].

1.2 Fundamentals of Directing Nanoscale Assembly at Surfaces

There are two competing types of interactions that control the formation of patterns at surfaces: (1) molecule–molecule and (2) molecule–substrate [78]. In most cases, bottom-up assemblies depend on the balance between (1) and (2); however, depending on the choice of surface (2) can be either the dominant interaction or can be almost suppressed, with various intermediate regimes. For example, graphite surfaces are essentially inert and therefore their participation in pattern formation is usually minimal besides providing regular and planar array of adsorption sites. On the other hand, reconstructed silicon surfaces are characterized by a high density of reactive unsaturated dangling bonds (DBs) that interact strongly with molecules upon adsorption, often causing the molecules to fragment as in the case of cyclo-addition reactions [79]. With respect to (1), most intermolecular interactions used so far are noncovalent in nature, that is, they may induce the formation of long-range ordered patterns, yet, are easily disrupted because of their weak bonding. This aspect has several advantages, including the ‘self-repair’ mechanisms that are well known in supramolecular chemistry: defects tend to disappear as the interactions locally break up the pattern forming a new ordered one devoid of defects. Notably, hydrogen bonding and metal–organic coordination are noncovalent interactions frequently employed to form ordered patterns in both 2D and 3D. van der Waals forces alone can usually lead to the formation of local patterns, yet their lack of directionality is usually a barrier to producing long-range patterns.

Stronger molecule–molecule interactions can lead to the formation of covalent bonds. While these are

often desirable to obtain more robust structures with interesting mechanical and electronic properties, they are significantly more difficult to direct and their use for nanostructure formation at solid surfaces has been explored only in the last decade. Some elegant examples of covalent architectures, together with a discussion of their challenges and limitations, will be provided in Section 1.7.

1.2.1 Noncovalent Interactions between Molecules

1.2.1.1 Hydrogen bonding

Hydrogen bonds are formed between an electronegative atom and a hydrogen atom bonded to a second electronegative atom [80]. The strength of the hydrogen bond depends on the electronegativity of the atoms; Table 1 classifies hydrogen bonds as very strong (e.g., $[F \cdots H \cdots F]^-$), strong (e.g., $O-H \cdots O=C$), or weak (e.g., $C-H \cdots O$) depending on the bond energy, which ranges from 40 to $<4 \text{ kcal mol}^{-1}$, respectively. The directionality of the bond increases with strength. For crystal engineering, the ‘strong’ hydrogen bond is perhaps the most useful type [81,82]. For example, in the systems we describe in this article, hydrogen bonds between carboxylic groups ($O-H \cdots O=C$) are often used to drive self-assembly.

1.2.1.2 Metal–organic coordination

The attraction between an organic ligand and a metal center provides an alternative route to creating directional associations at surfaces. Metal–organic coordination provides a stronger association than the commonly employed modes of hydrogen bonding (typically in the order of $50\text{--}200 \text{ kJ mol}^{-1}$ in 3D compounds) [84], and can confer various geometrical motifs due to the flexibility of the coordination modes available in transitional metals [85].

1.2.2 Molecule–Surface Interactions

The attraction between a molecule and an underlying surface is typically characterized as either physisorption or chemisorption, depending on the strength of the interaction. Physisorption generally refers to van der Waals interaction, and has a maximum interaction energy of about 60 kJ mol^{-1} for a small molecule [86]. Chemisorption implies higher interaction energy due to a significant charge rearrangement in the adsorbed molecule to facilitate the formation of a covalent or ionic bond with the surface. This is obviously the dominant case for molecules on semiconductor

Table 1 Properties of very strong, strong, and weak hydrogen bonds (X—H...A)

	Very strong	Strong	Weak
Bond energy (kJ mol ⁻¹)	63–167	17–63	<17
Examples	[F...H...F] ⁻ [N...H...N] ⁺ P—OH...O=P H—A ≈ X—H	O—H...O=C N—H...O=C O—H...O—H H...A > X—H	C—H...O N—H...F—C O—H...π H...A >> X—H
Bond lengths			
Lengthening of X—H (Å)	0.05–0.2	0.01–0.05	≤0.01
X...A range (Å)	2.2–2.5	2.5–3.2	3.0–4.0
H...A range (Å)	1.2–1.5	1.5–2.2	2.0–3.0
Bonds shorter than vdW	100%	Almost 100%	30–80%
X—H...A bond angle range (°)	175–180	130–180	90–180
kT at room temperature	>25	7–25	<7
Effect on crystal packing	Strong	Distinctive	Variable
Utility in 3D crystal engineering	Unknown	Useful	Partly useful
Covalency	Pronounced	Weak	Vanishing
Electrostatics	Significant	Dominant	Moderate

Adapted with permission from Desiraju GR and Steiner T (2001) *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford: Oxford University Press.

surfaces; on metal surfaces chemisorption strength depends on whether the metal has a d-band (the absence of which leads to relatively weak chemisorption), on the filling of the adsorbate-metal antibonding d-states, and on the orbital overlap between the adsorbate and the surface [87,88]. In general, for transition metal substrates, the reactivity of the surface decreases from left to right across the periodic table, and from top-to bottom [89]. We avoid using the total adsorption energy to distinguish between physisorption and chemisorption since complex molecules can interact with the surface over a large area, leading to a total physisorption energy that can be comparable to chemisorption energies for smaller molecules even in the absence of charge rearrangement.

