Engineering of Micro- and Nanostructured Surfaces with Anisotropic Geometries and Properties

Sameh Tawfick,* Michael De Volder, Davor Copic, Sei Jin Park, C. Ryan Oliver, Erik S. Polsen, Megan J. Roberts, and A. John Hart*

Widespread approaches to fabricate surfaces with robust micro- and nanostructured topographies have been stimulated by opportunities to enhance interface performance by combining physical and chemical effects. In particular, arrays of asymmetric surface features, such as arrays of grooves, inclined pillars, and helical protrusions, have been shown to impart unique anisotropy in properties including wetting, adhesion, thermal and/or electrical conductivity, optical activity, and capability to direct cell growth. These properties are of wide interest for applications including energy conversion, microelectronics, chemical and biological sensing, and bioengineering. However, fabrication of asymmetric surface features often pushes the limits of traditional etching and deposition techniques, making it challenging to produce the desired surfaces in a scalable and cost-effective manner. We review and classify approaches to fabricate arrays of asymmetric 2D and 3D surface features, in polymers, metals, and ceramics. Analytical and empirical relationships among geometries, materials, and surface properties are discussed, especially in the context of the applications mentioned above. Further, opportunities for new fabrication methods that combine lithography with principles of self-assembly are identified, aiming to establish design principles for fabrication of arbitrary 3D surface textures over large areas.

1. Introduction

An ultimate goal of materials manufacturing is to arbitrarily specify the composition and arrangement of features on a surface or within a volume, at high throughput and at low cost. For example, rapid advances in the dimensional limits and material capabilities of semiconductor fabrication technology have enabled continued miniaturization of electronics, and continually rapid advances in performance.1 Likewise, challenges in fabrication of complex and heterogeneous 3D surface structures continue to drive widespread research in new fabrication methods, especially at small scales.2 In many ways, the capabilities of fabrication technologies limit the pace of both research and commercialization of new materials and devices.3 Often, demonstrations of specific properties and/or applications drive specific advances in fabrication methods, yet commercialization happens only when a fabrication method becomes a scalable manufacturing process.

The ability to create highly organized micro and nanoscale surface structures in a wide variety of materials enables engineering of interfacial properties that are relevant to applications including energy, electronics, photonics, composite materials, and medical devices. This review focuses on the engineering of anisotropic surfaces: an emerging area that combines fabrication of complex surface architectures with novel physical properties. Broadly, the notion that a material can have anisotropic physical properties owing to surface patterns is well-founded in natural systems.4,5 For instance, the anisotropic wetting adhesion of rain droplets on a gecko lizard to climb vertical surfaces. However, the ability to fabricate anisotropic surfaces is traditionally limited by fabrication processes that enable only patterning of planar (2D) features such as micro- and nanoscale linear gratings. More recently, 3D assemblies of nanostructures have enabled more sophisticated surface designs. Both 2D and 3D anisotropic surface designs have enabled exciting studies of anisotropic physical properties including wetting, electrical and thermal transport, electromagnetic polarization, and cell and tissue growth.

We define surfaces with anisotropic properties are those which lead to anisotropic transformations of applied fields (i.e., mechanical, electromagnetic, optical and/or chemical). While anisotropic properties of bulk materials or thin films may arise from intrinsic crystallographic anisotropy, this is not an intended focus of the present review. Instead, we focus on anisotropy that results from the geometry and/or arrangement of surface features. Typically, the characteristic dimensions of
these surface features are comparable to or smaller than the characteristic dimension of the stimulus (e.g., wavelength of light, size of droplet). In many cases, the geometry of the surface features is anisotropic, and this is the primary driver of anisotropy in the property of interest. The constituent materials may have anisotropic properties themselves, and this is particularly true for nanostructured features such as nanotubes/nanowires, and block copolymer domains. However, anisotropy of the constituent material is not required to establish anisotropic surface properties.

Further, while the materials, fabrication processes, and applications of anisotropic surfaces may seem disparate, there are indeed many important connections in this multidimensional space. For example, essentially the same anisotropic surface design-linear grooves made by nanoimprint or interference lithography—can be used to establish anisotropic wetting, control optical polarization, and direct the alignment of cells such as neurons. However, the ability to fabricate this design in a variety of materials, from biocompatible polymers to mechanically robust metals, is essential for practical applications of these properties. This important need remains unmet. Likewise, the fabrication of complex 3D structures such as inclined and helical micro and nanopillars, and their applications as directional adhesives and circular polarizers, has stimulated creative approaches that utilize starting structures made by traditional lithography and etching methods, and transform these structures into more complicated forms. These approaches include directed mechanical deformation and capillary densification.

Therefore, the goals of this review are to:

1. Present a thorough “cookbook” of both well-established and newly developed techniques to fabricate 2D and 3D anisotropic features at different length scales and in different materials.
2. Classify these methods in a comprehensive manner, and critically analyze their capabilities and limitations.
3. Review the most important anisotropic surface properties, understand the physical principles causing these properties, and relate these principles and properties to the capabilities and limitations of the fabrication processes.
4. Identify future directions in the design, fabrication, and properties of anisotropic surfaces. These include the integration of self-assembly methods with top-down patterning, and surfaces with switchable and multifunctional anisotropic properties.

Our approach and perspective are in part inspired by the seminal publications that introduced microelectronics fabrication to the early stages of MEMS and lab-on-a-chip research. Now, we hope that a comprehensive review of fabrication methods for anisotropic surfaces, and their resulting physical properties, will catalyze increased synergy between fabrication and applications in this growing field.

### 2. Classification of Fabrication Methods

We consider methods that create two-dimensional (2D) and three-dimensional (3D) anisotropic surface features. First, fabrication methods for 2D anisotropic surfaces are summarized in Table 1. We define 2D features as having low aspect ratio (AR < 1), with no variation of geometry in the vertical direction (perpendicular to the substrate). In general, 2D anisotropic surfaces have features with elongated shape in the surface plane. For example, line patterns fabricated by nanoimprint lithography or using block copolymer self-assembly enable engineering of surface color and electromagnetic polarization. We define 3D features as having high aspect ratio (AR > 1), with variable geometry in the vertical direction. Exemplary 3D features include bent, inclined, zigzag, and helical pillars. Associated fabrication methods are summarized in Table 2. Between these limits, we define high-aspect-ratio vertical features as 2.5D. The substrate materials and process setup for all the methods presented in this review are summarized in Table 3.

In order to rigorously compare fabrication methods and feature geometries, it is important to establish a consistent nomenclature. Notably, in current literature, the adjectives *tilt*, *bent*, *slanted* and *inclined* are loosely used to describe any non-vertical micro- or nanopillar. In this review, we use the term *inclined* to denote a straight but non-vertical feature. We denote *bent* features as having a measurable radius of curvature, which typically results from a stress gradient. Further, the 3D geometry of *helical* structures made by different methods is difficult to...
the 2D and 3D processes according to their ability to control relative position and organization of the features on the surface. Examples are shown in SEM images in Figure 1 and 2, and a related symbology is presented which in turn corresponds to the classification tables.

For instance, “top-down” (subtractive) patterns made by photolithography have prescribed geometries and placement because the position and orientation of each feature follows the discriminate. We use the term helical to describe any structure (solid or hollow) that makes a generally spiral trajectory about a vertical axis.

All of the methods presented enable fabrication of 2D, 2.5D, and/or 3D structures over relatively large areas, albeit with different levels of control in the placement and order of the constituent features, as well as varying dimensional limits and material capabilities. To distinguish these attributes, we classify the 2D and 3D processes according to their ability to control relative position and organization of the features on the surface. Examples are shown in SEM images in Figure 1 and 2, and a related symbology is presented which in turn corresponds to the classification tables.

For instance, “top-down” (subtractive) patterns made by photolithography have prescribed geometries and placement because the position and orientation of each feature follows the

Table 1. Fabrication methods for anisotropic surfaces with 2D features.

<table>
<thead>
<tr>
<th>Process</th>
<th>Geometry (top view)</th>
<th>Feature size [μm]</th>
<th>Feature placement</th>
<th>Order</th>
<th>Packing density</th>
<th>Resolution limited by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interference lithography</td>
<td>two-beam</td>
<td>0.01 0.1 1 10</td>
<td></td>
<td></td>
<td>0.2 - 0.7</td>
<td>wavelength, refractive index</td>
</tr>
<tr>
<td>Nanoimprint lithography</td>
<td>same as master</td>
<td>0.01 0.1 1 10</td>
<td></td>
<td></td>
<td>0.3 - 0.7</td>
<td>mold robustness; molecular weight of resist</td>
</tr>
<tr>
<td>Block copolymer self-assembly</td>
<td>templated</td>
<td>0.01 0.1 1 10</td>
<td></td>
<td></td>
<td>0.3 - 0.7</td>
<td>molecular weight of blocks</td>
</tr>
<tr>
<td>Wrinkling</td>
<td>uni-directional</td>
<td>0.01 0.1 1 10</td>
<td></td>
<td></td>
<td>≈ 0.5</td>
<td>material combination</td>
</tr>
</tbody>
</table>

Table 2. Fabrication methods for anisotropic surfaces with 3D features.

<table>
<thead>
<tr>
<th>Process</th>
<th>Geometry (side view)</th>
<th>In-plane feature size [μm]</th>
<th>Feature placement</th>
<th>Order</th>
<th>Packing density</th>
<th>Aspect ratio (max)</th>
<th>Resolution limited by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inclined lithography</td>
<td></td>
<td>0.01 0.1 1 10</td>
<td></td>
<td></td>
<td>0 - 1</td>
<td>5</td>
<td>wavelength of light, refractive index of polymer</td>
</tr>
<tr>
<td>Multi-photon lithography</td>
<td></td>
<td>0.01 0.1 1 10</td>
<td></td>
<td></td>
<td>0 - 1</td>
<td>10</td>
<td>wavelength of light</td>
</tr>
<tr>
<td>Replica molding</td>
<td></td>
<td>0.01 0.1 1 10</td>
<td></td>
<td></td>
<td>0 - 1</td>
<td>20</td>
<td>mechanical robustness of mold</td>
</tr>
<tr>
<td>Metal-assisted chemical etching (MACE)</td>
<td></td>
<td>0.01 0.1 1 10</td>
<td></td>
<td></td>
<td>≈ 0.5</td>
<td>100</td>
<td>catalyst size and geometry</td>
</tr>
<tr>
<td>Glancing-angle deposition (GLAD)</td>
<td></td>
<td>0.01 0.1 1 10</td>
<td></td>
<td></td>
<td>≈ 0.5</td>
<td>10</td>
<td>interfacial energy between wafer and deposited polymer</td>
</tr>
<tr>
<td>Oblique angle polymerization (OAP)</td>
<td></td>
<td>0.01 0.1 1 10</td>
<td></td>
<td></td>
<td>≈ 0.5</td>
<td>10</td>
<td>interfacial energy between wafer and deposited polymer</td>
</tr>
<tr>
<td>Oriented nanostructure growth</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≈ 0.1</td>
<td>1000</td>
<td>catalyst size and geometry</td>
</tr>
<tr>
<td>Elastocapillary self-assembly</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1 - 0.5</td>
<td>10</td>
<td>mechanical robustness</td>
</tr>
<tr>
<td>Directed mechanical deformation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1 - 0.5</td>
<td>10</td>
<td>mechanical robustness</td>
</tr>
</tbody>
</table>

^ start from straight structures
the structures (and hence their density and order) can be arbitrarily controlled. We note that these methods are prescribed within the allowed resolution (or feature size). For example,

<table>
<thead>
<tr>
<th>Process</th>
<th>Materials (example)</th>
<th>Setup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interference lithography</td>
<td>Photocurable polymers</td>
<td>Laser, optics and translation stages</td>
</tr>
<tr>
<td>Nanoimprint lithography</td>
<td>Photocurable/thermoset polymer (PMMA)</td>
<td>Lithographic master fabrication; motion/force control</td>
</tr>
<tr>
<td>Block copolymer self-assembly</td>
<td>polymers (PS)</td>
<td>Wet chemistry; hotplate and/or oven</td>
</tr>
<tr>
<td>Wrinkling</td>
<td>polymers (PDMS), metals (Au)</td>
<td>Thin film deposition; thermal and/or solvent exposure</td>
</tr>
<tr>
<td>Inclined lithography</td>
<td>Photocurable polymers</td>
<td>Exposure/alignment tool; tilting and/or rotation stage</td>
</tr>
<tr>
<td>Multi-photon lithography</td>
<td>Photocurable polymers</td>
<td>Laser, optics and motion control stages</td>
</tr>
<tr>
<td>Replica molding</td>
<td>polymers (SU-8)</td>
<td>Master fabrication; UV; hotplate and/or oven</td>
</tr>
<tr>
<td>Metal-assisted chemical etching (MACE)</td>
<td>single crystal Si</td>
<td>Wet chemistry</td>
</tr>
<tr>
<td>Glancing-angle deposition (GLAD)</td>
<td>metals, ceramics</td>
<td>PVD system; in situ tilting and/or rotation stage</td>
</tr>
<tr>
<td>Oblique angle polymerization (OAP)</td>
<td>polymers (PPX)</td>
<td>PVD system; in situ tilting and/or rotation stage</td>
</tr>
<tr>
<td>Oriented nanostructure growth</td>
<td>Si, Ge, SiO₂, CNT</td>
<td>PVD; CVD (plasma optional) or wet chemistry</td>
</tr>
<tr>
<td>Elastocapillary self-assembly</td>
<td>CNT, polymer/semiconductor NWs</td>
<td>Controlled immersion or condensation</td>
</tr>
<tr>
<td>Directed mechanical deformation</td>
<td>Si, PUA, Epoxy</td>
<td>E-beam irradiation and tilting stage</td>
</tr>
</tbody>
</table>

Table 3. Comparison of process materials and setup for fabrication of anisotropic surfaces with 2D and 3D features.

Figure 1. Classification of anisotropic surfaces with 2D features. (a) Legend. (b-g) SEM images showing example surfaces with different feature shape, placement and order; (b) Multi-directional polymer gratings made by step-and-flash imprint lithography. Reproduced with permission,[19] copyright 2009 AIP. (c) Linear polymer gratings made by interference lithography. Reproduced with permission,[20] copyright 2010 ACS. (d) Block copolymer film with domain boundaries indicated by dashed lines. Reproduced with permission,[21] copyright 2008 AAAS. (e) Unidirectional block copolymer pattern made by templated assembly. Reproduced with permission,[22] copyright 2010 NPG. (f) Random arrangement of C60 rod crystals made by evaporative crystallization. Reproduced with permission,[23] copyright 2008 RSC. (g) Multiple domains of silver nanorods made by evaporative self-assembly. Reproduced with permission from http://www.nanopartz.com/.
photolithography is limited by optical diffraction which makes the process non-deterministic beneath this scale; however, the dimensions and location of each feature can be accurately prescribed within the diffraction limit.

On the other hand, “bottom-up” (additive) methods typically result in patterns that satisfy energy minimization under certain conditions. As a result, the order (packing) of the features is most likely local but not global, unless a pre-patterned template is used. Also, the type of order may be determined by the interactions among the features and/or their components. For example, self-assembly of spherical molecules of diblock copolymer can result in a hexagonally-packed arrangement of cylindrical domains; however, it cannot result in the square or rectangular arrangement. Moreover, the size of the building blocks and the spacing between them are coupled. Thus, the density of the structures can only be indirectly and partially controlled based on the lengths of the polymer. Self-directed mechanical stresses can also lead to self-ordered surface features, such as when micron-sized surface wrinkles are formed due to stress gradients caused by the deposition of thin metal films on PDMS substrates. In both examples, the resulting surface structures have order in small domains, typically called grains or crystals. The relative orientation of different domains is uncontrolled and cannot be deterministically defined.

