Freestanding Metallic and Polymeric Nanostructures: Directed Self-Assembly

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Abstract
Suspended, high aspect ratio structures can be extremely flexible, to the point where they are overly delicate, difficult, and expensive to fabricate on wafers by standard undercut and release. However, capillary forces that normally destroy such structures can be redirected in ways to directly self-assemble nanoscale structures on top of fabricated wafers. One class of methods reviewed uses capillary forces to transform droplets of liquid polymers into the suspended fibers and membranes. Another set of methods spontaneously grows freestanding intermetallic nanowires at selected locations on a device or wafer. Both approaches are one-step procedures that can be used to directly add three-dimensional (3-D) nanomechanical functionality to wafer-scale fabricated devices. These methods have the additional desirable property that they can be performed at room temperature in ambient air. The nanoscale structures provide high-resolution features that can be used in place of top-down nanolithography to build up complex 3-D nanoelectromechanical systems (NEMSs) devices and microsystems through templated growth. These new structures and geometries can provide potentially useful functions in novel forms. This point about novel forms and functions is illustrated through the presentation and consideration of possible applications of a few novel microsystems that could be built up from the basic nanostructures.

INTRODUCTION: DEFINING SELF-ASSEMBLY AND DIRECTED SELF-ASSEMBLY

Self-assembly refers to reactions or transformations that take place spontaneously. This is to say that excess energy in a system drives a transformation of the system from its current state into a lower energy state. Consider the simple case of pushing a ball up a hill which adds potential energy and is a non-spontaneous transformation. Releasing the ball at the top of the hill can produce the spontaneous reaction of falling as the ball seeks the minimum potential energy and can be viewed as self-assembly. In reality, the ball might not reach the minimum for a number of reasons, such as the rolling resistance is too high for the ball to start rolling, or the ball could be trapped in a local depression. A reaction that reaches an intermediate metastable state could also be viewed as a type of self-assembly. A metastable state can have a short or long lifetime depending on the height of the surrounding energy barrier and the magnitude of disturbances (e.g., in the case of a ball, wind, or ground vibrations and in the case of material systems, thermal fluctuations, and the related kinetics).

Based on this broad definition of self-assembly, one can classify all systems as either being in equilibrium, being pushed, or held away from equilibrium by applied forces, or in the process of spontaneously returning to equilibrium. Therefore, one might conclude that self-assembly is no more than a thermodynamic or kinetic concept. While this is true physically, there is a philosophical difference. Our engineering view is that self-assembly uses spontaneous transformations in nature to automatically make desired structures. That is, self-assembly is an alternative to the precisely specified (often called, “top-down”) manufacturing of a desired structure [We do not use the term “bottom-up” manufacturing to refer to self-assembly, since some self-assemblies are top-down (larger structures evolving into smaller, more precise structures, e.g., spinodal decomposition or capillary thinning of liquid threads) and others are bottom-up (smaller structures evolving into larger structures, e.g., nucleated growth of crystals and raindrops).]. We believe that self-assembly methods have the potential to replace top-down nanomanufacturing processes with simpler, faster, and lower-cost processes of comparable uniformity and precision. Of particular interest is the potential to use self-assembly processes that tend to converge toward a single common result. For instance, in polishing or in multilayer deposition, depending on the materials used and the processing conditions, a small defect can either grow or decrease in size with each processing step. Processes such as the latter, where uniformity and precision improves with processing time, are especially appealing. As an example illustrating this definition of self-assembly, growth of silicon boules from a melt, while a tightly controlled growth process, can be considered as a
type of self-assembly that produces a crystalline material with atomic-level perfection. Another example is the formation of micelles in a solution that is saturated with a surfactant, which can produce essentially monodisperse spheres. A liquid jet at a specific diameter and velocity can break up into a continuous stream of monodisperse droplets (via Plateau–Rayleigh instability).[1] Thin films of liquids can dewet from solid surfaces to form periodic arrays of droplets (via Rayleigh-Taylor instability).[1] The dewetting instability proceeds at a preferred spatial frequency (in mathematically analogous form to spinodal decomposition).[2] A few other examples are well-structured solidification growth fronts due to the constitutional supercooling of metal alloys (e.g., hexagonal cellular growth of Sn–Pb eutectic)[3] and the various (lamellar, spherical, cylindrical, gyroidal) phases of block copolymers.[4]

An appealing capability would be the ability to include self-assembly processes in the fabrication of devices. One or more of the fabrication steps might include self-assembly processes that occur at selected locations on the device. We refer to these types of processes as “directed self-assembly.” Especially appealing are those directed self-assembly processes that with approximate or simple directions cause macrostructured materials to evolve into more precise and uniform nanostructures. While there are numerous methods to grow nanostructures, there are few far methods to selectively grow or (after growth) place these same nanostructures at user-designated locations on a device.