1.2.2.1 Common surfaces for studies of molecular assembly

1. *Highly oriented pyrolytic graphite*. While its constituent graphene sheets have been the source of extremely intense investigation recently [90–98], highly oriented pyrolytic graphite (HOPG) holds its own place of importance in ambient and solution studies of molecules on surfaces. One reason for this is the ease with which a clean, flat surface can be prepared and used: an HOPG crystal can be cleaved with adhesive tape, and the exposed clean surface remains stable in air for hours. These properties are a direct consequence of the bonding between the carbon atoms. Each atom is sp² hybridized and bonded in-plane to three nearest-neighbors to form

graphene sheets, with the remaining electron contributing to a delocalized π-bond between the sheets.

The π system at the graphite surface is advantageous for studies of aromatic molecules, since π–π interactions stabilize the molecules on the surface. Long-chain alkanes can also adsorb stably, with their molecular axis oriented parallel to the HOPG surface [99,100]. In this configuration, the periodicity of the alternate methylene groups along the alkane molecule (2.51 Å) is very nearly commensurate with the spacing of the hexagons in the graphite surface (2.46 Å), providing strong molecule–surface interaction [101]. The subsequent formation of an alkane monolayer is stabilized by van der Waals interactions.

It is important to note that care must be taken in the interpretation of STM images obtained from HOPG surfaces, since defects in the graphite (e.g., those introduced by the rotation of subsurface graphene, etc.) [102–105] can be easily misinterpreted as molecular features [106,107].

2. *Cu(110)/Cu(111)*. The face-centered cubic (fcc) structure of copper leads to different atomic geometries on its low-energy faces: Cu(100) is fourfold symmetric, Cu(110) is twofold symmetric, comprising atomic rows, and Cu(111) is threefold symmetric, comprising close-packed atoms. The (110) and (111) surfaces (**Figure 1**) are extensively used as substrates in molecular assembly experiments. The surfaces present distinct characteristics to molecular adsorbates: besides the obvious difference in geometry, the open structure of (110) is associated with a higher adsorption reactivity than the closed (111) structure

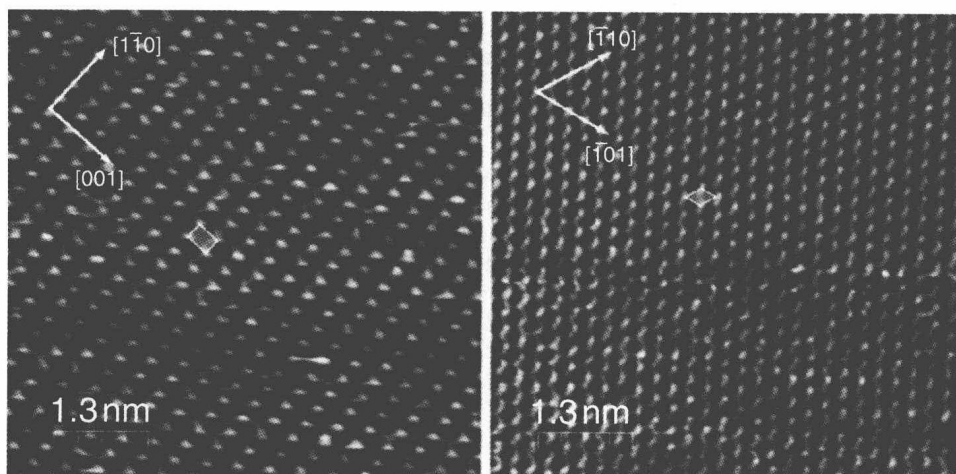


Figure 1 STM images of Cu(110) (left) and (111) (right). Unit cells are outlined in white, and surface directions are specified. STM image parameters: $V_b = -0.4$ V, $I_t = 1.5$ nA (left), $V_b = -0.2$ V, $I_t = 0.8$ nA (right). Courtesy of J. A. Lipton-Duffin.

[108]. The two surfaces are accordingly used in different contexts, with (111) being used to favor molecule–molecule interactions and (110) being used to impose a twofold symmetry on the molecular building blocks (see Section 1.5 for examples). The anisotropy of (110) has additional implications for the diffusion of adsorbates, which is enhanced parallel to the $[1\bar{1}0]$ direction [109,110].

3. *Au(111)*. The inclusion of an extra Au atom once every 22 atoms along $[1\bar{1}0]$ leads to a massive, strain-induced $(22 \times \sqrt{3})$ reconstruction of Au(111) [111,112]. The unit cell comprises both hexagonal close-packed (hcp) and fcc sites, with a narrow band of bridge sites between the two. These bridge sites form the characteristic herringbone bands evident in STM images (Figure 2). The spatial and electronic [113,114] inhomogeneities introduced by this reconstruction can lead to a templating effect for adsorbates introduced to the surface. Both atomic [115,116] and molecular [117] species have been demonstrated to preferentially adsorb at the ‘elbows’ of the herringbones.