The processes discussed herein generally span the 0.01–10 μm feature size range, which is beneath the scale achievable by traditional direct-write or machining methods. An overarching attribute of anisotropic surface fabrication methods is to sacrifice deterministic control over feature placement and order, in order to overcome the limitations of traditional lithography which can only fabricate straight vertical features (2.5D). For example, shadowing methods such as glancing angle deposition (GLAD) and oblique angle polymerization (OAP) enable fabrication of novel angled and helical features, but the placement of these features (and to some extent their dimensions) is random as determined by the local energetic conditions of formation. Metal-assisted chemical etching (MACE) is governed by random nucleation of etch sites on the surface, which influence the corresponding etching pathways. However, when an ordered template is used to define the diameter and location of the catalyst etching particles, the diameter and spacing of the resultant structures can be deterministically defined. The same holds true for many nanowires and nanotubes (e.g., Si, C) grown by CVD from catalyst particles on a substrate. Strategies that combine top-down and bottom-up methods are therefore the most typical and effective means of controlling long-range order, and in some cases establishing hierarchical order where the self-organization of nanostructures controls their formation at scales beneath the limits of template patterning. If the locations of nucleation and growth are specified in bottom-up techniques, true deterministic control of feature placement will result. However, in most present cases the spatial distribution of nucleation sites is random; and, patterning ordered features smaller than 5 nm remains a challenge for all scalable fabrication methods.

Notably outside the scope of this review are most subtractive fabrication methods including focused ion beam (FIB) milling and reactive ion etching (RIE). FIB milling can produce
arbitrary features, yet its serial nature precludes it from fabricating large-area surfaces. RIE can create anisotropic vertical features (e.g., nanopillars) in a variety of materials, and RIE is used widely to transfer anisotropic mask patterns into substrates, for example using nanoimprinted or block copolymer templates. Also beyond scope are methods of chemical and biochemical surface patterning, including contact printing, inkjet printing,[36] dip-pen nanolithography (DPN),[37] and gradient patterning.[38] These methods offer great potential to incorporate new reactive functionalities in surfaces, in combination with the physical methods discussed in this review.

In the following sections, we introduce each selected fabrication process, according to the 2D/3D classification of Tables 1 and 2. Then, we overview methods for the fabrication and assembly of anisotropic particles on surfaces. After that, we discuss six important application areas where anisotropic surface features give rise to anisotropic physical properties: wetting, adhesion, electrical conductivity, thermal transport, electromagnetic polarization, and cell/tissue interfaces.

3. Fabrication of Surfaces with 2D Anisotropic Features

3.1. Interference Lithography

Photolithography remains the standard technique in the fabrication of microelectronics, MEMS, and NEMS; and therefore can be a highly versatile means of fabricating anisotropic surface features that are compatible with microfabrication processes. Photolithography typically relies on the transfer of opaque geometries patterned on a clear mask by projecting ultraviolet (UV) or X-ray light through the mask onto a photosensitive polymer (known as photoresist or PR).[30] The resolution of photolithography is limited by the wavelength of the light according to

\[ C.D. = \frac{k}{N.A.} \lambda \]

where \( C.D. \) is the critical dimension representing the minimum feature size, \( \lambda \) is the wavelength of the light source used, and \( N.A. \) is the numerical aperture as seen by the wafer. The ratio of the depth of focus of the objectives to the thickness of the PR layer is an important factor limiting the minimum achievable feature size. At the nanometer scale, the resolution of photolithography is also limited by the size of the molecules of the PR.

Variations of photolithography developed to push the resolution below the wavelength of light include projection lithography where magnification objectives are used to focus the light beam; immersion lithography where a liquid with an index of refraction greater than one replaces the air gap between the objective and the mask; phase-shift masks where interference between diffracted UV light improves resolution; interference lithography; and deep-UV lithography where short wavelengths are used to limit diffraction and improve the resolution (Equation 1).[35]

Using interference lithography (IL), also known as holographic lithography, an interference pattern of two or more optical beams is used to define and fabricate periodic nanostructures. Surfaces patterned using interference lithography have been most widely used in photonic crystal waveguides and field-emission flat-panel displays, and as templates for assembly of nanostructures.[37] Interference occurs when multiple electromagnetic waves overlap in space, and the amplitude of the resultant wave is simply the sum of the amplitudes of the waves. In order to create an interference pattern for lithography, a single beam may be split into two or more beams, and then brought together again to create an interference pattern (Figure 3).[38] Alternatively, the beam may be passed through an optical element where diffracted beams overlap to produce an interference pattern. This interference pattern is used to expose the photoresist on the substrate, which is then developed to leave only the desired structures on the wafer. In order to produce a stable interference pattern, the multiple beams have to be coherent; therefore, their relative phase difference must be constant.

![Figure 3. Basic IL configurations. (a) Interference created by overlapping halves of a single beam using a mirror, where the angle of incidence is tunned by the angle between the mirror and the wafer. Schematic based on ref. [50]. (b) Two-beam interference created by splitting a single beam into two paths and projecting each path onto the substrate using pinhole optics. In (b) the interference pattern is modulated using a mirror to position one of the beams. Schematic based on ref. [42].](image-url)
Typical IL methods can create periodic structures over 1 cm$^2$ in area.\cite{34} Using a fringe-locking system,\cite{44} the patterned area can reach more than 50 × 50 cm\cite{46} with feature size approaching 20 nm.\cite{45}

Three-dimensional (3D) IL requires an interference pattern generated with 4 beams. 3D periodic photonic crystals with a FCC structure were demonstrated to have nearly perfect long-range order.\cite{47} Using multiple exposures after a phase shift, 3D anisotropic surfaces can be sculpted, such as a multi-layer grating-like structure shown in Figure 4d.\cite{48} 3D IL can also be done using a monolithic diffraction phase mask,\cite{49} but in this case control over the beam intensity and polarization is compromised.

Because the interference pattern is used to define features, attention must be paid to how the wave amplitude is spatially modified by diffraction, especially when patterning a large area. Usually, the geometry of the phase mask is modified to counter this effect. Also, the choice of materials is limited to photosensitive polymers, although patterns that are created by IL can then be used as a mask to etch other materials.

### 3.2. Nanoimprint Lithography

Nanoimprint lithography (NIL) is a high throughput mechanical embossing technique that enables direct patterning of soft polymeric surfaces. NIL was invented by Chou and colleagues in 1995. As shown in Figure 5, NIL uses a rigid master mold
which is pressed into a soft polymer.\textsuperscript{52} Chou et al. later showed that the lateral resolution of NIL could be as low as 10 nm and the depth resolution could reach a few nm.\textsuperscript{53} Nanoimprinted polymer surfaces can also be used as masks for patterning the underlying substrate, including metal, semiconductor, and oxide thin films. Therefore, NIL has been used in fabrication processes for organic electronics,\textsuperscript{54} photonics,\textsuperscript{55} biosensors,\textsuperscript{56} and nanofluidics.\textsuperscript{57} There are several excellent reviews of NIL and its applications, including those by Guo.\textsuperscript{58} Especially at the \(<100 \text{ nm scale}, \text{NIL has most frequently been used to create anisotropic patterns such as gratings or channels.}

Master molds for NIL are typically made using UV, electron beam, or interference lithography of photoresist (PR), followed by Reactive Ion Etching (RIE) of the substrate. Molds are typically made from hard materials, preferably with low surface energies, such as Si, SiO\textsubscript{2}, SiC, silicon nitride and sapphire. Hard master molds enable NIL to be a scalable, high throughput technique, because the master can be used many times. In order to prevent pattern distortion due to thermal expansion, the master and patterning material should have comparable coefficients of thermal expansion. Application of a low surface energy demolding agent to the master such as a PTFE-like coatings, can improve the fidelity of the pattern transfer, especially when the master mold has high surface energy or when very small and/or high aspect ratio features are desired.\textsuperscript{59}

In a typical NIL process (Figure 6a), the master mold is pressed into a plasticised thermoplastic at elevated temperature, which upon cooling and separation from the master retains the imprinted features of the master. NIL resists can be thermoplastics, thermosets, or thermally or UV curable liquids. If a thermoplastic is used as the resist, the material is softened by heating the material above the glass transition temperature before the mold is pressed into the resist. Alternatively, the polymer can be softened by adding a plasticizer such as a solvent or monomer.\textsuperscript{60} The applied pressure, temperature, and contact time vary depending on the selected resist.

Related techniques such as reverse NIL\textsuperscript{61} and step-and-flash imprint lithography (SFIL)\textsuperscript{62} use a polymerizable liquid to form the nanopatterned surfaces. In reverse NIL, a polymer is coated on top of the master mold and then cured using UV light, thereby allowing room temperature imprinting. Additionally, reverse NIL can be used to pattern multiple polymer layers forming complex anisotropic surfaces.\textsuperscript{63} In SFIL (Figure 2 and 6b), a transparent master mold is pressed over a pooled liquid (i.e., a photoresist). The liquid wicks in between the mold and the substrate, and then is cured using UV light. In contrast to NIL, SFIL can take place at room temperature. SFIL also enables local variation in the pattern density of the resist, such as by inkjet printing, which enables fabrication of variable density patterns. SFIL has been commercialized by Molecular Imprints, Inc.

Notwithstanding the limits to master mold fabrication, the resolution of the imprinting process is limited only by the mechanical properties of the mold and resist materials, and their surface interactions. The dimensional limits of NIL have been demonstrated by imprinting 5 nm wide lines using a SiO\textsubscript{2} master patterned using electron beam lithography (Figure 7a), and by imprinting 14 nm wide lines using a superlattice mask (Figure 7b).\textsuperscript{64} However, imprinting high aspect ratio (HAR) structures using NIL is challenging because HAR structures require high release forces due to their large surface area, but break easily during demolding, due to their narrow cross-sectional area. Alternatively, DRIE can be used to etch HAR structures using a NIL resist, but undercutting during DRIE limits the aspect ratio of these structures.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Process sequences comparing (a) nanoimprint lithography (NIL) and (b) step-and-flash imprint lithography (SFIL). Reproduced with permission.\textsuperscript{68} copyright 2004 IOP.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Limits of nanoimprint lithography. (a) 5 nm wide line imprinted using SiO\textsubscript{2} master. Reproduced with permission.\textsuperscript{64} copyright 2004 AIP. (b) Lines with 14 nm pitch imprinted using superlattice mask. Reproduced with permission.\textsuperscript{64} copyright 2004 AIP. (c) Reduction of feature roughness by guided transient liquefaction. Reproduced with permission.\textsuperscript{66} copyright 2008 NPG.}
\end{figure}
Significant promise for NIL has been buoyed by its compatibility with roll-to-roll processing.\cite{65} This poses to be especially useful for manufacturing of electronic and optical components on flexible substrates, such as for organic photovoltaics and displays. However, an important issue for roll-to-roll NIL is the fabrication of a cylindrical master from the planar Si or ceramic template. Also, for semiconductor fabrication and optical applications, the surface roughness of nanoimprinted structures is vital. To this end, it has been shown that melting and solidification of nanoimprinted structures, under mechanical constraint, can greatly reduce the roughness of imprinted surfaces (Figure 7c).\cite{66} Using this “self-perfection” process it is also possible to change the aspect ratio of the imprinted structures. Advances in the resolution and fidelity of NIL will also be enabled by new resist materials and master mold fabrication methods.

3.3. Block Copolymer Self-Assembly

Block copolymers (BCP) consist of at least two covalently bonded immiscible polymer chains, which undergo phase separation when processed, thereby forming ordered nanoscale domains. BCP form a variety of intricate morphologies depending on the number and type of blocks, their relative length and arrangement, and their relative solubility.\cite{9,10} Due to their ability to form nanoscale domains with long range order, BCP assemblies can be used for nanolithography, photonic crystals,\cite{69} membranes,\cite{70} and wave guides.\cite{71} BCP-based lithography is a core technology to reduce the critical dimensions of CMOS devices, as described in the International Technology Roadmap for the Semiconductor Industry (ITRS).\cite{8} We recognize that BCP are by definition anisotropic at the molecular level, but without patterning or orientation control, BCP typically result in surfaces with isotropic properties. Therefore, consistent with the theme of this article, the remainder of this section will focus on diblock copolymer (DBCP) thin films, which represent a scalable anisotropic nanostructured surface. See Park et al. for a comprehensive review of BCP assembly.\cite{72}

DBCP consist of two covalently bonded homopolymer subunits (\(A\) and \(B\)), and have a set of equilibrium morphologies shown in Figure 8. In general, BCP reach their final morphology via a self assembly process, typically after spin-coating followed by thermal or solvent annealing. The BCP self assembly process is driven by the tendency of the blocks to separate and reach a thermodynamic minimum. The Flory-Huggins interaction parameter quantifies the driving force for polymer phase separation. Combinations of blocks with high Flory-Huggins interaction parameters will undergo strong phase segregation forming distinct domains. For a DBCP having strong segregation of its domains, its equilibrium morphologies can be predicted solely by the relative volume fractions of the blocks.\cite{9}

The morphology orientation of DBCP thin films, which is largely dictated by the interaction with the substrate, must be controlled to fabricate anisotropic surfaces. Specifically, anisotropic surfaces can be made from thin films of DBCP having either lamellar or cylindrical morphologies. Lamellar morphologies consist of alternating planar layers of blocks \(A\) and \(B\). Cylindrical morphologies consist of hexagonally packed cylinders of either block in a matrix of the other block, and the block having the smaller volume fraction will form the cylinder. Cylindrical morphologies with hexagonally packed cylinders parallel to the substrate will result if the interaction between one of the blocks and the substrate is very strong. The orientation of domains in relation to the substrate is a common issue and can be addressed for lamellar morphologies by a variety of alignment methods including shear fields, thermal gradients, electric fields, and physical confinement.\cite{72} Reciprocating shear fields in particular have shown ability to controllably orient lamellar phases either parallel or perpendicular to the substrate. Cylindrical morphologies have been demonstrated with line widths as small as 8nm, extending up to tens of microns and having excellent long range order.\cite{73}

Even with good domain alignment, many defects are present in BCP films. By pre-patterning the substrate to guide BCP assembly, the defect density can be reduced, and the orientation of the domains can be specified. BCP films can have very low defect density and excellent long range order are achieved by annealing the BCP over a chemically or topographically patterned surface. Both chemically and topographically-driven patterning require the use of lithography before BCP assembly. If nanoscale domain sizes are desired, UV, electron beam, or interference lithography is necessary.

Chemical patterning of BCP typically involves patterning in the substrate and then either modifying the exposed substrate using oxygen plasma for example\cite{72} or using reactive ion etching (RIE) to form trenches which are then backfilled with polymer brushes.\cite{21,78} The process for chemical patterning of a substrate for BCP thin films is shown in Figure 9a, and results

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**Figure 8.** Diblock copolymers. (a) Equilibrium morphologies as determined by the volume fractions of the two blocks. Reproduced with permission,\cite{77} copyright 1991 AAAS. (b) TEM images of lamellar and cylindrical morphologies. Reproduced with permission,\cite{78} copyright 2010 NPG.
3.4. Wrinkling

Wrinkle formation results from stress gradients or property mismatch across the thickness of planar materials, and wrinkles are ubiquitous in nature especially on leaves and skins. Many studies have shown that wrinkles can be formed with scales ranging from nanometers to millimeters. Theoretical insights into the mechanics of wrinkle formation have enabled engineering of dimensionally controlled uniform wrinkles. Promising applications of wrinkled surfaces include microfluidic sieves, diffraction gratings, and templates for guiding cell proliferation and colloidal crystal assembly.

In 1998, Bowden et al. formed wrinkles in thin laminated films and suggested their use in facile fabrication of diffraction gratings. A multilayer film consisting of 5 nm Cr or Ti (adhesion layer) and 50 nm Au was deposited by evaporation onto a 1 mm thick PDMS slab. Upon cooling, wrinkles formed with 15–50 μm period and 1.5 μm depth (Figure 10b). The spontaneous formation of this 2D network of random surface wrinkles was attributed to thermal stresses during the evaporation of the metal; this was confirmed because the wrinkles disappeared when the samples were reheated to 110 °C after the deposition. The large mismatch in coefficient of thermal expansion (αPDMS = 20 αmetal) caused compressive lateral buckling of the metal film upon cooling. This pioneering study also showed that the direction of wrinkle formation can be specified by micropatterning the PDMS. Channels with 800 μm width, 10–20 μm height, and 100 μm separation caused the wrinkles to arrange perpendicular to the channels as shown in Figure 10d. The waves are aligned perpendicular to the channels because stresses in the direction orthogonal to the channel sidewalls significantly drop at the vicinity of the sidewalls, and reach zero at the step edge. Hence physical guidance facilitates fabrication of an ordered anisotropic surface by wrinkling.