This entry reviews the recent developments in these types of directed self-assemblies. One major class of methods uses viscoelastic extensional flow and capillary thinning of polymeric liquids to form “air-bridges,” which are nanofibers or membranes that are suspended over free-space or air-gaps. A second class of methods stimulates at selected locations the nucleated growth of freestanding metal alloy nanowires. This entry first reviews these methods. Then, we consider the broader use of the structures in the three-dimensional (3-D) fabrication of micro- and nanoelectromechanical systems (MEMSs and NEMSs). Then, applications of the structures that are enabled by the resulting high aspect ratio structures are considered.

**SELF-ASSEMBLY STRATEGY I: CAPILLARY FORCE-DRIVEN SELF-ASSEMBLY OF POLYMERIC LIQUIDS**

Capillary forces, which are well known for causing the undesirable collapse of overly flexible microcantilevers and beams during wet-etching, can be redirected to directly self-assemble the suspended fiber air-bridges from liquid polymers. The basic “brush-on” method, as shown in Fig. 1, can produce well-ordered arrays of nanometer diameter fibers by simply hand-brushing a solution of dissolved polymer over an array of microscale pillars.[5] Due to its large surface area, the initially drawn liquid film is unstable. It breaks up into threads that span the pillars in the direction of brushing. Then, these liquid bridges, which are extended beyond their limit of stability, continue to thin due to capillary forces (specifically, the Laplace pressure, \( \gamma/r \), where \( \gamma \) is the surface tension of the liquid and \( r \) is the radius of the fiber).[6,7] Rather than breaking, evaporation of the solvent causes the fibers to reach a stable diameter as the polymer solidifies.

Very high aspect ratio fibers (sometimes as high as 20,000:1) have been produced this way (Fig. 2A), including a hand-brushed array of fibers of 37 ± 6 nm diameter.[8,9] The fibers, as shown in Fig. 2A, can often form on the sidewalls of the pillar array. Other interesting nanostructures that resemble trampolines (Fig. 2B) and tennis nets (Fig. 2C) have been formed (by a modified process in which monomers polymerize as the liquid is being brushed over the substrate).[9] The potential of the brush-on approach to be developed into a manufacturable batch fabrication process is illustrated by the last array where over 1000 contiguous tennis-net-shaped membranes formed without an intervening defect.[9] The fabrication process is quite robust, enabling defect-free arrays of identical structures to be produced, even with crude hand applications. The level of uniformity and repeatability demonstrated for the fabrication of nanofiber arrays currently recommends them for prototyping of various suspended MEMS and NEMS devices, especially those that are very flexible. Nanofiber air-bridges have been produced in seconds with numerous types of organic polymers and block copolymers, nanomaterial–polymer composites, and biopolymers—including actin, fibrin, and DNA.[9,10]
Underlying Principles That Control Fiber Formation

The mechanism that causes the fibers to form might at first appear similar to the known processes of fiber spinning. In terms of the use of solvated polymers, the process would be classified among the solution spinning method referred to as "dry spinning" (which includes electrospinning).[11] In dry spinning, the polymer is extruded from a spinneret. The steady-state diameter of the fiber is attained at some distance past the spinneret where the fiber has solidified through drying. However, in the brush-on method, the polymer is drawn a relatively short distance and is detached from the applicator prior to the polymer thinning and solidifying. There can be a considerable force present due to surface tension and surface wetting that can further drive fluid transport and fiber shaping.

A macroscopic demonstration of the capillary force-driven formation of a fiber is illustrated in Fig. 3A under controlled conditions in a capillary breakup extensional rheometer (CaBER).[12] In the CaBER, a liquid bridge is formed by filling the gap between two parallel circular plates with the test liquid. An axial step strain is imposed on the sample by rapidly separating the plates by a predetermined distance (at a speed that exceeds the capillary breakup time), and then, the diameter at the midpoint between the two plates is optically monitored over time. In Fig. 3A (and modeled in Fig. 3B), the 6-mm diameter plates are separated by a fixed distance.[6] Capillary forces can also drive the filament to break (referred to as "capillary breakup," which is commonly observed when a thin falling stream of water breaks up into drops); however, this breakup process is inhibited by the presence of the dissolved polymer solute, resulting in the formation of a stable filament.