Although the Au(111)- $(22 \times \sqrt{3})$ surface can be prepared on a single-crystal metal sample using the usual ultrahigh vacuum (UHV) techniques [118], it can also be prepared on thin films of gold deposited on mica [119–121]. The films can be easily prepared by vacuum deposition of gold onto mica, with subsequent flame-annealing to improve the quality of the substrate, or can be purchased commercially. Gold on mica substrates is amenable to study in ambient, or in solution.



Figure 2 STM image of the Au(111)- $(22 \times \sqrt{3})$ herringbone reconstruction. Obtained from http://ipn2.epfl.ch/LESEN/jvb/collection/coll_au111.htm.

4. *Si(001)*. The electronic properties of Group IV semiconductors have made them the cornerstone of modern devices [122]. Growing useful nanostructures on a semiconductor surface is therefore of considerable interest, since this approach offers the opportunity to integrate novel technologies with established ones. We focus here the Si(100) surface, which is nearly ubiquitous in the microelectronics market [123].

The Si(001) surface has been described in many insightful reviews [124–126,123], so we will provide only a brief sketch of the surface structure. The

Si(001) surface reconstruction is $c(4 \times 2)$ at low temperature, and (2×1) at room temperature [127, 128]. This surface periodicity results from formation of asymmetric silicon dimers [129], with the $2 \times$ periodicity aligned along $[\bar{1}10]$ (traditionally, a surface that is $2 \times$ along the equivalent $[110]$ is referred to as (1×2) .) The dimerization results in a reduction of the number of surface DBs from one per atom to one per dimer. These remaining DBs mean that even the dimerized surface is quite reactive; exposure to hydrogen passivates the surface through the formation of one of several hydrogen terminations, depending on conditions of preparation [130]. Reactive DB sites can persist as defects after passivation [131], or can be introduced in a controlled manner by desorbing a hydrogen atom with a voltage pulse from the STM tip [132].

1.3 Patterned Bonding between Molecules and Surfaces

In this section, we will provide an overview of two rather different methods of spatial control over molecular bonding at surfaces. In Section 1.4.1, we will discuss chemical chain reactions that lead to the formation of molecular lines covalently bonded to a silicon surface. In Section 1.4.2, we will discuss a more general technique for molecular positioning through the selective patterning of substrates to delineate reactive regions on a surface. This approach can be used to guide covalent molecule–substrate bonding or to confine molecular self-assembly to a predefined area.

1.3.1 Chemical Chain Reactions

Self-propagating directed growth via chemical chain reactions represents an extremely appealing mechanism for fabricating molecular architectures. As a general schema, the growth of a molecular architecture via a chemical chain reaction requires a nucleation site, at which a molecule will attach in such a way so as to create a second nucleation site. Attachment of a molecule at this site will create a third nucleation site, and so on. The power of this technique lies in the simplicity of its execution: once the initial nucleation sites are created, the subsequent chemical chain reaction can be carried out quickly, and in parallel, that is, the growth of multiple structures can be carried out simultaneously.

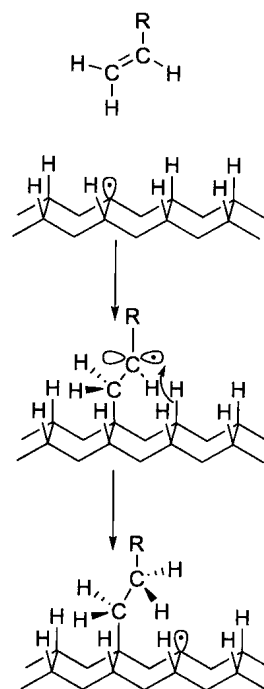


Figure 3 Schematic illustration of an alkene reacting at a silicon dangling bond in the first step of a chemical chain reaction. From Lopinski GP, Wayner DDM, and Wolkow RA (2000) Self-directed growth of molecular nanostructures on silicon. *Nature* 406: 48–51.

The seminal work on molecular architecture formation through a chemical chain reaction is described by Lopinski *et al.* [133]. The nucleation site for the chemical chain reaction was a single silicon DB on an otherwise H-terminated Si(001). **Figure 3** shows a schematic of the reaction of an alkene at the DB site: the alkene moiety ($\text{CH}_2=\text{CH}-\text{R}$) interacts with the surface DB to form a C-centered radical at the carbon–carbon double bond, and the radical abstracts a hydrogen from a neighboring silicon dimer (this mechanism was confirmed with density functional theory modeling [134]). After exposing a slightly defective H:Si(001) surface to 3l of styrene (1), Lopinski *et al.* observed molecular lines up to 130 Å in length. High-resolution imaging confirmed the spacing of the features within the line to be 3.8 Å, corresponding to the dimer spacing on Si(100). The longest observed lines therefore indicate a $34 \times$ propagation of the chemical chain reaction.