For a film on a substrate, the properties can be related to the average wavelength of the wrinkles as shown in Equation (2)

$$\bar{\varepsilon} = \frac{3}{2\pi d} \left( \frac{\lambda}{2\pi d} \right)^3 \quad \text{or} \quad \lambda = 2\pi d \left( \frac{\bar{\varepsilon}}{3\bar{\varepsilon}_s} \right)^{1/3}$$

where \( d \) is the film thickness, \( \lambda \) the wavelength, \( \bar{\varepsilon} \) the reduced elastic modulus of the film (or substrate) and \( \bar{\varepsilon}_s \) is the reduced elastic modulus of the substrate, \( E_{f0} \) is the reduced elastic modulus of the film (or substrate), and \( \nu_f \) and \( \nu_s \) are the Poisson's ratio of the film (or substrate) respectively. Equation (2) indicates that the wavelength is proportional to the film thickness. For strain values higher than a certain threshold, the
wavelength is independent of the applied strain and only the amplitude varies. The amplitude of the wrinkles depends on the initial strain and follows the relation $A \sim \lambda^{1/2}$. Notably the bulk value of $E_f$ can’t be used for very thin films (typically <100 nm thickness), whose elastic modulus is different than the bulk value of the same material. Consequently, techniques have developed to experimentally predict the elastic modulus of thin films from the periodicity of the wrinkles, by applying small strains to thin films laminated on substrates, or by poking thin films floating on liquid surfaces (Figure 11b).\

An even simpler method for forming wrinkles involves surface oxidation of PDMS to establish the required stiffness mismatch. With an adequate plasma exposure dose, a hard film of SiO$_2$ with $E_f = 70$ GPa, $v_f = 0.17$ and thickness $d$ dependent on the plasma power and time can be formed on the surface of PDMS. This compares to soft bulk PDMS having $E_f = 7.1$ MPa and $v_f = 0.5$. When this oxidized PDMS substrate is pre-stretched and then released after oxidation, wrinkles form. With unidirectional stretching and plasma doses ranging from 4-50 kW, the wrinkle period ranges from 100–900 nm and the amplitude is below 100 nm. Incidentally, cracking of oxidized PDMS surfaces followed by stretching can create long nanochannels whose width can be mechanically tuned by the amount of stretch.

Alternative methods to create wrinkle patterns include osmotically driven wrinkling where a droplet of solvent (e.g. ethanol) locally deforms the surface layer of a soft film (e.g. PDMS with oxidized surface), creating a hierarchical morphology. In this study, responsive wrinkles were created by controlling the swelling of the soft substrate to reverse the wrinkling. These could be used in microfluidics, for example to deposit line patterns of colloidal particles.

4. Fabrication of Surfaces with 3D Anisotropic Features

4.1. Inclined Lithography

Typically, polymer features made by photolithography have straight sidewalls, and conventional lithography methods do not enable variation of the lateral feature dimensions (i.e., slope,
undercut) in the vertical direction. Certain photoresists such as SU8 enable the fabrication of high aspect ratio micropillars; however, these remain straight unless special exposure techniques are used. To overcome the limitation of straight features, inclined lithography (IncL) was developed. IncL enables the formation of 3D geometries such as inclined micropillars and truncated cones, by tilting the wafer with respect to the light source and optionally rotating the wafer and/or the mask during UV exposure. For example, as shown in Figure 12, Beuret et al. fabricated multi-directional inclined structures in commercially available thick PR by using tilting and rotating assembly of two masks and the wafer.

3D structures made by inclined lithography have lateral dimensions and height (defined by the PR thickness and exposure depth) both in the range of 1–100 μm. For instance, inclined SU8 pillars with an aspect ratio (height/width) exceeding 4 have been realized in 100 μm thick SU8. The angle of inclination is limited by the refraction of light entering the mask as shown in Figure 12a and has a theoretical limit in air of ∼39°, measured from the normal to the substrate. Immersion lithography can thus achieve larger inclination angles, such as 56.2° in water and 71° in glycerol. The spacing between individual structures can be as small as the feature size, and is also limited by the wavelength of the exposure light. However, to our knowledge, submicron 3D features made by inclined photolithography have not been demonstrated.

Combinations of standard vertical and inclined lithography allow the fabrication of asymmetric pillars with both straight and inclined sidewalls as shown in Figure 12. For example, two masks can be stacked (or a double-side mask may be used) such that the two patterns have a desired offset. This configuration enables simultaneous exposure of the PR at different angles by allowing the transmission of UV at the angle defined by the offset double mask. This technique can also be used to make hollow conical microwells. Additionally, Tabata et al. fabricated solid conical structures in PR using a rotating mask along with a LIGA process. The mask has a clear circle with radius R, and is offset from the center of rotation as shown Figure 12. The difference in exposure dose from the center to edge leads to the formation of the cone. Moreover, when a reflective substrate (e.g. Si wafer) is used, the reflection of the exposure light can result in parasitic patterning of material near the base of the structures. This limitation can also be an opportunity; for example, crosslinking of the SU-8 along the reflected path can give V-shaped geometries (Figure 13).

Arrays of structures made by inclined lithography have been exploited to create anisotropic wetting or adhesive surfaces. These
surfaces have found several applications in microfluidics where they are used as filters, droplet fragmentation devices, truncated microchannels, and 3D mixing channels. The main limitation of anisotropic structures fabricated by inclined lithography remains the performance of the PR as a functional material (and not as a sacrificial material). For example, the mechanical, electrical and thermal properties of most PR are inferior to the properties of metals, silicon or other inorganic materials. Nonetheless, this limitation can be addressed by coating or infiltration of polymer structures with inorganic films or nanoparticles.

4.2. Multi-Photon Lithography

Two-photon absorption polymerization (TAP) can fabricate arbitrary 3D structures in polymers, with feature sizes as small as \( \approx 100 \text{ nm} \). This capability is particularly useful for photonic crystals and broadband circular polarizers.

TAP occurs due to two-photon absorption (TPA) where an electronic transition occurs in a molecule that absorbs energy from two photons simultaneously. The sum of the two photon energies should be equal to the energy required for the transition, and the second photon needs to be absorbed within several femtoseconds after the absorption of the first photon. It need not be the case that the photons have the same amount of energy, but often this is the case for convenience. TPA was first predicted theoretically in 1931 but was not demonstrated until 1961 when a laser was used, thus providing the requisite high photon density within a short time. Nowadays, an ultrafast laser is typically used to drive TPA, and the laser pulses are focused to a small spot using an objective with high numerical aperture.

TAP is analogous to a chemical reaction involving two molecules, where both molecules must be present to complete the reaction. For TPA to happen, two photons must be present at the same place at the same time, and therefore (as in the chemical analogue) the reaction rate is proportional to the concentration of photons (intensity) squared. Assuming the absorbing molecules are uniformly distributed, the reaction rate for single-photon absorption does not depend on the area, because the cross sectional area dependence of intensity (number of photons per unit area \( \times \) time) is cancelled out by the number of molecules (concentration \( \times \) area). However, in TPA, the areal dependence of intensity prevails because the reaction rate is now proportional to the square of the number of photons in the beam. Therefore, the reaction rate will be the greatest where the laser spot is focused most tightly, which leads to high spatial resolution along the central axis of the beam. Also, assuming a perfectly Gaussian beam, the radial variation in intensity is sharper with TPA, thus giving a tighter concentration of events close to the center of the beam. These attributes make TPA have a significantly higher spatial resolution than single photon absorption.

TAP is used to fabricate structures by local polymerization of a photocurable resin; once the focal spot has polymerized, the laser (or the sample) is moved to expose the next part of the desired structure. Therefore, with a successive series of exposures, an arbitrarily complex 3D structure can be defined. After TPA, as in traditional photolithography, the polymer can be developed to remove the unpolymerized region (Figure 14). Alternatively, the polymer structure may be used as a template for deposition of a second material, such as a metal. For example, arrays of micrometer-scale gold helices were made by filling a positive photoresist template with Au by electroplating (using an ITO seed layer), and dissolving the photoresist.

While TAP can create arbitrary features, its main disadvantage is its low throughput due to serial exposure of each voxel. If the intensity needed to polymerize the monomers is sufficiently low, the throughput can be increased by splitting the beam such as using a digital micromirror array. Current limits to feature size \( \approx 100 \text{ nm} \) may be overcome using new resin chemistries or using stimulated emission depletion (STED) which was shown to achieve resolution of \( < 100 \text{ nm} \). As discussed by Klat et al., this was demonstrated with visible light by subtracting STED pulses (with minimum intensity at the focal point) from a focused excitation pulse, and exploiting the nonlinear relation between the intensity of the STED pulse and the residual population of the fluorescent state. For a more detailed review of multiphoton processes we refer to a past review.

4.3. Replica Molding

Replica molding (RM) is a means of copying micro and nanoscale structures using a master template and a polymer as a transfer medium. Typically, a soft polymer such as polydimethylsiloxane (PDMS) or polyurethane (PU) is used to cast a negative of a hard master mold. Optionally, the negative is used to cast a replica (thus copying the master). In contrast to nanoimprint lithography (NIL), RM can produce surface features over a wide range of length scales (nm-mm), and its use of a soft/flexible negative allows a wide variety of replica materials and geometries to be made. Additionally, the match between the master and the subsequent transfer materials for RM is determined largely by the physical (e.g., wetting) and chemical compatibility of the materials and is not aided by mechanical pressure. Broadly, RM is categorized as a soft lithography process, and related techniques include solvent-assisted micromolding, microtransfer molding, micromolding in capillaries, microcontact printing, and nearfield conformal photolithography. Comprehensive reviews of soft lithography and its application to nanostructure patterning have been published previously.

Figure 14. Polymer surfaces made by two-photon absorption polymerization. (a) SU8 grid. Reproduced with permission, copyright 2004 NPG. (b) SU8 nanobridges spanning microgrooves. Reproduced with permission, copyright 2005 IOP.
Thus, RM is widely capable of replicating anisotropic features of a master mold, as shown schematically in Figure 16, and for the example of slanted nanohair arrays in Figure 17a. The compliance of the PDMS negative enables detachment of the negative without damage to the slanted structures, and slanted nanoscale hairs with inclination angles up to 60° have been made. The flexibility of the negative also allows for structures to be molded onto curved substrates, and the negative can be mechanically compressed to reduce the height of the replicated structures. Further, deforming the PDMS negative enables casting of anisotropic structures. In this case, application of a demolding agent greatly reduced the separation force and increased the yield of slanted structures. Nevertheless, it is still challenging to replicate slanted or reentrant structures without dissolving the mold.

RM using PDMS has been shown to have high fidelity even on the nanoscale as demonstrated by replication of an individual SWNT on a substrate. The ultimate resolution of PDMS replication has been experimentally determined to be 0.4 nm, which is limited due to the nanoscale roughness of the PDMS even when replicated against a flat silicon wafer. As a result of its nanoscale fidelity and compatibility with a wide range of length scales, single-step RM of hierarchical structures is possible. For example, composite microstructures of SU8 and vertically aligned CNTs have been replicated using PDMS negatives (Figure 17b). This process captures both the microscale shape of the CNT structures, and their nanoscale texture which matches the alignment and bundling.
of the CNTs on the sidewalls. The mechanical integrity of the SU8/CNT master enabled RM of textured walls with aspect ratios of up to 50:1, and multidirectional structures with thin slanted walls.

Development of new materials for casting negatives and replicas would greatly increase the applicability of RM. Recently, Gratton et al. used highly fluorinated perfluoropolyether (PFPE) elastomers instead of PDMS or PU as the molding material.[121] PFPE is not easily swelled by organic solvent, allowing for use of a wider range of organic replica materials. Also, casting of microposts in low melting point metals has been demonstrated using a PDMS master.[122] The fabrication of micro and nanostructures in metals and ceramics is a particularly important commercial application of replica molding, and demands further development in scalable master fabrication and processing methods.

4.4. Metal Assisted Chemical Etching

Metal assisted chemical etching (MACE) of silicon was first demonstrated in 2003 by Peng and colleagues, who achieved top-down fabrication of silicon nanowires (SiNWs) from single-crystal silicon wafers as shown in Figure 18.[124] In contrast to bottom-up growth of SiNWs by CVD, MACE relies on catalytic etching of silicon in a solution of hydrofluoric acid (HF) in the presence of a metal catalyst and an oxidant. MACE can result in the formation of vertically-aligned or inclined SiNW that follow a specific crystal orientation.[125] Because MACE is a top-down technique, it results in the fabrication of single crystalline SiNW of controlled diameter and orientation when combined with catalyst patterning. SiNWs made by MACE have been used in solar cells with up to 11.4% conversion efficiencies.[26]

Formation of SiNWs by MACE occurs due to the simultaneous oxidation of the silicon surface into SiO₂ at the catalyst-silicon interface, and the anisotropic etching of the formed SiO₂ by the HF solution. Therefore, the projection of the etched area is determined by the arrangement of catalyst on the top surface. The metallic catalyst, which is usually a noble metal such as Ag, Au, or Pt, can be deposited by PVD on a template of self-assembled polystyrene nanospheres, a block co-polymer film, or a membrane of anodic aluminium oxide (AAO). When the catalyst metal is deposited on the surface prior to MACE, an etching solution of HF and H₂O₂ (oxidant) is typically used (Figure 19). Alternatively, a random etching pattern can be established using a solution of HF with a dissolved metal salt such AgNO₃. This causes etching by simultaneous precipitation of Ag⁺ ions and formation of an interconnected 2D network of metal nanoparticles that catalyze anisotropic etching of silicon.
In both cases, the area of the silicon surface that is not covered by the metal catalyst is not etched, thus a forest of vertically aligned or inclined SiNW is formed. MACE using a metal salt solution typically gives SiNWs with 50–200 nm diameter. MACE using an ordered metal mesh as a template gives SiNWs with narrow diameter distributions. For example, masking using nanosphere lithography gave SiNWs with average diameter of 200 nm, a BCP-templated mesh gave 22 nm diameter SiNWs, and using anodic aluminium oxide (AAO) template SiNWs as small as 8 nm diameter were made. In general, the etching rate is ~1 µm/min and depends on the [HF]/[oxidant] concentration ratio and the etching solution temperature with an optimum temperature ~55 °C.

Most studies of MACE have produced vertical SiNWs; however, it was recently shown that inclined SiNWs can be formed when the etch chemistry is adjusted to manage the oxidation versus the etching rates of the single crystal wafer substrate. For example, preferential etching in the <100> direction caused SiNWs to be etched at β = 54.7° and 45° from the surface of (111) and (110) wafers, respectively. This preferential etching of the inclined crystal planes occurs only at slow etching rates when using a low concentration of H2O2 oxidant relative to the HF concentration. Anisotropic etching perpendicular to the wafer surface occurs at high H2O2 concentration. Thus, the etching direction depends on a competition between the total strength of the back bonds of silicon atoms in a particular crystal direction and the relative rates of oxidation and etching at the catalyst-silicon interface. In silicon, the atoms on the {100} plane have two back bonds, while the atoms on the (111) plane have three back bonds to the atoms underneath them.

As a result, it is generally more favorable to dissolve atoms along the <100> direction (box orientation) for wafers of non-(100) orientation. When the rate of etching of SiO2 is higher than the rate of oxidation of Si (high [HF]/[H2O2] ratio), the etching proceeds in the inclined direction following the <100> direction. Conversely, the Si at the catalyst-Si interface is adequately oxidized at sufficiently low [HF]/[H2O2] ratio, insuring anisotropic vertical etching. It is also known that all the Si back bonds (on the different planes) are generally weakened due to the formation Si-OH terminated atoms at high oxidant concentration which effectively suppresses the effect of the back bond anisotropy and leads to vertical etching regardless of the crystal plane orientation. On the other hand, when the solid area of the metal mask is sufficiently greater than the open area, etching according to the crystallographic directions is suppressed and SiNWs are formed perpendicular to the wafer surface due to the limited mobility of the metal catalyst.

In addition to vertical and inclined etching, in-plane and out-of-plane rotation and folding of catalyst metal patterns have been demonstrated using MACE to fabricate 3D Si geometries as shown in Figure 20. Star-shaped catalyst geometries were defined by e-beam lithography and rotation of the star-shaped catalyst along the vertical etching direction was observed for a wide range of [HF]/[H2O2] etch ratios thus creating a spiral. The mechanism can be explained by local variability in etching rates depending on the geometry of the catalyst boundary. In particular, line width has been identified as an important factor which is correlated to the etching rate. The mechanism of geometry-dependent etching rate in MACE is not understood, but speculations about electrophoretic forces driving the motion of the catalyst layer can explain the etching trajectories and catalyst deformations observed in recent studies.