The dynamic evolution of polymer solutions into fibers is influenced by four time scales that can be related through three dimensionless parameters listed in Table 1.[6,14,15] These parameters vary over time with the characteristic length $R$, which we associate with fiber radius. Table 1 shows that as radius decreases, inertial effects become increasingly unimportant compared to viscous effects, and that elastic effects become even more important. Gravitational forces characterized by the Bond number $B_0 = \rho g R/\gamma$ and inertial forces characterized by the Ohnesorge number also will be vanishingly small for fibers with small radii $R$, especially for nanofibers. Evaporative fluxes associated with mass transfer to the surroundings (characterized by $h$) remain important at all scales. Even though total mass transferred per unit time may decrease as the thread shrinks, the relative importance of evaporation remains unchanged.

At scale sizes below around a millimeter, the dominant forces involved in fiber formation are primarily surface tension, viscous resistance to flow, and resistance to stretching of the polymer chains. Very large molecular stretch rates can result from the surface tension-driven capillary thinning of the thread, even when there is no external driving of the flow. The competition between capillary necking and viscoelastic stretching results in a process that may be called elasto-capillary thinning, which is characterized by the elasto-capillary number (see Table 1).
The first theoretical description of fiber formation from polymer solutions in volatile solvents during CaBER experiments was developed by Tripathi, Whittingstall, and McKinley.\(^6\) Numerical simulations showed that the necking filaments, rather than break, will thin to an equilibrium diameter, \(R_{\text{mid}}\), if the time scale for mass transfer is sufficiently small compared to the time scale for capillary breakup. These competing trends are combined into the dimensionless processability parameter \(P = \eta h / \gamma\). The extent of the strain hardening in the tensile stresses exerted by the elongating molecules (as measured by the magnitude of the elasto-capillary number \(Ec\)) controls the axial uniformity of the filaments formed.

A purely viscous asymptotic theory (for the case \(Ec = 0\)) also was developed that estimates a final equilibrium diameter, \(R_0\), if the time scale for mass transfer is sufficiently small compared to the time scale for capillary breakup. These competing trends are combined into the dimensionless processability parameter \(P = \eta h / \gamma\). The extent of the strain hardening in the tensile stresses exerted by the elongating molecules (as measured by the magnitude of the elasto-capillary number \(Ec\)) controls the axial uniformity of the filaments formed.

The processability parameter \(P\) provides a convenient guide to adjusting the polymer properties to obtain fibers of desired diameters. The properties of viscosity can be controlled by the percent solvent used and polymer molecular weight, and the evaporation rate and surface tension can be controlled by the choice of solvent or surfactant additive. Therefore, it should be possible to process numerous polymers that have a variety of useful functional properties into the suspended fiber structures.

The features shown in Fig. 3C for the rather idealized geometry of the CaBER tests in Fig. 3A and B can be fully appreciated by examining the electron microscope images of the results of brush-on experiments in Fig. 4.\(^5\) In Fig. 4A and B, 950 kDa polymethyl methacrylate (PMMA) in chlorobenzene (MicroChem C9 e-beam resist that is dried to \(\sim 22\) wt.% PMMA) is hand-brushed over a cylindrical pillar array at a speed of 30 mm/s. First note that the nanofibers primarily form in the direction of brushing in Fig. 4A. In Fig. 4B, there are thicker fibers in the brushing direction than in the cross direction. Apparently, brushing not only induces unstable capillary bridges (like those in Fig. 4A) to form in the brushing direction, but less liquid is able to bridge between pillars in the cross direction, leading to thinner fibers or (through capillary breakup) no cross fibers at all. In agreement with this observation, at slower brushing speeds, fibers of equal size are found in both directions. Another feature evident in these two SEM pictures is that there is strong wetting over the top and sidewalls of the pillars, leading to the fibers being attached beneath the top surface to the sidewalls. The polymer structures are shown after they have dried, so that the buildup on the pillars has little resemblance to droplets. In Fig. 4C, by using 50 kDa polyvinyl acetate (PVAc), the filaments are also attached to the sidewalls, and in this case, the droplet shape is more pronounced (even with these pillars being square and flat-topped). Visual examination of these particular images led to the association of the suspended polymer formation process with the capillary thinning theory described by Fig. 3C.