Because it MACE can directly form vertical or inclined nanowires with controlled diameters over large areas, MACE is potentially advantageous over CVD growth of SiNWs because it does not require high temperature conditions. The ability to form inclined NWs is particularly advantageous for fabrication of smart materials, including anisotropic adhesives and wetting surfaces. However, more studies are needed on fabrication of structures with variable local densities, and different heights and geometries on the same substrate, which would be important steps toward 3D surface engineering using MACE.
The geometry and density of the deposited structures are determined by both physical and chemical effects. GLAD anisotropic structures grow when the substrate and source material interact such that Volmer-Weber growth occurs.[134] This happens when the newly condensing adatoms have a greater affinity to one another than to the substrate, thus forming isolated islands on the substrate. As deposition proceeds, the islands locally shadow the ballistic vapor flux from the source, which leads to vertical growth of the islands into individual 3D structures. Hence, the nucleation and growth dynamics are governed by the source-substrate interfacial interactions and the mobility of the deposited material on the substrate, which in turn are dependent on the substrate temperature and surface roughness.

Moreover, rotation of the substrate during GLAD enables the controlled formation of four types of archetypal pillar structures, as shown in Figure 21b–e: straight, inclined, zigzag, and helical. A substrate fixed at an angle \( \alpha \) leads to the growth of pillars inclined by an angle \( \beta \). To create zigzag pillars, the substrate inclination is changed from \( +\alpha \) to \( -\alpha \) after a given deposition time which determines the thickness of each segment. Continuous rotation during deposition will cause formation of helical structures with a vertical pitch dependent on the deposition and rotation rates. At high rotation rates, the pillars grow perpendicular to the substrate, thus forming straight pillars.

GLAD has been demonstrated using several PVD methods including e-beam evaporation, sputtering, and pulsed laser deposition.[27, 135] In order to make any of these systems suitable for GLAD, the vapor flux must be highly directional, with the mean free path larger than the distance between the source and the substrate. As noted above, in situ substrate rotation is needed to achieve straight, zigzag, and helical pillars.

The lateral dimensions of GLAD structures are typically in the range of 10–1000 nm. The height is typically heights are in the range of hundreds of nanometers to a few microns. The column spacing \( a \) is comparable to the feature size, and can be estimated as

\[
a = (1 + 1/ \cos \alpha) \delta
\]

where \( \delta \) is the column diameter.\[136\] This simple relation takes into consideration only the geometrical shadowing effect and not diffusion of the deposited material. GLAD structures can also grow from pre-patterned seeds where photolithography can be used to control the position and density of the based on the position of the seeds.\[117\]
Structures have been demonstrated by evaporating or co-sputtering multiple sources as shown in Figure 22. GLAD of anisotropic sculptured organic films has also been demonstrated. In one case, GLAD of Alq3 gave highly uniform helical structures with less surface roughness and no broadening effects. These structures also exhibited photoemission of circularly polarized light.\[138\]

### 4.6. Oblique Angle Polymerization

Oblique Angle Polymerization (OAP) is analogous to GLAD except that the precursors polymerize into individual anisotropic structures on the surface of a substrate. OAP was first introduced by Pursel et al. in 2005 who showed the formation of helical structures.\[142\] For OAP, a nozzle is typically directed at a shallow angle (~10°) with respect to the substrate, whereas the nozzle is perpendicular to the substrate in traditional polymer CVD. Notable applications of OAP include surfaces with anisotropic wetting and adhesion,\[13,143\] and templates for metal deposition that enable biosensing by Surface Enhanced Raman Spectroscopy (SERS).\[144\]

In the case of parylene deposition by OAP, a dimer is evaporated at 150–175 °C and then pyrolized into a monomer precursor resulting in a chemical structure such as poly-p-xyylene (PPX) that leaves the nozzle at pressure of ~10 mTorr.\[142\] Because the flux is directed onto the substrate at a shallow angle, a network of molecular strands nucleates on the substrate without forming a continuous film due to shadowing effects. (Figure 23) The strands then start to aggregate into columns of 200–400 nm diameter, which are inclined with respect to the substrate. The density of the columns is ~107 mm². The inclination angle is a function of the nozzle orientation and is approximately 55° for a nozzle directed at 10° with respect to the substrate. When the substrate is rotating, helical structures with a pitch of ~2 μm can be formed. Detailed analysis of the effect of deposition parameters on the structure of OAP films was reported by Cetinkaya and Demirel.\[145\] Pursel et al. demonstrated OAP in a commercial polymer PVD system with modifications including the insertion of a 1/4 in. diameter nozzle for precursor injection, and the addition of the substrate rotation and inclination motors. The dimer used was para-chloro-xylylene, and the deposited polymer consisted of a benzene ring with two para-methylene groups and one chlorine side group, having the chemical formula C₈H₇Cl. Demirel et al. used chloro-(2,2-paracyclophane dimer to fabricate slanted columns of poly(chloro-p-xylylene) (PPXC) having 50–100 nm diameter and up to 50 μm thickness with an inclination angle of 45°.\[146\] Cetinkaya et al. demonstrated columnar nanostructures of poly(chloro-p-xylylene) and poly(bromo-p-xylylene) thin films, and co-deposition of nanostructured poly(o-trifluoroacetyl-p-xylylene-co-p-xylylene).\[146,147\]

### 4.7. Oriented Nanostructure Growth

Synthesis of aligned one-dimensional (1D) nanostructures such as carbon nanotubes (CNTs) and semiconducting or oxide nanowires (NW) allows the bottom-up fabrication of
Figure 21. Glancing Angle Deposition (GLAD). (a) Setup of the substrate with inclination and rotation capability, and illustration of shadowing effect and growth of inclined pillars. The four archetypal structures of GLAD. (a-c) Reproduced with permission, copyright 2011 RSC. (b) Inclined pillars (MgF$_2$), (c) zigzag pillars (MgF$_2$), (d) helical pillars (MgF$_2$), and (e) straight pillars (Si). Reproduced with permission, copyright 2007 AIP. Reproduced with permission, copyright 1996 AAAS.

Figure 22. Multi-material GLAD methods and structures. (a) Two deposition sources located at different angles and directions with respect to the substrate. (b) Two deposition sources located at the same angle but opposite directions. (c) Two deposition sources located at the angle and the same direction from the substrate. Reproduced with permission, copyright 2011 RSC. (d) Si/Ta nanorods resulting from the configuration shown in (b), where ($d_1$, $d_2$) are the schematics corresponding to ($d_3$, $d_4$). Reproduced with permission, copyright 2008 Elsevier. (e) Co/Cu multi-section nanorods deposited from the configuration shown in (c) where ($e_1$) is the schematic, ($e_2$) is the SEM image, and ($e_3$) is the EELS elemental mapping. Reproduced with permission, copyright 2007 IOP. (f) TiO$_2$/SiO$_2$ zigzag nanorods resulting from the configuration shown in (a) with $\alpha_{TiO_2} = 60^\circ$ and $\alpha_{SiO_2} = 85^\circ$ and substrate rotation by 180° between the deposition of different layers where ($f_1$) is the schematic of the SEM shown in ($f_2$). Reproduced with permission, copyright 2010 RSC.
SiNWs with deterministically placed kink locations and angles for example, Tian et al. demonstrated a strategy to fabricate zigzag systems are seen with inorganic NWs particularly SiNWs. For development of scalable approaches for defining the position and spacing of the individual nanostructures over large areas. Waals interactions). An overall challenge in bottom-up fabrication (CVD), plasma enhanced CVD (PE–CVD), supercritical gas or liquid phase methods such as chemical vapor deposition (CVD), plasma enhanced CVD (PE–CVD), supercritical precipitation, or electrochemical deposition. In general, the geometry and orientation of a 1D nanostructure is determined by the precipitation reaction and/or by external forces that act on the structure during growth. External forces can be from the synthesis environment (e.g., gas flows or applied electric fields), the substrate, and/or from neighboring structures (i.e., van der Waals interactions). An overall challenge in bottom-up fabrication of 1D nanostructures with anisotropic organization is the development of scalable approaches for defining the position and spacing of the individual nanostructures over large areas.

In principle anisotropy of individual 1D nanostructures can be controlled by the motion of the catalyst particle, and model systems are seen with inorganic NWs particularly SiNWs. For example, Tian et al. demonstrated a strategy to fabricate zigzag SiNWs with deterministically placed kink locations and angles (Figure 24a,b). By Au catalyzed VLS synthesis, 120° kinks were introduced at predetermined intervals by purging the growth furnace for 15 s, then reintroducing the growth gases. The growth gases were SiH4 and H2 at a pressure of 40 Torr, and during purging, the flows were stopped and the chamber was pumped down to 3 mTorr. Purging dropped the reaction concentration in the super-saturated catalyst seed, and reintroducing the growth gases led to the saturation of the catalyst seed and heterogeneous nucleation of the kink segment. The angle of the kink was dictated by the most thermodynamically favorable growth direction according to the Si crystal structure. Additionally, pine-tree-like lead sulfide (PbS) nanostructures were made using CVD, by Bierman and Lau et al. The growth of this complex architecture was attributed to a screw dislocation along the trunk. According to the Eshelby theory, an axial screw dislocation exerts a torque at the free ends of the trunk, resulting in the twist of the rod along the axial direction. Zhang et al. fabricated SiO2 helical nanowires by CVD and attributed their formation to asymmetric growth chemistry around the catalyst. Wang et al. fabricated highly dense helical SiO2 NW forests by the liquid-vapor-solid mechanism using a gold catalyst with contact angle anisotropy (CAA), where the deposition temperature was 350 °C. CAA occurs when the catalyst size is larger than the NW size and the center of mass of the catalyst is shifted with respect to the NW center of mass. This in turn leads to CAA and hence asymmetric work of adhesion for new atoms attaching on the catalyst-NW interface (NW growth), which results in asymmetric growth rates across the NW. Nanosprings have also been made from boron nitride and silicon carbide.

Because of the widespread work on CNT synthesis for different applications, many methods have been developed to control both the anisotropic organization and the individual structure of CNTs. CNTs can be synthesized on substrates in the horizontal orientation (parallel to the substrate) or vertical orientation (perpendicular to the substrate), depending on their interaction with neighboring CNTs and with the substrate. In common CVD methods, CNTs grow from nanoparticle seeds in the tip- or base-growth mode, described by, respectively, whether the catalyst nanoparticles are advancing with the tip of the CNT or pinned to the substrate. In the tip growth mode, the convective gas flow on the substrate can lift the CNTs early during growth, thus enabling the CNTs to align with the flow direction. The alignment of the CNTs to the substrate can also be caused by van der Waals interactions between the CNTs and the substrate. As a result, HACNTs have been grown directly on crystalline substrates, such as ST-cut single crystal quartz and a-/r-/c-plane sapphire. On sapphire, atomic step edges (a few angstroms high) become faceted upon annealing, and physically guide CNTs during growth. However, in all these methods the density of horizontally-aligned CNTs is still low (10–50 CNTs/μm). Recent reports demonstrate how the density can be increased by optimizing the gas-catalyst combination by performing multiple re-growth cycles or transfer printing. Nevertheless, in order to be a potential replacement for Cu as horizontal interconnects in CMOS electronics, CNTs must be organized at very high packing densities and with enhanced control of local position and orientation. Other applications of anisotropic films of HACNTs include RF transistors, flexible devices and interconnects, and polarization-sensitive near field detectors.

When the catalyst seeds are densely distributed on a 2D planar substrate, CNTs self-assemble into “forests” of vertically
insertion of $C_2$ into the heptagon pairs shifted the geometry thus forming the helical twist. The diameter and pitch of the CNT helices were approximately 100 nm and 500 nm respectively. Thermal CVD on substrate bound Fe catalyst nanoparticles was also used to fabricate helical CNTs, though the alignment was poor compared to the co-pyrolysis method.\footnote{166} CVD of helical CNTs from floating catalyst was achieved by injecting a xylene-ferrocene mixture having dissolved indium isopropoxide and tin isopropoxide (sources for In and Sn respectively) in a CVD furnace. Formation of helices was explained by asymmetric growth on compound catalyst nanoparticles (Fe-In) due to different carbon precipitation rates in the segregated phases of the particle.

### 4.8. Elastocapillary Self-Assembly

Because of the inverse relationship between capillary pressure and interface curvature, capillary forces provide a versatile and accessible means of manipulating micro- and nanoscale structures.\footnote{170} This is especially true for structures with a low bending stiffness, such as thin films and high aspect ratio pillars.\footnote{171} Incidentally, the aggregation or stiction of small-scale structures upon evaporation of processing liquids was initially seen as an unwanted effect, for example causing narrow photoresist lines to collapse\footnote{172} and suspended MEMS devices to be pulled down to the substrate.\footnote{173} Researchers since learned to use this effect to their advantage, initially for the assembly and folding of microsystems,\footnote{174} and later to manipulate arrays of flexible pillars.\footnote{175} Recently, techniques to control the arrangement and spacing of nanostructures and manipulate their interactions (e.g., surface texture, adhesion) have enabled the fabrication of anisotropic assemblies using capillary forces.

Typical capillary self-assembly processes simply involve wetting of the processing substrate, followed by evaporation of the liquid. As the liquid evaporates, the surface tension of the moving meniscus draws the structures (e.g., nanopillars) together, as illustrated in Figure 26a. The resulting densification is a balance between elastic and capillary forces, called elastocapillary aggregation, and the size of the resulting assemblies can be predicted analytically by modeling the structures as slender elastic beams.\footnote{29} It is interesting to note that elastocapillary aggregation primarily happens as the densifying liquid withdraws from the structures rather than during the initial infiltration step. This has been confirmed by freeze drying experiments\footnote{171,176} and using environmental ESEM to watch infiltration and evaporation of liquid on CNT forest microstructures in situ.\footnote{25} After evaporation, the stable aggregated geometry is determined by equilibrium between adhesive forces (e.g., van der Waals attraction) and mechanical interlocking between the structures. For typical CNT forests, the aggregated configuration

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**Figure 24.** Complex morphologies of inorganic nanowires (NWs). (a) Deterministic formation of kinked SiNWs by purging, re-introduction of reactant, joint growth, and subsequent arm growth. (b) Kinked SiNW segment made by pulsed method. (a, b) Reproduced with permission,\footnote{148} copyright 2008 AAAS. (c) Pine tree PbS NW made by VLS. Reproduced with permission,\footnote{149} copyright 2008 AAAS. (d) SiO$_2$ nanosprings grown from Au catalyst. Inset shows Au particle and TEM image of helical SiO$_2$ NW. Reproduced with permission,\footnote{154} copyright 2006 IOP.
of structures are used to shape an assembly. Capillary enables the directed formation of bent CNT micropillar arrays, or complex truss-like or twisted microarchitectures, which preserve the local anisotropy of the aligned CNTs. While CNT forest micropillars behave as anisotropic foam that shrinks laterally upon capillary densification, extensive studies have also been performed on the assembly of arrays of isolated pillars that are initially uncoupled. In particular, the spontaneous formation of intricate twisted aggregates of polymer nanopillars (Figure 26g) was observed. This hierarchical aggregation behavior was attributed to the balance among capillary forces, elastic forces, and adhesion between the pillars, and as a result the size and stability of nanopillar assemblies can be manipulated via the pillar geometry and surface chemistry.[29]

Importantly, very little equipment is required to perform capillary self-assembly. In many reports, the substrate is simply submerged[171,180,181] or dipped[179,182,183] in a beaker containing solvent. However, in order to locally direct the capillary forces that act upon the structures, more advanced approaches were developed where the substrate is either drawn in a specific direction from the beaker[177] (Figure 26h) or where the liquid is controllably condensed onto the substrate.[185,186] Many liquids have been used for capillary aggregation. For CNT densification, acetone, IPA, toluene, methanol, ethanol, hexane, cyclohexane, diocetyl ether, dimethylformamide, tetrahydrofuran, water, liquid nitrogen, oleic acid, glycerol and several machine oils have been used.[178,180,182] Besides CNT forests, capillary self-assembly was also applied to Si nanowires,[185] hydrogel nano-rods,[175] epoxy,[179] PMMA,[176,186] cyclic olefin copolymers[176] polyurethane,[175] and photoresist lines.[172]

Despite its simplicity, it is clear that capillary self-assembly can manufacture both highly complex and very delicate structures. For instance, CNT walls with a thickness below 300 nm and aspect ratios exceeding 100:1 were demonstrated,[120] and iteration of CNT growth and self-assembly steps can build corrugated microstructures with re-entrant curvature.[187] Using electron beam lithography and plasma etching of horizontally folded CNTs, cantilevers with a width of only 170 nm were created and used as a switch (Figure 26h). The ability to control the aggregation of individual nanopillars demonstrates the applicability of capillary self-assembly to the limits of advanced lithography methods (nm scale) and perhaps beyond.

Last, composites of nanopillars or CNTs with responsive matrices such as hydrogels have been used to change the orientation[188] or shape of nanostructure patterns in response to varying in humidity or pH.[189] These are described further in the next section, and will enable novel surfaces whose anisotropic properties can be switched dynamically on demand.

### 4.9. Directed Mechanical Deformation

Arrays of bent or inclined pillars can also be fabricated by a number of methods that first create straight pillars, and then apply asymmetric stresses to cause bending.[24,192–194] In the first fabrication step, vertical micro- or nanopillars are fabricated by etching or molding from a master template. Exemplary studies have used pillars with diameter 0.1–1 μm and height of 1–10 μm. The pillars are subsequently bent by directional metal deposition, electrochemical coating, e-beam irradiation, thermal

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**Figure 25.** Anisotropic CNT morphologies. (a) Zigzag CNTs fabricated by PECVD. Reproduced with permission.[164] Copyright 2004 ACS. (b) Helical CNTs fabricated by CVD from Ferrocene-In catalyst precursor. Reproduced with permission.[149] Copyright 2008 Wiley.
Kim et al. demonstrated several approaches to make bent polymer nanohairs for applications in unidirectional wetting and dry adhesives. First, they fabricated a silicon master template using lithography and dry etching (DRIE) as shown in Figure 27a. The holes were 100 nm diameter and 1 μm deep, with tapered side walls as a result of the DRIE process. The treatment, or a combination of these methods. This step induces a stress gradient across each pillar, causing bending due to a mechanical effect analogous to the thermal actuation of a bimetallic strip. These anisotropic arrays have found applications in unidirectional wetting, anisotropic adhesion, chemical and biological sensing, and actuation.

Kim et al. demonstrated several approaches to make bent polymer nanohairs for applications in unidirectional wetting and dry adhesives. First, they fabricated a silicon master template using lithography and dry etching (DRIE) as shown in Figure 27a. The holes were 100 nm diameter and 1 μm deep, with tapered side walls as a result of the DRIE process. The
pills touched during irradiation, they remained bent due to van der Waals forces that overcame elastic restoring forces. At lab scales, both of these techniques are serial (as limited by the field of view of the e-beam at the required intensity) and relatively expensive because of the high operation costs for most commercial FEG SEM systems.

Directional thermal stresses provide a more scalable method for bending of nanohair arrays. For example, Yoon et al. coated PUA nanohair arrays with 6–12 nm Pt by oblique e-beam evaporation.\(^{[198]}\) Annealing for 30 minutes at 120 °C caused bending of the pillars to \(\approx 20^\circ\) from their initial vertical orientation, and these bent pillars had directional adhesion properties. The authors noted that the pillars bent toward the metal-coated side upon thermal annealing, (most likely because of greater thermal expansion of the polymer. Upon e-beam irradiation, the pillars bent toward the polymer side. Chu et al. presented a different approach where metal was deposited on Si pillars at elevated temperature (up to 1000 °C).\(^{[24]}\) Internal stresses resulting from the mismatch in thermal expansion coefficient caused the pillars to deflect upon cooling to room temperature. The bending angle was controlled from 2–52° depending on the thickness of the Au film (250–400 nm).

Stresses generated during anisotropic electrodeposition can also induce bending of polymer nanopillars. Kim et al. used UV-curable epoxy resin (UVO114, Epotek) to make straight nanopillars using a PDMS mold.\(^{[194]}\) After demolding, the nanopillars were coated with 30–100 nm thick Au by oblique e-beam evaporation or sputtering. The metal film deposited on only one side of the pillar arrays due to shadowing effects. This film functioned then as the electrode for deposition of Polypyrrole (Ppy) from an aqueous solution containing 0.1 M pyrrole (Py) and 0.1 M NaDBS (0.5–0.7 V vs Ag/AgCl reference electrode). As selective deposition of the Ppy progressed on each pillar, the resulting mechanical strain gradients caused the nanopillars to bend in one direction.

Active anisotropic surfaces are a class of materials having reversibly anisotropic building blocks which respond to external stimuli by changing their shape. For example, polymer nanopillar arrays embedded in a hydrogel matrix can be actuated directionally due to isotropic expansion of the hydrogel.\(^{[199]}\) Anisotropic inclined or bent nanopillars are formed by capillary aggregation before they are embedded in hydrogel. The nanopillars straighten as the hydrogel swells; and restore their original inclined or bent shape as the hydrogel contracts. By changing the chemistry of the hydrogel, these surfaces can respond to electric, chemical, or light stimuli.\(^{[199]}\) These active composite surfaces can have many applications in photonics, wetting surfaces, and microfluidics, where the structural geometry and the resulting performance anisotropy can be reversibly

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**Figure 27.** Fabrication of bent nanohairs by self-directed mechanical deformation: (a) Fabrication process for PUA nanohairs with oblique metal coating. (b) Bending towards metal-coated side, induced by thermal annealing. (c) SEM image after process (b). (d) Bending towards non-coated side, induced by e-beam irradiation. (e) SEM image after process (d). Reproduced with permission,\(^{[198]}\) copyright 2009 Elsevier Ltd.
controlled.\[^{200}\]\(^{200}\) In addition, composites of CNT microstructures and hydrogels allow direct electrical measurement of shape changes, due to modulation of the resistivity of the CNT network, thus enabling integration of responsive materials with microsystems.\[^{201}\]\(^{201}\)

5. Fabrication and Assembly of Anisotropic Particles

Even more diverse anisotropic surface designs are enabled by the bulk synthesis of anisotropic particles and their subsequent assembly onto surfaces. In many cases, assembly of anisotropic particles can create surface topologies that cannot be achieved by other approaches, and this will undoubtedly be buoyed by further innovations in anisotropic particle design and synthesis. In this section, we briefly discuss: (1) the synthesis of particles with anisotropic shape and/or chemical features; (2) the assembly of anisotropic particles into superstructures; and (3) the coating of surfaces with anisotropic particles and superstructures, to create surfaces with anisotropic properties.

To accommodate for the diversity of attributes that can arise by control of both particle shape and chemistry, Solomon and Glotzer proposed a classification scheme for particles based on their anisotropic dimensions, as shown in Figure 28.\[^{202}\]\(^{202}\) This methodology is one step towards a rule based approach whereby surface structures are designed based on knowledge of how the anisotropy attributes of a particle influence its assembly capabilities.

Within this classification scheme, patchy particles comprise a large class of building blocks whose surface exhibits multiple functionalities, often with an isotropic core.\[^{203}\]\(^{203}\) This is a distinguishing attribute because all other methods discussed in this review create structures with only one surface functionality. Janus particles, named after the two-faced Roman god, Janus, are a special case of patchy particles involving two distinct patches of equal areas. Janus particles were first introduced by Casagrade et al. in 1989,\[^{204}\]\(^{204}\) but have received wide attention since they were discussed in de Gennes’ Nobel lecture in 1991.\[^{205}\]\(^{205}\) More recent work by Lahann and co-workers has produced multi-compartment polymer microstructures via electro-hydrodynamic co-jetting.\[^{206}\]\(^{206}\) This method involves applying a high voltage between an electrode and a plate on which a drop is placed, creating a jet of liquid comprised of two immiscible flows. The liquid jet can either be fragmented into particles or sustained to produce a long fiber, which in turn may be sectioned into microcylinders.\[^{207}\]\(^{207}\) Several thorough reviews on Janus particles and their synthesis have been written by Perro and co-workers, Walther and Muller, and Pawar and Kretzschmar.\[^{203,208}\]\(^{203,208}\) A possible ultimate limit to the size scale of patchiness is represented by the fabrication of Au nanoparticles with striped monolayer coatings.\[^{209}\]\(^{209}\) where mobility enabled by the particle curvature allows mixed monolayers of immiscible molecules to segregate into nm-scale stripes.\[^{210}\]\(^{210}\)

While electro-hydrodynamic co-jetting is limited to production of cylindrical and spherical particles due to surface tension effects, more complex shapes can be produced using microfluidic strategies. One such technique, called stop flow lithography (SFL), enables remarkable control over particle anisotropy and was first demonstrated by Doyle and colleagues. In SFL, an optical microscope is combined with microfluidics to produce custom-shaped particles in the 10–1000 \(\mu\)m range.\[^{211,212}\]\(^{211,212}\) The process begins by flow of a UV-curable polymer through a PDMS channel. The particle shape is formed in the device by focusing the UV light through a mask placed in the field diaphragm of an inverted microscope. Spatial control of chemistry is achieved through the use of multiple streams of immiscible fluids to create particles having well-defined compartments. Variations on this technique include stop flow inference lithography, lock and release SFL, and railed SFL.\[^{213,214}\]\(^{213,214}\) Applications of these particles, which can have virtually any 2D shape within the dimensional limits of lithography, include bar-coded biosensors as demonstrated by Pregibon et al.\[^{215}\]\(^{215}\) Alternative strategies such as nanoskiving (where anisotropic particles are controlled.\[^{200}\]\(^{200}\)
made by by microtoming), seeded emulsion, and particle replication in nonwetting templates (PRINT), are highlighted in several excellent reviews.\cite{203,212,216,217}

To assemble anisotropic particles into larger structures and onto surfaces, a thorough understanding of the relevant forces between particles is necessary.\cite{218} In general, strategies can be classified by the nature of interaction that holds the structures to one another and/or to the surface, i.e., covalent bonding, or non-covalent interactions (van der Waals forces, Hydrogen bonding); and by the forces that direct the particles to their assembled position and orientation, e.g., capillary forces, electrostatic forces, magnetic forces, and gravitational forces. We will highlight two strategies emphasizing the roles of forces in assembly: the assembly of twisted structures of nanoparticles and the assembly of proteins and DNA.

Recent work by Srivastava et al. created twisted semiconductor nanoribbons (Figure 29c) composed of several layers of cadmium sulfide (CdS)/cadmium telluride (CdTe) nanocrystals. The twisted ribbons were assembled via the slow oxidation of tellurium (Te) ions in a solution of CdTe nanoparticles.\cite{219} During the process, the exposure of the solution to visible light for 72 hours induced a twisted conformation, and the intensity of the light (61, 45, 38 and 21 μW) controlled the pitch of the helix (250–1500 nm). The twisting was attributed to the relief of mechanical shear stress during assembly, caused by photooxidation of CdS. At the microscale, twisted assemblies have been created by stacking of dumbbell-shaped microparticles to form chiral columns.\cite{220} First, a modified seeded growth procedure (Stober and Fink\cite{221}) was used to create dumbbell-shaped silica nanoparticles with paramagnetic lobes.\cite{222} After synthesis, the colloidal solution of particles was placed in a shallow liquid cell, and a magnetic field was applied. Under the applied field, the dumbbells assembled into twisted columns, and the chiral angle was determined by the dimensions of the lobes.\cite{223,224}

In contrast to engineered particles, peptides have the unique feature of undergoing distinctive sequence-specific self assembly\cite{225,226} as well as the ability to recognize other particles,\cite{227} giving them the potential to uniquely direct the assembly of inorganic building blocks into nanostructures. Due to this capability, many inorganic nanoparticle superstructures, including nanoparticle chains, flowers and double helices have been designed and synthesized by peptide based methods.\cite{228}

For example, peptide directed self-assembly of nanoparticles can form alpha helices and beta sheets to form peptide-particle hybrids.\cite{226} In a HEPES buffer solution, parallel beta sheets of peptides (C₁₂-AYSSGAPPFF) spontaneously form and take

Figure 29. Anisotropic particles and their assembly into superstructures. (a) Electrohydrodynamic co-jetting of two polymers, which enables the formation of two- and three-compartment microcylinders. Reproduced with permission,\cite{206} copyright 2009 Wiley. (b) Railed stop-flow lithography method, with images of railed disc particle within and outside of the device. Reproduced with permission,\cite{214} copyright 2008 NPG. (c) Twisted ribbons of semiconductor nanoparticles. Reproduced with permission,\cite{219} copyright 2010 AAAS. (d) Twisted columns of stacked peanut-shaped particles. Reproduced with permission,\cite{223} copyright 2009 Wiley. (e) Lock and key assembly of polymer particles. Reproduced with permission,\cite{224} copyright 2010 NPG. (f) Stacking of lithographically made polymer particles, controlled by the depletion interaction. Reproduced with permission,\cite{248} copyright 2007 ACS. (g) Double emulsion droplets. Reproduced with permission,\cite{217} copyright 2011 RSC. (h) DNA icosahedron formed by 3D origami method. Reproduced with permission,\cite{231} copyright 2009 NPG.
on a left-handed helical conformation due to the aliphatic tails of the peptides. When mixed with a reactive acid (HAuCl₄), gold nanoparticles precipitate onto the peptide forming a gold nanoparticle helix.

DNA-directed assembly is also sequence-specific, and can be performed with greater ease because of the ability to rapidly prototype complimentary DNA strands. While DNA assembly has been studied for nearly 30 years,[229] recent work has shown potential to tile surfaces and build complex nanostructures out of DNA. In 2006, Rothemund invented the DNA origami principle where a long strand is folded by many short staple strands, and used this technique to build 2D shapes.[230] Shih and colleagues extended this technology to produce 3D DNA origami.

Both groups developed software to design DNA sequences to achieve a desired assembly.[231] Rothemund also demonstrated assembly of DNA triangles to lithographically patterned positions on a silicon wafer.[232] The same features that allow DNA origami enabled Rothemund et al. to test DNA-directed algorithmic control. They demonstrated tiling of DNA strands into a 2D Sierpinski pattern in solution, using designed DNA strands that followed specific assembly rules.[233] For a more comprehensive review of biologically based strategies refer to Ulijn et al.[234] and Chen et al.[235]

Other emerging strategies combine two or more interactions to achieve anisotropic assembly in solution. For example, the “lock and key” strategy uses geometry and depletion forces to assemble spherical particles as shown in Figure 29c.[236] A spherical key (silica particle) fits into the cavity of a lock (spherical particle with a spherical cavity. Short range attraction between lock and key pairs arises when a depletant is added to the solution. The depletant induces a short range depletion attraction, which arises from entropic considerations caused by excluded volumes.[237] The depletion interaction potential is proportional to the overlapping excluded volume between particles, which is determined by the surface shape and roughness. The overlap of the exclusion volumes and therefore the depletion attraction is maximized when the key particle is fitted into the lock particle, therefore causing site-specific assembly. Using roughness to control the depletion interaction instead of particle geometry, Badaire et al. suppressed lateral aggregations between cylinders and platelet like colloidal particles, causing them align face-to-face and form long columns in solution. This was done by roughening the particle surface which, when combined with addition of a depletant, controlled aggregation of the anisotropic particles into columns.[238]

Using these anisotropic building blocks, hierarchically engineered surfaces can be fabricated. For the particles and their ordering to impart anisotropic properties to a surface, one must choose a surface attachment strategy with the appropriate control. Perhaps the simplest method of surface attachment is gravity driven assembly, where a horizontal surface is submerged in a particle solution, and the particles settle to the surface. For example, Smith et al. assembled silica nanotubes partially filled with metallic cores into an array of columns by allowing gravity to orient the wires as they settled (Figure 30c). The “heavy” metallic end was therefore favored to be closer to the substrate, and assembly of vertically oriented rods occurred only when the concentration of rods was high enough to form a self-supporting film of standing rods.[239] Despite the influence of gravity, the nanowires could still diffuse by Brownian motion after assembling.