Returning to discussion of Fig. 3C, as \(P\) decreases below 0.01, thinning becomes more dramatic, but control of the
final diameter becomes increasingly difficult, and breakage becomes increasingly likely unless the elasto-capillary number Ec is increased. Therefore, to obtain small diameter fibers while minimizing the risk of breakage, rather than continue to reduce P to levels below 0.01, it is preferable to reduce the initial diameter of the fluid droplet R, or equivalently the initial radius of the thread R_i, and/or increase the relaxation time \( \lambda \) of the polymer chains. This may be achieved by increasing the molecular weight of the solute and by increasing the background viscosity of the solvent. The latter approaches have been adopted in nature by silk spinning organisms such as the silkworm (Biombyx mori) and orb-weaving spiders (such as Nephila clavipes). The silk proteins (fibroin and spidroin) are of high molecular weight \( (M_w \geq 275,000 \text{ g/mol}) \) and self-assemble during spinning to form nanocrystallite-reinforced threads of less than 10 \( \mu \text{m} \) diameter.\(^{16,17}\)

A detailed evaluation of elasto-capillary thinning was developed for one of the first polymers employed in brush-on (PMMA, 500 KDa, 22 wt.%).\(^{18}\) The key results are shown in Fig. 5 as a plot of fiber diameter and as a function of Ec and P. The colors represent the ratio of the radius of the final fiber to radius of the initial thread \( h_f \). For purposes of explanation, the initial thread radius is considered to be 100 \( \mu \text{m} \) and the fiber is assumed to break at 10 nm (or log \( h_f = -4 \), though thinner fibers have been formed in experiments). The key result is that increasing the value of the elasto-capillary number improves control on the nanofiber diameter, since at larger values of Ec, the value of processability parameter varies over a much larger range than for very small values of Ec.

Various elasto-capillary processes are related in Fig. 3D in terms of two dimensionless parameters. The parameters are the Ohnesorge number \( (Oh) \) and an intrinsic Deborah number \( (De) \).\(^{13}\) These parameters measure the relative importance of elasticity and inertial effects \( (De = \lambda/\eta R) \). The elasto-capillary number is given by the tangent line \( Ec = De/Oh \). Inertial forces play significant roles in some microscale non-Newtonian free surface phenomena including inkjet printing and electrospinning; however, they are generally unimportant for the more viscous materials employed in hot melt and pressure-sensitive adhesion, silk-spinning, and the nanofiber brush-on method.

Beyond forming simple fibers, a bead-on-a-string (BOS) morphology is also possible for specific values of \( De \) and \( Oh \) near and below unity (blue region in lower left of Fig. 3D). Fig. 6A shows a (possibly) well-known example of self-assembly of BOS structures from saliva, which is due to the presence of highly flexible long chain glycoproteins.\(^{19}\) Fig. 6B shows time-lapse images of the formation of BOS structures with a model, non-volatile fluid.\(^{20}\) Once formed, the liquid structures can be stable for an extended period of time, which provides a wide processing window for the material to permanently solidify into the desired shape through drying of the solvent,\(^{5}\) polymerization,\(^{9}\) or crosslinking.\(^{21}\) A \( De - Oh \) phase space (Fig. 6C) has been identified that delineates the regions for BOS structures with no beads (normal fiber), beads of one diameter, and beads of multiple diameters.\(^{19}\) (Note that this region is found within the blue zone in Fig. 3D.) For \( De \) and \( Oh \) both slightly above unity, fibers without beads form. Between \( 0.2 > De > 0.05 \) and \( 1 > Oh > 0.5 \), there are nearly vertical

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**Fig. 5** Simulated dependence of fiber radius \( h_f \) as a function of processability parameter and elasto-capillary number. The result, for a specific geometry described in Crest et al.\(^{18}\) shows that increasing the elasto-capillary number enables thin fibers to resist breakup to much smaller values of processability than for negligible values of Ec.

**Fig. 6** Macroscale self-assembly of BOS structures (A) from saliva and (B) a PEO–water–glycerol solution. The sequential time-lapse images in (B) are at 25 ms/frame. Beads of three sizes form with each smaller set of beads forming at increasingly later times. (C) A \( De - Oh \) phase-space showing three regions of no beads or string only, single-size beads, and dual sized beads. The specific geometry modeled is shown in the simulated shapes on the right.

**Source:** (A) and (C) From Bhat, Appathurai, et al.\(^{19}\) © 2010 Nature Publishers. (B) From Oliveira, Yeh, et al.\(^{20}\) © 2006 Elsevier.
and horizontal bands on the phase diagram where beads of one diameter form. Below these bands, BOS structures with beads of two diameters form. The transition from one to two bead sizes along the $Oh$ axis of the plot corresponds to (see Table 1) reduce the viscosity of the solution. Along the $De$ axis, the transition from one to two bead sizes corresponds to increase the inertial time scale (Table 1), which can be achieved by increasing the initial thread diameter during application or using a solvent with lower surface tension. In practice, $De$ and $Oh$ are adjusted by brushing speed (to control $f_b$), and molecular weight and concentration of the polymer (to control $\lambda$). The $De$-$Oh$ phase space makes it possible to specify the appropriate concentration and molecular weight of any number of polymers (together with brushing speed) that will form BOS structures. As a result, this type of self-assembly is not limited to a specific polymer.