In general, diffusive motion and surface forces dominate the assembly of sub-micron structures. As a result, direction by evaporative or capillary assembly is an especially useful means of ordering particles, by crystallization at the liquid-air interface or by packing at the three-phase contact line.[240] In one example, CdTe nanotetrapods (100 nm arms) were collected from solution at the three-phase contact line, and positioned within lithographically pre-patterned cavities on a substrate during evaporation of a droplet.[241] When the cavity width was approximately the width of two arms the tetrapods oriented reliably with two arms facing towards the channel. Further, anisotropic surfaces can guide the crystallisation of materials into anisotropic assemblies, for instance when evaporation of C₆₀ dissolved in m-Xylene on horizontally aligned CNT films results in crystalline C₆₀ rods oriented along and combined with the CNTs.[242]

External forces such as electric or magnetic (e-fields, m-fields)[223,243] can be employed to override weaker forces (Brownian, surface) and create a temporary directional force between particles and the target substrate. For example, Carbon et al. and colleagues aligned nanorods by induction of a dipole during evaporation to functionalize a surface with aligned CdSe/CdS nanorods.[244] An electric field applied during evaporation of a droplet containing CdSe/CdS nanoparticles induced lateral alignment of the rods on the surface during evaporation. Hu et al. demonstrated this approach to align CdSe and CdTe nanorods across electrode gaps measuring several hundred nanometers.[245] These assemblies are of particular interest for making light-emitting devices, optical sensors and solar cells.

Chemical cues on anisotropic striped or decorated particles can also be used to control assembly and surface attachment. Chen et al. demonstrated assembly of a kagome lattice of Janus particles, which sediment onto a surface as shown in Figure 30a.[243] The Janus particles were made by sequential GLAD onto opposite faces of polystyrene microspheres, followed by treatment with octadeconethiol to render the faces hydrophobic. Because of the two distinct hydrophobic phases separated by a charged waist, each particle could interact with two other particles. Assembly was induced by screening electrostatic repulsions by adding NaCl to the solution. Short range hydrophobic attractions then directed assembly of the metallic faces into the Kagome lattice where each particle touches four others.

Overall, synthesis of anisotropic particles and their subsequent assembly on surfaces can clearly produce more diverse shapes and chemistries than top down methods discussed in previous sections of this review. However, capabilities to position and orient particles on surfaces cannot yet compete match the performance of lithography, and this limits the potential for integration. Therefore, lithography, and top down fabrication of anisotropic surfaces is a complementary technology to direct the placement of anisotropic particles. Applications will be further improved as modeling methods provide new pathways for particle assembly and surface functionalization with a higher degree of control.[246] Further, the organized attachment of anisotropic particles to surfaces offers great potential for the design and implementation of responsive surface behaviors.
on these surfaces were measured for many liquids including DI water, buffer solutions with different pH (8.0–11.0), and solvents. Consistently, the contact angles from the view parallel to the stripes ($\theta$) were 2–10° larger than the view perpendicular to the stripes ($\theta$). This data agrees with predictions using the Cassie (for $\theta$) and the modified Cassie (for $\theta$) theories where Cassie state is the state where the droplet is sitting on a composite substrate. This composite support can be two materials with different surface energies or can be solid and air in case of rough surfaces). Cassie’s theory can be written as

$$\cos \theta_c = f_1 \cos \theta_1 + f_2 \cos \theta_2$$ (5)

where the subscripts $S$, $L$, $V$ denote solid, liquid, and vapor, respectively; $\gamma$ is the surface energy, and $r_i$ is the radius of the three-phase contact line at the respective stripe.

6. Properties of Anisotropic Surfaces

6.1. Wetting

Anisotropic wetting is the occurrence of different apparent contact angles on a solid surface depending on the direction of view (Figure 31). Recent studies have demonstrated highly elongated droplets, unidirectional spreading of liquids, and anisotropic adhesion of droplets to engineered surfaces. These anisotropic surface architectures hold promise for several potential applications including open-channel microfluidics and self-cleaning surfaces (Figure 32–35).

For example, there is an enormous toolbox to design surface regions and/or compartments of particles with materials (i.e., polymers, gels, or surface-bound molecules) that change size or chemical affinity as a function of temperature, pH, light, or applied fields, and so on. These active surfaces could enable dynamic switching of optical spectra (e.g., transparency, surface plasmon resonance), adhesion, wetting, and other useful properties.

monolayers of alternating hydrophilic/hydrophobic surface chemistries. Upon wetting the chemically patterned surfaces by SWCNT aqueous solutions, cylindrical droplets were formed on the hydrophilic stripes. The flow inside these droplets during evaporation led to the controlled alignment and placement of individual SWCNTs along the middle of the hydrophilic stripes.

Wetting on physically textured anisotropic surfaces has been studied more extensively, in part because such surfaces are more accessibly fabricated, such as by nanoimprint lithography (Figure 31c). Recent studies have demonstrated wetting anisotropy ($\Delta \theta = \theta_2 - \theta_1$) ranging from $22^\circ$ to $79^\circ$ on micro- and nanoscale patterns, and enabled a detailed analysis of the anisotropic wetting theory. In general, for anisotropically rough hydrophobic surfaces, $\theta_1$ is larger than $\theta_2$. Moreover, for the same liquid volume, the droplet can have several different stable geometries (and hence different $\Delta \theta$) depending on the number of channels pinning the droplet. Also for a constant droplet volume, as the number of channels pinning the droplets decreases, both the average contact angle and the anisotropy become greater. The number of channels pinning the droplet depends on the droplet size and on how the droplet is formed (e.g., from a needle, free falling, or by condensation). For example, Chen et al. fabricated PDMS channels (with intrinsic contact angle $\theta_{ic}$) having $25 \mu m$ width and $30 \mu m$ depth. Using droplets of $1 \mu L$ volume, they reported $\Delta \theta = 20^\circ$ and explained that the droplets are trapped on the outer edges of the channels. Thus the droplets become squeezed in the direction of view parallel to the channels and stretch in the direction normal to the channels. The geometry of the contact line between the droplet and the substrate is found to be most accurately represented with a cubic curve,

$$\left(\frac{2|x|}{A}\right)^3 + \left(\frac{2|y|}{B}\right)^3 = 1$$

(7)

where $A$ and $B$ are the droplet lengths in the two orthogonal directions. Importantly, it was observed that the $A/B$ ratio (i.e., how stretched the droplet is) linearly correlates with $\Delta \theta$, while the size of the droplet is inversely proportional to $\Delta \theta$.

The highest anisotropy yet known, $\Delta \theta = 79^\circ$, was achieved using a surface made by interference lithography, where parallel PR lines ($\theta_{ic} = 76^\circ$) with $300 nm$ width and $1500 nm$ period (1/4 duty cycle) and $500 nm$ height were patterned on Si ($\theta_{ic} = 38^\circ$). Here, droplet sizes ranged from $1.5 \mu L$ to $30 \mu L$, resulting in $\theta_1 = 130^\circ$ and $\theta_2 = 51^\circ$. When the same pattern geometry was formed on top of a $300nm$ thick SiO$_2$ layer ($\theta_{ic} = 5^\circ$), the results change slightly giving $\theta_1 = 125^\circ$ and $\theta_2 = 43^\circ$.

Other examples of chemically patterned anisotropic surfaces include uniform $200 nm$ wide hydrophilic mica channels (10 nm depth) separated by $800 nm$ wide hydrophobic stripes of L-$\alpha$-dipalmitoyl-phosphatidycholine (DPPC) monolayers. The monolayer stripes were formed by an oscillating meniscus during the withdrawal of the sample from the organic monolayer solution. The anisotropic properties of these channels were demonstrated as templates for selective adsorption from solution. For example, when these substrates were withdrawn from colloidal solutions, only the hydrophilic channels were coated with gold particles, dye, and FeCl$_3$ by simple capillary filling. Applications in open channel microfluidics were demonstrated by fabricating complex microfluidic networks based on chemically directed flow through the hydrophilic channels. Space efficient gas-liquid reactions were performed in these networks in a compact microfluidic device along the flow in sidewall-free microchannels (Figure 32c). Further, anisotropic wetting surfaces made by chemical patterning can be used to control the alignment and placement of 1D nanostructures such as SWCNTs. Sharma et al. used microcontact printing to chemically pattern thin stripes ($175–900 nm$ wide) of self-assembled
suggesting that the surface follows the Cassie model (composite) with no interactions with the Si or SiO$_2$ substrate. On the other hand, after spin coating silica nanoparticles atop the SiO$_2$/PR structures, the contact angles changed to $\theta_h = 38^\circ$ and $\theta_v = 8^\circ$, thus retaining $\Delta \theta = 30^\circ$ in a fully hydrophilic Wenzel regime. More recently, the same group fabricated PR line patterns with different lithography duty cycles (affecting the line width and spacing), and studied the effect of the duty cycle on the wetting anisotropy. Coating the sample with CF$_4$ increased the overall hydrophobicity, and decreased the anisotropy to $\Delta \theta < 30^\circ$. These surfaces have potential applications in microfluidic flow and mixing as well as evaporation-driven self-assembly.

Unidirectional liquid spreading is a special case of anisotropic wetting where liquid droplets are pinned in three directions, and wet the surface in only one direction as shown in Figure 33. Accordingly, the droplet has three distinct contact angles: for the view parallel to the spreading, the contact angle is symmetric ($\theta_l$); and for the view perpendicular to the spreading direction there are two distinct contact angles, pinned ($\theta_{l,p}$) and spreading ($\theta_{l,s}$). Unidirectional spreading has typically been achieved using arrays of high AR (>10) bent or bent nanopillars. Kim et al. fabricated stepped nanopillars by molding and e-beam irradiation, resulting in bending angles of 60°. A 50 µL droplet exhibited the Cassie-Wenzel transition and spread in the direction of bending at a velocity of 50 µm/s, while remaining pinned in all three other directions, until it eventually reached a steady configuration (In contrast to a droplet in the Cassie state, a droplet in the Wenzel state has no air pockets underneath, so the liquid surface is in full contact with the textured solid substrate). The time evolution of unidirectional spreading on an anisotropic surface fabricated by Chu et al. is shown in Figure 33. This study used silicon nanopillars of diameter $d = 500$ nm and 750 nm, height $H = 6$ µm and 10 µm, and spacing $l = 3.5$ µm. The nanopillars were fabricated by RIE, followed by oblique angle e-beam evaporation of a thin film of Au; and then bent due to differential thermal contraction upon cooling. By comparing pillar arrays of different dimensions, the critical angle ($\theta_{cr}$) which determines the spreading in each direction was derived independently from the intrinsic contact angle of the pillar material,

$$
\theta_{l,r,s} = \tan^{-1} \frac{(H/l) \cos \varphi}{1 \mp (H/l) \sin \varphi} \quad (8)
$$

If $\theta_{l,r,s} > \theta_{cr}$, the droplet propagates, and otherwise it pins.

Anisotropic wetting adhesion is the phenomenon by which the roll-off angle of a liquid droplet depends on the orientation of the substrate with respect to gravity. Zheng et al. observed and analyzed the anisotropic wetting adhesion of the *Morpho aega* butterfly, and showed (Figure 34) that a 3 µL droplet rolls off in the radially outward direction with respect to the butterfly body when the wing is tilted by +9°, while the droplet stays pinned when the wing is tilted up to ~90° in the opposite direction. This fascinating property is caused by the hierarchical structure of the wing surface, which has flexible microscale patches that overlap like roof shingles (Figure 34d-g). The individual patches have anisotropic nanoscale texture with a stepped down topography in the direction facing outward from the body as well. Hence, the roll-off is a result of the droplet being in the Cassie state (with trapped air lubrication) when the wings are inclined downward with respect to the butterfly body; and when the wings are inclined upward the droplet is in the Wenzel state and has strong adhesion.

Engineered anisotropic wetting adhesion was demonstrated using a film of poly(p-xylene), PPX, made by OAP as shown in Figure 35. The film can hold a droplet of up to 45 µL against gravity when substrate is vertical and the nanorods are tilted upward, and when the substrate is horizontal and inverted. When the substrate is vertical and the nanorods are tilted downward, the droplet falls. The contact angle of the droplet on the film is 120° (superhydrophobic), yet the droplet adheres to...
the surface due to contact line pinning on asperities. The maximum droplet retention force that can be applied by the surface is \( \sim N \gamma d \) where \( N \) is the nanorod density (40 \( \times \) 10^6/mm^2), \( \gamma \) is the surface tension and \( d \) is the nanorod diameter (150 nm). Potential applications of these films in passive droplet transportation were demonstrated by directional liquid transport induced by vibration (Figure 35d).

Looking forward, it will be extremely beneficial to apply the principles of anisotropic wetting surfaces to mechanically durable materials that have widespread industrial applications. Combinations of engineered textures with the high thermal conductivity and corrosion resistance of aluminium and copper will be especially useful for applications in heat exchangers and turbomachinery. Additionally, the long-term performance of anisotropic wetting surfaces, including the effects of exposure to harsh, wet, and dusty environments, must be studied.

### 6.2. Adhesion

The use of anisotropic micro/nanostructures that have anisotropic adhesive properties enables the locomotion of insects and reptiles on a variety of surfaces including vertical walls and even ceilings,\(^{256, 257}\) and synthetic mimics of these surfaces is finding applications in robotics, household products, and biomedical devices. When climbing on a vertical surface, the body weight of an animal generates a large downward force which needs to be supported by a strong adhesion of its feet. At the same time the animal should be able to easily detach one or more feet for further locomotion without breaking the contact of the other feet.\(^{258}\) This is achieved using anisotropic adhesives which can be released easily in one direction, while providing strong adhesion in another direction.

In both insects and reptiles such as gecko lizards, these adhesion pads typically consist of arrays of angled branching hierarchical fibers with spatula-shaped tips as shown in Figure 36a. Interestingly, these architectures emerged independently in various animal groups as the optimal evolutionary attachment structures.\(^{256}\) Because of the small contact size and large aspect ratio of the fibers, they are able to conform to both rough and smooth surfaces. This way, millions of adhesive contact points are created between the foot and the climbing surface. The fibers adhere via van de Waals forces, possibly in combination with capillary forces.\(^{257, 259}\) The latter is a topic of debate; for geckos some researchers reject the influence of capillary effects, while others have shown an important influence of the humidity on spatula adhesion.\(^{259}\)

Analysis of these natural structures has determined that adhesion anisotropy is often established by angled fibers.\(^{260, 261}\) which yield a different tribological behavior along and against the pillar orientation.\(^{260–262}\) This effect was studied in detail in the feet of the green bush cricket,\(^{261}\) and the gecko,\(^{257, 263, 264}\) which have dendritic fibre arrangements with an angle of 30° to 70° to the surface. A different mechanism of adhesive anisotropy was observed in spider legs, for instance in A. See-manni and C. Salei,\(^{265}\) where the contact area is composed of long setae which are only covered on one side with fine tips. Depending on the sliding direction of the counter surface, the spatula shaped tips are pushed onto the surface or bend away from it, hereby altering the adhesion properties.\(^{259}\) Yao and Gao report detailed numerical modeling of anisotropic adhesion using a strongly anisotropic pad mimicking the gecko’s foot.\(^{261}\)

Synthetic anisotropic dry adhesives are a recent engineering achievement for which ingenious fabrication methods have been developed. Most engineered anisotropic dry adhesives utilize arrays of angled polymer microposts or nanofibers. For example, these are created by flipping over vertical fibers by pressing them between heated rollers,\(^{262}\) by drawing\(^{266}\) or even by rupturing them in an angled direction. Arrays of angled fibers have been made by the methods described in this review such as e-beam irradiation of an FE-SEM,\(^{193}\) while others directly define the angled geometry using inclined
Murphy et al. \[273\] developed a fabrication method where polymer microposts are dipped in uncured polyurethane (PU) and then pressed against a counter surface to create the mushroom shapes shown in Figure 36 b. These structures gave shearing forces of 100 kPa in the forward direction and only 20 kPa in the reverse direction. The anisotropy was controlled by the tip angle, where higher tip angles facilitated easier detachment. Sameoto et al. proposed a more deterministic fabrication method utilizing a two-step lithography mold fabrication, which allows to control of the offset of the cap on the supporting pillar. \[268\]

Further efforts have sought to create hierarchically branched structures that increase the number of contact points while retaining sufficient stiffness to prevent mechanical buckling. \[6\]

Jeong et al. developed an hierarchical anisotropic dry adhesive by a two-step UV-assisted replica molding technique, which is also mentioned in Section 4.3. \[267\] This design, shown in Figure 36 c, not only enables an adhesion anisotropy of more than 10:1 (26 N/cm² – 2.2 N/cm²) due to the inclined features, but also enables adhesion to rough surfaces (<20 μm) due to its compliant hierarchical tips. Hierarchical adhesives have also been made using SU8, \[274\] porous AAO templates, \[186\] modified soft lithography processes, \[6, 258, 260, 268\] and angled etching of a Si master mold. \[267\] Anisotropy has also been introduced by coating one side of the pillars with a metal layer. \[269\]

The performance of anisotropic adhesives is typically quantified by comparing adhesion in the forward and reverse lateral directions (parallel to the target surface), and in some cases adhesion perpendicular to the target surface. Lee et al. reported 4.5 N/cm² adhesion in the forward direction and 0.1 N/cm² in the reverse direction for slanted pillars fabricated by pressing between heated rollers. \[262\] In the case of slanted pillars generated by e-beam irradiation, the shear force was 11 N/cm² in the the forward direction, and 2.2 N/cm² in the reverse direction. \[193\] This adhesion force was maintained over 100 cycles without degradation. By combining these slanted pillars with oblique metal deposition, the same group reported a shear attachment of 31 N/cm² in the first direction, and 4.1 N/cm² in the second direction. \[269\]

Pressing and shearing an array of vertically aligned CNTs against a surface causes the CNTs to align with the shearing direction, and create an anisotropic adhesive with a strong shear adhesion force (100 N/cm²), and much lower lift-off force in the normal direction (10 N/cm²). \[270\] It is however unclear if the induced CNT deformation is permanent, and how the nanotubes react to subsequent loading in different directions. \[272\]

Besides the use of angled fibers, adding spatulas to the tips of microfabricated features can introduce anisotropic adhesion. Murphy et al. \[273\] developed a fabrication method where polymer microposts are dipped in uncured polyurethane (PU) and then pressed against a counter surface to create the mushroom shapes shown in Figure 36 b. These structures gave shearing forces of 100 kPa in the forward direction and only 20 kPa in the reverse direction. The anisotropy was controlled by the tip angle, where higher tip angles facilitated easier detachment. Sameoto et al. proposed a more deterministic fabrication method utilizing a two-step lithography mold fabrication, which allows to control of the offset of the cap on the supporting pillar. \[268\]

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Besides the use of angled fibers, adding spatulas to the tips of microfabricated features can introduce anisotropic adhesion.