The values of $De$ and $Oh$ for BOS self-assembly are easily met for very high molecular weight linear chain polymers, where at modest concentrations, the polymer chains can become highly entangled. For example, aqueous solutions of 2–5 M Da polyethylene oxide (PEO) at 2–3 wt.% concentration were used in brush-on formation of the BOS structures in Fig. 7.[8,22] No less remarkable than the formation of the beads is the enormous degree the fiber can thin without breaking. We have observed beads of upward of 25 $\mu$m form on millimeter long strings of diameters as thin as 50 nm. Much less than 1% of the mass of the structure is contained in the string. Based on this geometry, such a structure can have a very low stiffness together with high mass, resulting in a structure with a very low resonant frequency. These mechanical properties will be described further, below in Applications.

Other Methods of Fabricating Suspended Nanofibers

First, let us compare the brush-on method to conventional planar processing for forming arrays of suspended air-bridges. Planar lithographic processing is quite labor-intensive requiring several hours of processing (including spacer deposition, bridge deposition, resist spin-on, photopatterning, development, etching bridge layer, and undercut etching of bridge). Also, care is required in material selection, temperature control, and deposition to reduce the potentially damaging effects of built-in stress. However, with fiber drawing, a suspended bridge of nanometer-scale diameter and millimeters of length can be drawn in a few seconds and without sagging. Laser-assisted 3-D direct writing is another alternative to planar lithographic processing. Most notable are the methods that use two-photon absorption (TPA) to expose the photopolymer. The resolutions as high as 120 nm using a 780-nm femtosecond laser have been reported.[24] The brush-on method can be compared with this method in that smooth fibers (often substantially thinner than the 120-nm TPA resolution) are formed automatically during the drawing process, without the need for a subsequent development process.

Traditional fiber manufacture is geared toward producing continuous streams of optical fibers and textile yarns. However, with the development of electrospinning[25,26] and its demonstration of producing uniform diameter fibers as small as 50 nm[27] (as well as 20 nm beads on 3 nm strings,[28] hollow fibers of 200 nm diameter,[29] and porous fibers[30]), there is a growing interest in electrospun fibers as a nanomaterial and as a structural element for device fabrication.[25,26] Traditionally, electrospun fibers are spun to lengths of kilometers and collected as randomly oriented mats. Recently, there has been interest in orienting electrospun fibers and consideration that electrospinning might have a role in device patterning. Two studies have demonstrated local electrospinning, where a drop of polymer solution is placed on one electrode and fibers are spun out to nearby counter electrodes.[31] Similar to this is a study where polydimethyl siloxane (PDMS) is electrospun between a 500-$\mu$m gap resulting in a BOS micron scale string.[21] The liquid structure is solidified by exposing it to UV light to cure and crosslink the polymer. Most recently, a near-field method was demonstrated in which a single tapered pipette at about 200 V was used to direct-write nanofiber air-bridges over the surface of a micromachined device.[32] This last method is a serial direct-write method. Another serial method has been demonstrated in which drops of polymer are delivered to a surface and then a stylus or pipette is used to locally draw or dry spin a fiber between the deposited droplet and the next deposited droplet.[5,33–35] This method and the near-field electrospinning method show a wide variation in control of fiber diameter.[31,33,35] In comparison, the brush-on method is a parallel method, and therefore establishes steady-state conditions over a large area of the substrate, resulting in good uniformity.[9] On the other hand, no studies have been reported on the dimensional repeatability when a brush-on application is repeated, so that a complete comparison with the serial method remains incomplete.
Related Parallel Methods of Forming Suspended Polymer Fibers

Receding Liquid Front

Nearly identical to the brush-on method is the method demonstrated by Lin et al., in which the same capillary-force-driven principles appear to be involved. DNA nanofibers are patterned on top of PDMS pillar arrays. Herein, instead of brushing the solution over the pillar array, the array is held parallel to the surface of the DNA solution, the tops of the pillars are inserted slightly below the surface, and then the array is tilted so that a liquid front recedes across the pillars. This forms unstable capillary bridges between pillars in a direction perpendicular to the receding liquid front. The capillary bridges then rapidly thin as their solvent (buffer solution) drains and dries, leaving behind the DNA air-bridges.

Brush-on During Initiated Polymerization

Another variation on brush-on method is to start with monomers that rapidly polymerize during brushing. Results of this method are shown in Fig. 2 for the soluble protein fibrinogen that is insoluble protein fibrin by the enzyme thrombin. It appears that in addition to fibers, membranes can form (Fig. 2B) with anchors at 45° to the direction of brushing. These membranes form at slower brushing speeds, which suggests that polymerization is rapid enough in the transverse direction to stabilize the initially brushed-on fluid film as a four-point supported membrane rather than breaking up further into parallel fibers. In Fig. 2C, which results at the slowest brushing speed, liquid threads that span between two pillars, wet down to the base of the pillar forming a membrane septum that is anchored between two pillars and the substrate. The filamentary protein actin and the organic polymer polynorbornylene were also polymerized during brush-on to form nanofiber air-bridges, which in a few instances even reached diameters as small as 4 nm. Polymerization, through its increasing the viscosity of the solution over time, tends to retard and arrest capillary breakup, and in this way serves a similar role as evaporation does in Fig. 3C.

Thermal Methods

There appear to have been only limited efforts to draw nanofibers by melting and resolidification. These were serial, direct-write approaches. One parallel thermal approach is considered by Rathfon et al. Here, a thin sheet of polymer (50–120-nm-thick) is placed on top of a micropillar array. Heating the film to slightly above the glass transition temperature leads to nucleation of holes, followed by breakup of the film into liquid threads and fibers. These studies were motivated by their potential to isolate one of the two effects in the brush-on method. Specifically, the film breakup and capillary thinning step can be studied, while the brush-on application step is completely eliminated. Performing the experiments slightly above the glass transition temperature also slows the thinning process to hours or longer, enabling its careful observation. The thread thinning rate (or waist diameter $R_{\text{mid}}$) has been observed to follow an exponential decay

$$R_{\text{mid}} = \frac{GR}{\gamma} \frac{1}{3} \exp \left( -t/3\lambda \right)$$

where $G$ is the shear modulus of the polymer and all other parameters are defined above. This result is consistent with theories of viscoelastic thinning, where the thinning slows down with time (as opposed to simple Newtonian fluids, for which thinning accelerates with decreasing fiber diameter). Thinning decreases at an even slower linear rate once the polymer chains become nearly fully extended, both for the theory and the experiments with the breakup of the thin films. The slowing, while it does not completely stabilize the fibers, does enable the heating to be stopped and the thinning arrested precisely once the desired fiber diameter is reached.

In early experiments, fiber formation events were observed to begin at different times for different fibers, with the result that some fibers broke before other fibers formed. The problem was identified as due to uncertainties related to the random nucleation of holes in the film. The film remains stable until holes nucleate. This problem is overcome by prenucleating holes in the film. A focused laser has been used to locally form holes. Only near the center of the beam is there enough heat for the film to melt and dewet to the cooler, solid region of the film. Once the holes are formed, the film is heated above the glass transition temperature and fibers form at the same time throughout the film. Fig. 8A shows four (relatively large) holes formed in a polystyrene film by a laser after a period of thermal annealing. Away from these holes, many randomly nucleated holes of various diameters (because they nucleate at different times) are also evident. Fig. 8B shows the same film after full thermal annealing. Very well-defined fibers result from the prenucleated holes, while the randomly nucleated holes evolve into a more random network of fibers, similar in appearance to Ostwald ripening or coarsening of soap bubble rafts.

Viscoelastic Fingering

Fig. 9 shows the result of drawing very long fibers normal to the top surface of a micropillar array. A droplet of solution PMMA ~1-mm-thick is applied to a glass slide. The array is contacted by and then retracted 10 mm/s to a distance of 50 mm. Most notably, the bases of many of the
fibers are bifurcated, at least at two scale sizes, as well as each base appearing self-similar, but not identical, suggesting a fractal process of self-assembly (e.g., the similarities among snowflakes). These structures appear to be related to the Saffman–Taylor viscous fingering instability, where injecting a lower viscosity Newtonian fluid into a higher viscosity Newtonian fluid above a critical velocity results in a radial (fractal-like) pattern of fingers. The number of fingers $N$ initially formed by a classical Saffman–Taylor instability is given by

$$\frac{2\pi R}{N} = \lambda = \pi b Ca^{-1/2}$$

where $\lambda$ is the average spacing between fingers at the radius $R$ of the liquid film, $b$ is the initial film thickness, and the dimensionless capillary number that relates viscous forces to capillary forces is given by