Figure 34. Anisotropic wetting adhesion on a butterfly wing. (a) Butterfly with arrows showing the radially outward (RO) direction. (b) A water droplet rolls off the wing in the RO direction when it is tilted by 9°. (c) A water droplet is pinned even when the wing is tilted 90° against the RO direction. (d,e) Low and high resolution SEM images showing the lamellar morphology of the wing. (f,g) Low and high resolution AFM images of the micro- and nanoscale morphology of the wing. Reproduced with permission. \[5\] copyright 2007 RSC.
leaves residue, and anisotropy allows easy detachment. However, leave residue, and anisotropy allows easy detachment. However, from an industrial point of view, large scale production of complex hierarchical and anisotropic designs at low cost requires further work. Finally, future developments will include active anisotropic structures which can be switched through external stimuli. For instance, dry adhesives using nickel cantilevers that are driven by magnetic fields showed a 40:1 on:off ratio.\(^{[277]}\) We may eventually have surfaces that can switch from non-adhesive to adhesive states on demand, and/or where the direction and amount of anisotropy can be adjusted dynamically.

### 6.3. Electrical Conductivity

As the scale of electronic components has decreased, their complexity has increased, thereby accelerating demands for new materials for electrical interconnects. In particular, anisotropic conductive films (ACFs) have been used in electronics packaging for more than 30 years. In 1977 the first liquid crystal displays (LCDs) were manufactured using ACFs to make electrical contact (Figure 37a) between the circuit board and the multiple liquid crystal cells within the display via a thin indium tin oxide (ITO) layer. This allowed for a lighter, thinner package and eliminated the need to solder to the thin ITO layer coating the LCD display.\(^{[279]}\) Nowadays, a variety of materials with anisotropic electrical conductivity (AEC) have been developed, including patterned thin films, electrically conductive adhesives (ECA), and polymer-nanostructure composites where the nanostructures are shaped and/or organized to give anisotropic conductivity. Anisotropic electron and ion transport is also of interest for battery electrodes, electrochemical actuators,\(^{[280,281]}\) and photovoltaics. In these materials, the nanostructures are engineered to perform electron transfer reactions on their surface, and shape anisotropy is useful to direct electrons to a typically planar current collector.

ECAs are the largest category of materials that have been engineered to exhibit AEC. ECAs include anisotropic conductive adhesives (ACA) and ACFs, wherein the individual components are isotropic but the final matrix is anisotropic. ECAs typically comprise an organic or polymeric binder matrix with a metal filler (5–10% by volume), that allows electrically conductive paths to be made between individual devices and the main circuit board.\(^{[282,283]}\) Because of the low volumetric loading of the metal particles, these materials form a conductive path only where the particles are squeezed between the contact pads, and not through adjacent particles (Figure 37b). As a result, parallel electrical lines with pitch as small as \(\approx 30 \mu m\) can be created, whereas solder bump joining tends to encounter flow restrictions with pitches smaller than 200 \(\mu m\).\(^{[279]}\) Currently, both thermosets and thermoplastics are used for the adhesive matrix. The most common conductive particles have a plastic core, coated with a metal such as gold or silver, then coated with a polymer shell.\(^{[282,284]}\) During mechanical deformation under pressure and temperature, the polymer shell is damaged and the particles form an electrically conductive path via the metal underneath the shell. Alternatively, the use of magnetic particles has been successfully demonstrated where their alignment is controlled by a relatively weak magnetic field.\(^{[285]}\) In these designs, the matrix material primarily determines the strength of the connection, thus allowing somewhat independent tuning of the mechanical properties. On the other hand, soldering relies on a single soft metal for both mechanical and electrical function. Applications of anisotropic ECAs include flat panel displays (FPDs), LCDs, chip-on-glass (COG), flexible circuits, rigid board circuits, radar systems, and ultrasound transducers.\(^{[282,286]}\)

In order to achieve multi-use flexibility and smaller feature sizes, conductive pathways formed from anisotropic nanostructures are the ideal solution for ACFs. While there are many types of anisotropic nanostructures, carbon nanotubes (CNTs) are sought after, especially as fillers for polymer-nanostructure composites, because of their mature growth methods and excellent combination of mechanical and electrical properties.\(^{[280,287]}\) CNTs can exhibit ballistic electron transport over micron lengths at room temperature, and bundles of aligned CNTs still show greater conductance axially versus laterally.\(^{[288,289]}\)
The most common approach to create CNT-based ACFs uses a low volumetric loading of slightly aligned CNTs in polymers to create a highly conductive pathway, which typically has an anisotropic factor on the order of 4.\textsuperscript{281,290} Overall, the use of aligned CNTs, or the assembly of CNTs into films, results in a material with an electrical conductivity that is dominated by the network properties. The junctions between CNTs within the network not only reduce the electrical conductivity through increased contact resistance, but also allow flow of electrons parallel to the interface planes, thus reducing the film's achievable anisotropic properties.\textsuperscript{291}

Although CNT-CNT junctions limit the properties of aligned CNT networks, the application of these materials in electronics is still promising. Flexible interconnects of horizontally aligned CNTs (HA-CNTs) have been made by growth of vertically aligned CNT patterns, followed by mechanical rolling and transfer printing to PDMS as shown in Figure 38.\textsuperscript{164} These HA-CNT sheets showed a highly anisotropic DC conductivity of 36:1 parallel:perpendicular to the direction of CNT alignment.\textsuperscript{292} Further, these sheets have been used as substrates for growth of ZnO NWs. Bridging between adjacent CNTs by the ZnO increased the electrical conductivity of the film while maintaining its anisotropy, and enabled coupling of the photoelectric properties of ZnO to the CNTs. Organic crystals have also exhibited anisotropic transport up to 100:1 in orthogonal directions of the crystal lattice.\textsuperscript{293} but their overall conductivity is not sufficient for high performance interconnects.

Future implementation of anisotropic nanostructures into electronics will require patterning commensurate to contact pitches on devices. Additional improvements in electrical anisotropy through junction control or chemical coating on the nanostructure networks is also needed to maintain tightly defined electrical pathways. Nevertheless, the inherent anisotropy of nanostructured films and networks such as CNTs, along with their mechanical durability and adhesive properties, encourages further development.

6.4 Thermal Management

Thermal management of heat dissipated by integrated circuit components is currently the largest challenge in microelectronics.\textsuperscript{299} and this is exacerbated by reductions in the size of system components. In order to maintain current performance trends, high performance materials for directing thermal loads to locations in the system where they can be efficiently removed, are needed. In order to transport heat most effectively, materials should have a high thermal conductivity in the desired transport directions while having a low thermal conductivity in transverse directions. This anisotropy minimizes the need for insulation,
and reduces heat transfer to undesired areas. Having reached the limits of bulk materials, the current trend is towards high thermal conductivity, anisotropic nanostructures.\[296\] Additionally, for packaging, thermal interfaces must have low coefficients of thermal expansion (CTE) close to that of semiconductor materials, thereby minimizing mechanical stress at the joining plane. Crystalline nonmetallic materials have received the most interest in this regard, because their CTE values are much lower than bulk metals, and they have comparable thermal conductivity. The use of nanostructures with dimensions comparable to typical phonon mean free paths of 10–100 nm enables engineering of thermal transport.\[297\] Accordingly, carbon nanotubes (CNTs) have received a lot of attention due to their exceptional thermal conductivity, which is phonon-dominated and is relatively insensitive to mechanical deformation.\[288,298\] Additionally, because CNTs are 1D nanostructures and natively anisotropic, they may be considered as building blocks to provide directed thermal transfer from a load to sink without losses to the surrounding environment. Specifically, individual CNTs have been shown to have a thermal conductivity of over 3000 W/m K at room temperature, which exceeds both copper (400 W/m K) and diamond (2300–3320 W/m K).\[288,299,300\] Boron-nitride nanotubes (BNNTs) are also of interest because they have thermal conductivity of 350 W/m K near room temperature.\[301\] Also, BNNTs are electrically insulating, and have fewer defects at diameters of 10 nm and below. However, existing BNNT growth methods are not as versatile as CNT growth methods\[302\] and require higher temperature and more complex precursor chemistry. As a result, BNNT thermal interfaces are at a much earlier stage of development.

In order to integrate CNTs in a practical thermal interface, they need to be arranged in a branched network or aligned array that provides a large number of parallel conduction paths along with a large effective contact area.\[303\] An exemplary configuration uses a vertically aligned CNT array between two parallel plates, which may represent a heat generating component (e.g., microprocessor) and a heat sink. While individual CNTs have exceptional conductivity, the junctions within CNT networks and arrays, and the interfaces themselves, lead to increased phonon scattering and ultimately reduce the thermal conductivity in the desired axial direction, while also increasing it in the transverse direction.\[304\] Additionally, without a binder material (which further increases phonon scattering), CNT arrays do not typically meet the mechanical properties required by high strength applications. For example, typical polymer matrices have lower thermal conductivities, \(~5\) W/m.K, than even the as grown, undensified CNT arrays themselves, which are in the range of 18 to 265 W/m.K based on volume averages.\[305\] And, in aligned CNT-polymer composite interfaces the ratio between axial and transverse thermal conductivity has been shown to be between 2 and 5, illustrating that the final structure is still anisotropic although the overall thermal conductivity is significantly lower than metals.\[305\] Potential reasons for the decrease in thermal conductivity are phonon scattering within the individual CNTs by the polymer matrix, interfacial thermal resistances between the CNTs and the matrix, and impurities or defects in the CNTs.\[300,305,306\] Future work minimizing the defects detrimental to the thermal conductivity of these composite matrix materials will potentially allow for high performance thermal interfaces to be realized. Because junctions in the CNT networks limit thermal transport so much, it is possible that there is a maximum limit for achievable thermal conductivity. Spatially separated aligned CNTs could provide enhanced anisotropy, but the conductivity will determined by the packing fraction. Future system concepts may utilize multiple modes of cooling such as conduction through anisotropic nanostructure arrays along with heat transfer to liquids.\[307\]

6.5 Manipulation of Electromagnetic Waves

The anisotropic conductivity of anisotropically patterned metal surfaces also enables directional manipulation of electromagnetic waves. In general, the dimensional limits of the fabrication
technique and/or the size of the constituent nanostructures determine the wavelengths that can be addressed. Wire grid polarizers, which have been made for decades, are perhaps the most prominent example and can be designed across a broad range of wavelengths. Within the limits of lithography-related techniques, optical applications are most typical including linear [308] and circular [28] polarizers and infrared (IR) detectors. [309] Here we focus on recent work enabled by the fabrication of anisotropic surfaces with optically-active sub-micron features.

Perhaps the simplest example is the use of metal gratings fabricated by NIL as passive optical elements such as broadband polarizers [310] and color filters [311]. For example, gold gratings fabricated by nanoimprint lithography were recently used as filters that reflect a particular color and direct the absorbed light to a photovoltaic layer below. [312] The color of the gratings was simply related to the spatial frequency of the imprinted pattern; periods of 420, 280 and 220 nm correspond to cyan, magenta, and yellow, respectively. At smaller length scales, NIL can manipulate optical properties via plasmon resonances of metals, which in general depend on the structure dimensions, shape, and texture. Of particular interest are Metal-Insulator-Metal (MIM) resonator structures, with applications ranging from waveguides [313] to negative index materials. [314] Al/ZnSe/Al nanoresonator arrays, comprising periodic strips whose geometry determines the position of a single peak in the transmission spectrum, have been demonstrated as polarizing color filters. [315] While these structures were made by sequential thin film deposition followed by ion milling, there is certainly potential for more cost-effective fabrication using multi-layer imprint methods.

More complex anisotropic structures such as arrays of gold micro-helices and double helical nanowire structures can function as broadband circular polarizers [28, 103]. The gold helices are analogous to split ring resonators viewed in an oblique angle except that the linear birefringence is absent; therefore, their polarization eigenstates correspond to circular polarizations instead of elliptical polarizations. When a beam of light is passed perpendicular to the axes of the helices, depending on the handedness of the helices, either the right-handed circular polarization (RCP) or the left-handed circular Polarization (LCP) is transmitted while the opposite polarization is absorbed (Figure 39). The optical spectrum can be simulated and is

Figure 38. Fabrication and characterization of a horizontally aligned (HA-CNT) film, before and after coating with ZnO NWs. Schematic (a) depicts: (1) CNT forest “blade” growth from lithographically patterned catalyst; (2) and (3) folding of CNTs to horizontal orientation using mechanical rolling and surface tension; (4) deposition of Au contacts using shadow mask pattern; and (5) ZnO NW growth. A schematic of the final device (b) is accompanied by SEM images of the ZnO NW morphology on a HA-CNT sheet with ~1.5 μm thickness. Graph (c) depicts the I–V curves before and after ZNW growth in the parallel (along the CNTs) and perpendicular (normal to the CNTs) directions. Reproduced with permission,[292] copyright 2010 Wiley.
determined by the dimensions (e.g., pitch, number of turns, diameter) of the helices.

Anisotropic assemblies of nanostructures such as aligned CNT arrays can also function as polarizers. Because CNTs are conductive, they absorb waves with polarization parallel to their axes and transmit waves with polarization perpendicular to their axes. Aligned CNT optical polarizers typically achieve polarization greater than 0.9,[309,316] where 1.0 represents perfectly polarized light. CNT arrays have also been used as IR polarimeters,[309] and it was suggested that the intensity and polarization of an incident beam can be measured by employing two sheets of aligned CNTs placed at 90°. Each of the aligned CNT sheets will be able to measure the magnitude of the electric field in the direction of CNTs; therefore, and putting the two components of the vector together, the polarization state of a beam could be determined.[309] Further, it was recently shown that horizontally aligned CNT films can also function as terahertz polarizers, because CNTs have high terahertz conductivity along their axis. For example, the terahertz absorption spectrum of an aligned HA-SWNT film (2 μm thickness) mounted on a sapphire window depends strongly on the angle of the polarization terahertz field and the CNT axis (Figure 40).[316] Even though the CNTs are quite wavy on the sub-micron scale, they behave as perfectly straight on the millimeter scale of the terahertz waves and therefore absorb essentially no terahertz radiation when the field is perpendicular to the CNTs.

The polarization capability of individual anisotropic elements is emphasized by the use of individual CNTs as polarization-sensitive near-field probes.[160] Here, Au nanodisks were placed in proximity to individual horizontally aligned SWNTs grown on quartz. When the substrate was illuminated with light polarized perpendicular to the CNTs, the CNTs were excited by near-field coupling with the Au disks. The strength of this coupled excitation was measured by resonant Raman spectroscopy of the CNTs. Therefore, the CNTs served as directional probes of the local electric field in the metal structures. This phenomenon will be useful in photonics and molecular sensing devices.

Further advances will be enabled by improved dimensional control in fabrication of metallic nanostructures, and improved 3D fabrication with the general aim to enable arbitrary manipulation of electromagnetic fields. In fabrication of metallic surfaces, one critical issue that couples fabrication to applications is the high sensitivity of surface plasmon resonance modes to the size, shape, and spacing of nanostructures. Improved methods to assemble nanostructures made by bottom-up methods, such as CNTs, will also be very fruitful. For example, calculations show that the optical properties of square grid arrays of vertical CNTs could be tuned exquisitely by the CNT diameter and grid spacing, and these arrays could function as deep-UV photonic crystals and near-perfect absorbers.[317] However, current limits to precision placement of catalyst particles prevent these CNT grid arrays from being realized.

6.6. Bioengineering

Anisotropy is inherent in many biological tissues, and therefore anisotropic surface topographies with sub-cellular dimensions are highly relevant to biology and medicine. For example, muscle tissue actuates directionally and without the global order of the cells organs would not function properly. Similarly, the brain is able to send and receive signals from all over the body because the nervous system comprises a highly branched bidirectional network of nerves. Synthetic anisotropic surfaces have been used to explore how cells sense and respond to surface texture, and to develop grafts for repair of damaged tissue by providing directional physical cues. Relevant surface designs include micro and nanoscale grooves patterned by various lithography methods, assemblies of aligned nanofibers or CNTs, and wrinkled thin films.

Overall, it is not surprising that cells respond to micro- and nanoscale features, because cell bodies are generally ~10–25 μm diameter, and subcellular components such as protein complexes and lipid bilayers are ~1-25 nm. Early on, Whitesides and colleagues established that cell viability could be directed by microscale patterns of extracellular matrix (ECM) on flat surfaces.[318] Since then, research has shown that cells respond to physical cues as small as 10 nm.[319–321] The lower limits of many fabrication methods discussed in this paper are commensurate with these dimensions, and thus a wealth of scientific understanding is within our grasp. While in general it has been shown that cells respond to anisotropic topographical cues, it is important to remember that the particular responses depend on the substrate feature size, texture, and chemistry, as well as the cell type.

The means by which cell shape and alignment are influenced by the surface of a culture substrate is known as contact
Anisotropic surfaces have enabled fundamental studies of contact guidance as well as applications of aligned cell and tissue constructs cultured on anisotropic surfaces. Early work by Clark et al. cultured baby hamster kidney (BHK) cells, Madin Darby canine kidney (MDCK) cells, and chick embryo cerebral neurons, on PMMA microgrooves. Photolithography and reactive ion etching were used to pattern grooves with 4–24 μm width and 0.2–1.9 μm depth. The researchers observed that BHK and MDCK cells align with the grooves, and that found alignment was influenced more by groove depth than width (pitch). For MDCK cells the alignment behavior within cell colonies was different than the alignment behavior of isolated cells. Alignment of neurite outgrowth from chick neurons was observed on 2 μm depth grooves but not 1 μm depth grooves; and both MDCK cells and chick neurites bridged across deeper grooves. As a result, it was concluded that alignment behavior depends on both the cell type and groove dimensions, particularly depth.

In 1991, Nagata et al. studied the effect of substrate topography on neuron growth by culturing rat and mouse neurons from the peripheral (PNS) and central (CNS) nervous system on aligned neurite bundles. They found that PNS neurons were always aligned with the bundles, whereas CNS neurons exhibited both parallel and perpendicular alignment (but not random alignment). Two years later, the same group cultured CNS and PNS neurons on quartz grooves (1–8 μm wide, 0.5–0.8 μm deep). These dimensions were chosen to be similar to a tightly aligned neurite bundle, which is what neurons might encounter while developing inside the body. Again it was found that CNS neurons extended neurites perpendicular and parallel to the grooves, whereas PNS neurons were always parallel.

Rajniczek and others expanded on this pioneering work by showing that perpendicular contact guidance of neurons depends on the type of neuron, the age of the neuron, and the groove dimensions. In their study, quartz substrates were patterned using electron beam lithography and dry etching, giving grooves with 1–4 μm width and 0.014–1.1 μm depth. The percentage of neurites bridging grooves was linearly related to the groove depth. In particular, hippocampal neurons grew on quartz grooves and MDCK cells align with the grooves, and chick neurites bridge across deeper grooves. As a result, it was concluded that alignment behavior depends on both the cell type and groove dimensions, particularly depth.

Anisotropic surfaces have enabled fundamental studies of contact guidance as well as applications of aligned cell and tissue constructs cultured on anisotropic surfaces. Early work by Clark
influences cell behavior. They also found that perpendicular or parallel contact guidance depended on the type of cell media used (Epilife versus DMEM/F12), which indicates that the chemical environment of the cell may influence the mechanisms of contact guidance, perhaps by presenting a positive or negative signal.

Another anisotropic surface design for cell culture uses aligned fibers, and this design is promising because fibers can be made into long constructs, without the size limits of substrate patterning methods. Gertz, et al. compared the growth of embryonic rat motor neurons on surfaces of laterally aligned electrospun polylactic acid (PLLA) nanofibers, randomly aligned fibers, flat PLLA, and flat glass. The early development of neurites was accelerated on the fiber substrates, and the resulting neurites followed the direction of the fibers. Similarly, Hurtado, et al, showed that P4 rat pup dorsal root ganglia (DRG) aligned on electrospun PLLA fiber substrates (Figure 41). The same group also performed in vivo studies using electrospun PLLA fiber nerve grafts. The spinal cord of a rat was transected and then a nerve graft of aligned PLLA nanofibers was placed at the site of injury. After 1-4 weeks the neural regeneration was more robust inside the aligned PLLA graft as compared to control grafts made from PLLA films and randomly oriented fibers. In a similar study, Kim, et al. showed robust PNS tibial nerve regeneration inside an aligned electrospun graft compared to grafts with unaligned electrospun fibers and a graft filled only with saline.

As nanofabrication capabilities have advanced, many recent studies have focused on how cells respond to anisotropic textures with nanoscale lateral feature dimensions. Kim et al. studied cardiomyocyte development using arrays of grooves (200–1600 nm pitch, 200–500 nm depth) in polyethylene glycol (PEG), fabricated by a UV-assisted molding method. Previous cultures of cardiomyocytes on flat substrates did not replicate the in vivo organization of cardiac tissue. The groove dimensions chosen by Kim, et al. corresponded to their measurements of aligned collagen fibril diameters observed under cardiomyocytes from explanted cardiac tissue. On the flat substrate, the cardiomyocytes had random alignment and random direction of contraction; on the grooved substrates, the cardiomyocytes aligned and contracted parallel to the grooves. Increased conduction velocity was also observed on the grooved substrates. These findings suggest contact guidance induced by the ECM of aligned collagen fibrils directs the orientation and mechanical behavior of cardiomyocytes in the body.

Yim et al. cultured bovine pulmonary artery smooth muscle cells (SMC) on PMMA and PDMS groove arrays (350 nm width, 350 nm depth), patterned by nanoimprint lithography. Although SMCs showed no alignment on flat substrates, SMCs cultured on grooves were elongated and parallel to the grooves, which is more similar to their in vivo morphology. The cells also demonstrated greater motility along the axis of the grooves, which could be an important finding for applications in wound healing. Interestingly, cell behavior was similar on PMMA and PDMS, despite the different stiffness and surface chemistry of the two materials.

Another study observed axon alignment from adult mouse sympathetic and sensory ganglia using nanoimprinted PMMA grooves (200–2000 nm pitch, 300 nm depth). Fast fourier transform (FFT) image analysis indicated better alignment and homogeneity on ridges wider than 100 nm (200–500 nm pitch). Scanning electron microscopy showed a growth cone with filopodia extending both parallel and perpendicular to the grooves (Figure 41).

In addition to surfaces with linear grooves, more complex anisotropic pattern designs have been shown to alter cell function or direct cell migration. For example, Jiang, et al. demonstrated that cells polarize on a patterned self-assembled monolayer and that their migration can subsequently be controlled. Microchannels with periodic arrow-like (ratchet) shapes have been used to direct cell migration, potentially enabling continuous label-free sorting of multiple cell types. This technique has also been applied to sort Escherichia coli cells by length by incorporating them into a microfluidic device with curved channels where only the shortest cells can follow the tightest curves. Vandeperre et al. formed wrinkles in a PDMS substrate by solvent infiltration and then cultured fibroblasts on these substrates. They observed that filopodia align with the wrinkles and that integrin binding is limited to the tops of the ridges. The data suggested that the
nanoscale topography may direct filopodia alignment, but that micro-scale patterns may be necessary for the focal adhesions to form.\textsuperscript{[341]} Engelmayr et al. designed an accordion-like scaffold with micro-scale honeycomb structure to control the growth cardiac cells (Figure 43).\textsuperscript{[342]} The scaffold was constructed of poly(glycerol sebacate) and its properties were tuned to resemble the anisotropic stiffness of the adult rat right ventricular myocardium. The cardiomyocytes aligned parallel to the preferred direction on the scaffold and showed electrical anisotropy.

Additionally, there is a possible connection between cell alignment on anisotropic textures and the surface tension forces that give rise to anisotropic wetting. Lenhert et al. cultured three cell types (osteoblasts, \textit{M. grisea}, and \textit{P. graminis}) on polystyrene groove arrays (0.4–3.0 $\mu$m pitch, 0.1–0.25 $\mu$m depth).\textsuperscript{[343]} The resulting cell shape (the lengths of the major and minor axes) was then compared to the shape of a water droplet on the same surface. A linear relationship was found between cell shape and droplet shape. This finding suggests that capillary forces may affect cell morphology, and that substrate wetting behavior should be considered in quantitative models of cell shape, especially on anisotropic textures.

Finally, the growth of elongated nanosstructures enables studies of cell and tissue response to even smaller features. Many studies have used CNTs as culture substrates,\textsuperscript{[344]} owing to the ability to control CNT diameter ($\approx$1–100 nm), organization (e.g., random, vertical, horizontal), and chemical functionalization, as well as their attractive combination of mechanical and electrical properties. An initial study on immobilized CNT biocompatibility found that human skin fibroblasts demonstrated increased alignment and double migration velocity on aligned CNT sheets compared to flat glass and flat plastic.\textsuperscript{[345]} More recently, Abdullah et al. cultured Chinese hamster ovary (CHO) cells on aligned multi walled carbon nanotubes (MWCNT).\textsuperscript{[341]} The MWCNTs (10 nm diameter) were fabricated as a vertical forest by chemical vapor deposition (CVD), and then drawn to create an aligned sheet that was subsequently transferred to a glass slide. The CHO cells aligned parallel to the MWNT, but did not have an elongated morphology. Additionally, CHO cells were less clustered on CNT substrates as compared to flat glass. These results indicated that contact guidance directs cell behavior even on features as small as 10 nm.

![Figure 42](image1.png) **Figure 42.** Aligned polymer fibers specify the direction of DRG neurite growth. DRG isolated from P4 rat pups were cultured on (a) film, (b) random fiber, and (c) aligned fiber substrates. Random (d) and aligned (e) electrospun polymer fibers were visualized by scanning electron microscopy. Reproduced with permission,\textsuperscript{[333]} copyright 2011 Elsevier Ltd.

![Figure 43](image2.png) **Figure 43.** Microstructured honeycomb cardiac scaffold. (a) Schematic diagram of the honeycomb design. (b) SEM image of the poly(glycerol sebacate) PGS structure created by excimer laser microablation. (c) Fluorescence microscopy image of neonatal rat heart cells cultured for one week on honeycomb scaffold with F-actin stained green and cell nucleus stained blue, showing that cells completely fill the anisotropic pores in the pattern and cell alignment is generally parallel to the widest part of the pattern. All scale bars 200 $\mu$m. Reproduced with permission,\textsuperscript{[342]} copyright 2008 NPG.
in vivo study immobilized aligned CNTs in a poly[styrene-b-isobutylene-b-styrene] (SIBS) matrix and implanted it in guinea pigs for 1–26 weeks.\textsuperscript{146} The immune response was similar between the aligned CNT/SIBS capsule and the control SIBS capsule, which provides a promising early indication of the biocompatibility of immobilized aligned CNTs.

Practical applications of anisotropic surfaces for tissue engineering and in vivo applications are beginning to emerge and improved treatment of many disorders will require an in-depth understanding of how cells shape or align in response to complex directional cues. Although features with biologically relevant length scales can be made using many techniques, the ability to precisely vary the dimensions over a wide range will lead to better understanding of how topography mediates biological function and development, and more complex and hierarchical designs (especially in 3D) are needed to accurately mimic the cellular environment. It will also be interesting to study surfaces patterned with both physical and chemical cues, such as varying stiffness or protein gradients. Development of hybrid surfaces that more closely mimic the in vivo biological environment will be essential to both fundamental studies and regenerative medicine. In addition to aiding regeneration of inherently anisotropic tissues such as muscles and nerves, new surface designs could enhance directed differentiation of stem cells,\textsuperscript{347} enable cell improved cell separation methods, and be used in new adhesives and bandages.

7. Conclusion and Outlook

We reviewed and classified widespread methods to fabricate surfaces with arrays of asymmetric 2D and 3D features. Surfaces made by these methods have represented important advances in control of wetting and adhesion, electrical and thermal conductivity, optical properties, and cell culture and tissue engineering.

While a tradeoff between geometry and order is prevalent in existing fabrication methods, it was emphasized that many applications of anisotropic surfaces do not require precise placement of features. For instance, control of adhesion and wetting can be achieved by patterning anisotropic structures with locally random placement. On the other hand, further advances in optical metamaterials and photonics can be realized only by ab initio design of features with controlled placement, geometry, and size. These typically require more expensive lithographically-based methods, or methods that combine self-organization with lithographically patterned templates. Growth of cells and tissues can respond to imperfectly ordered patterns; however, the role of substrate order on cell behavior phenomena is not comprehensively understood. Biointerfaces also involve a hierarchy of length scales that extend beneath the limits of many current fabrication methods, and must incorporate building blocks such as DNA and proteins.

Clearly, there are great opportunities and challenges for further developments, toward an eventual goal to enable design and fabrication of heterogeneous surface features over large areas. Because fabrication process innovations are often motivated by specific applications, processes have been developed in the context of relatively small sets of materials and feature geometries, and the a priori control material, geometry, and feature dimensions is not yet possible. Moreover, the most diverse library of anisotropic surface designs can be made in polymers, yet for many commercial applications to be realized, innovations are needed in scalable fabrication of metal and ceramic surfaces (e.g., for controlling wetting and thermal/electrical transport), and biomaterials (i.e., proteins and gels) for new cell and tissue interfaces.

In the future, new methods to create 3D surface features at sub-micron scales will be especially useful for new biomaterial interfaces, optical metamaterials, and novel multifunctional sensing interfaces that combine transduction of physical, chemical, biological, and/or optical properties. Improved understanding of the morphological evolution of films during PVD,\textsuperscript{348} as well as crystallographically patterned nucleation and growth of sub-nanometer scale structures, could enable deterministic fabrication of anisotropic materials and surface patterns with unprecedented order. And, 3D structures made from natural filaments such as collagen and actin may be achieved by extending recent innovations in manipulation of nanotubes and nanowires using capillary forces. Responsive surfaces that enable changes in surface geometry and properties upon ambient stimulations will become omnipresent, and will be aided by combining chemical synthesis of anisotropic particles with directed placement onto pre-patterned templates. And, high-throughput metrology techniques and standards are needed to measure and implement dimensional control of complex surface textures, which is especially important for manufacturing. Therefore, the most impressive advances in this field will combine basic understanding of interface properties with novel fabrication principles that can be adapted to large-scale production.

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