$$Ca = \frac{\eta V}{\sigma} = \frac{\eta}{\sigma} \left( \frac{vR}{2b} \right)$$

where $V$ is the average radial velocity of liquid in the film and $v$ is the velocity normal to the film. These equations show that thickening of the film or decreasing the initial aspect ratio $R/b$ decreases the number of fingers. The Saffman–Taylor analysis has recently been experimentally shown to apply to viscoelastic fluids (PDMS oils) and elastomers (crosslinked PDMS) in studies of loss of adhesion in response to normally directed pulling. The value of $N$ for viscoelastic materials is correctly predicted by using an appropriate value of viscosity. The value used for $\eta$ corresponds to the complex and frequency-dependent shear modulus $G$ divided by the frequency $\omega$ that is representative of the experiment. Earlier work by this group shows how the number of fingers decrease with time and aspect ratio (also referred to as “confinement factor”).

The bifurcated fibers in Fig. 9 look as if they were also generated by a viscoelastic fingering instability. However, because the fluid contains a volatile solvent, a direct comparison with the Saffman–Taylor analysis could be substantially more involved. Specifically, the drying and solidification of the liquid polymer leads to dramatic changes in viscosity over the time frame of the pulling. Further drying and flow following pulling of the fiber may occur that further transform the shapes of the bifurcated fibers. However, in agreement with the Saffman–Taylor predictions, which show less fingering with increasing aspect ratio of the initial droplet, the branching was not observed for the same pulling conditions when repeated with much narrower, sharply tapered pillars. Branched fibers like those in Fig. 9 might be useful for some applications; e.g., fiber optic splitters or combiners.

**Single-Ended BOS Fibers**

Fig. 10 presents an isolated result where single-ended fibers are formed from the brush-on method. Here, a solution of 25 wt.% PMMA (996 KDa) in chloroform was brushed over an array of 10-μm diameter pillars. It is quite intriguing that the fibers remain supported and cooriented, not to mention that there is also a BOS structure. Typically, if one draws a very long fiber and it breaks before the polymer fully solidifies, there is elastic recoil of the fiber, and at the same time, the fiber relaxes into a multicooled shape (as shown in Fig. 11). So, the possibility of forming arrays of relatively short but straight fibers is especially interesting. However, the mechanism of formation has not been studied. So, there are several questions one could ask. Does each fiber break free from the applicator or does it form a bridge that later breaks from the opposing post? Does a fiber end break free due to elastic fracture of a solidified fiber or does it break free by the capillary breakup of the liquid polymer? These questions do not begin to touch on the dynamics of thread formation, thinning, breaking, and (possibly) shrinkage in length, but could be studied by repeating...
these brush-on experiments for a range of parameters (from Table 1.)

SELF-ASSEMBLY STRATEGY II: SELECTIVE MENISCUS-CONTROLLED SPONTANEOUS CRYSTALLIZATION OF FREESTANDING NANOWIRES FROM LOW-TEMPERATURE METAL ALLOY MELTS

One key reason why polymer materials are so widely used in the manufacture of everyday products is that they usually can be processed at temperatures much lower than that required to process metals. However, there are cases of metal alloy systems that can be processed close to, or even below, room temperature. Mercury amalgams, used in dental fillings, are mixtures of mercury and other metals that rapidly solidify to form alloys of interlocking crystal-lites that have high melting points and good corrosion resistances. While the use of amalgam fillings has been out of favor due to concerns about mercury poisoning, most reports indicate that mercury is strongly bound in the alloy filling and there is scant evidence of any mercury health hazards to patients. The resulting alloys consist of interlocking crystallites of plates and rods. A somewhat less aggressive and a much less toxic metal that melts at a temperature slightly above room temperature (29.15°C) is gallium.

Intermetallics correspond to line compounds (fixed stoichiometry) or ordered phases (somewhat variable stoichiometry) found on the phase diagram. Fig. 12A shows the Au–Ga diagram. Three line compounds are indicated, including AuGa₂, which is 67 at.% Ga. To the left of the line compound, at 56.4 at.% Ga, is one of the eutectic points. A melt of this concentration, when cooled through the eutectic point, will spontaneously phase-separate into AuGa and AuGa₂. While eutectic solidification is widely used for the solidification of alloys (such as solders), the region to the right of the AuGa₂ line is useful for the self-assembly of metallic nanostructures. The region under the liquidus line contains the two phases of the AuGa₂ line compound and a gallium-rich phase of Au–Ga liquid—which persists as a liquid down to ~27°C (300 K). Below 27°C, the liquid (which is nearly 100% Ga) solidifies. Fig. 12A is annotated for tie-line analysis between the AuGa₂ line and the liquidus curve. The analysis enables one to calculate the percentage of each of the phases present in the two-phase region. The red asterisk corresponds to an overall composition of ~75 at.% Ga. A liquid solution of this concentration when cooled into the two-phase region produces an amount of line compound proportional to the depths b/(a + b) and an amount of liquid a/(a + b). Since the length of b increases with decreasing temperature, the fraction of solid precipitate increases with decreasing temperature. The Ag–Ga phase diagram in Fig. 12B produces the ordered ζ phase, rather than a line compound of a single stoichiometry. The phase exists up to 425°C as an

Fig. 10 Single-ended beaded fibers that formed following brush-on of 25 wt.% PMMA (996 Kg/mol) in chloroform. Source: From Pabba.

Fig. 11 Coiling in PMMA fibers due to elastic recoil prior to complete drying of the solvent. (A) On AFM tip following retraction by AFM approach motor from the pool of solvated PMMA. (B) Long fiber that snapped from the solvated PMMA during hand drawing. The red color is due to scattering from laser light that is guided through the fiber. Source: (A) From Harfenist, Cambron, et al. © 2003 IEEE.

Fig. 12 Phase diagrams for binary solutions of (A) Au–Ga, and (B) Ag–Ga. Central portion (which lacks grid lines) has been updated with newer data. Source: (A) and (B) Adapted from Predel. (B) New information from Gunnaes, Karlsen, et al. © Elsevier.
ordered phase and remains a solid, though as the disordered ζ phase, up to 611°C. The ordered phase has a composition that varies between 24 and 33 at.% Ga (Ag₃Ga to Ag₂Ga). For a tie-line analysis between the Ga liquidus curve and the ζ phase, the ordered phase composition corresponds to the right side of the region. That is, the composition is much closer to Ag₃Ga than to Ag₂Ga. Quite stable alloy compounds can be precipitated from room temperature gallium-rich Ga–M melts of a number of different metals M. In many cases, nanometer scale structures are formed. A variety of materials and structures are considered below.

Identification of Ga–M Alloy Systems That Form Nanostructures Near Room Temperature

An examination of 31 binary gallium–metal (Ga–M) phase diagrams[45] shows that there are 21 that have a similar two-phase region down to nearly room temperature, in which one side of the region is an ordered crystalline phase and the other is a gallium-rich liquid.[47] The ordered phases or line compounds found on the Ga-rich side of the phase diagram can form at room temperature and remain an ordered phase from a few hundred to several hundred degrees above room temperature. For instance, the corresponding line compounds for Ga with Fe, Co, and Ni are FeGa₃, CoGa₃, and Ga₄Ni, only begin to separate into a mixed liquid and solid phase with temperatures of approximately 825°C, 840°C, and 350°C, respectively.

Nanostructures readily form (in from minutes to hours) at the interface between a liquid gallium droplet and a plane of several elemental metals (Fig. 13). Crystalline structures form in from minutes to a few hours. For slower reactions, liquid gallium might still cover the interface, but it can then be removed by etching with dilute HCl. For faster reactions, the gallium can be completely absorbed into the bulk of the metal leaving the resulting crystals exposed to air. All of these structures, when identified by electron-energy dispersive spectroscopy (EDS), were identified as the ordered phase or line compounds that have the highest gallium content of all the ordered phases for the specific Ga–M phase diagram. Apparently, gallium is such an aggressive solvent that it readily establishes conditions similar to those found on the gallium-rich side of the phase diagram. Gallium becomes saturated with the Ga–M ordered phase, which precipitates (more precisely, heterogeneously nucleates) at the Ga–M interface, followed by continued growth into the gallium. One can imagine that on the metal side of the interface, gallium diffuses into the metal, and at these low concentrations, other intermetallics (such as the β′ ordered phase in Fig. 12A) are thermodynamically predicted. However, this would require the gallium concentration at room temperature to rise to between 2% and 22%. Also, gold is in the solid phase, so the diffusion rate and ability of the new alloy to transform and grow should be dramatically slower than the formation of the gallium-rich phases. Therefore, it appears that in regions rich in gallium, near-equilibrium conditions for ordered phase growth are possible, while in regions rich in the solid metal, equilibrium cannot be established. It also seems that gallium can dissolve away and transport most of the metal at the interface, and use it for the sustained growth of the gallium-rich nanostructures—before the metal can be incorporated into metal-rich alloys.

Various nanostructures are observed for the resulting ordered phases in Fig. 13, including (A), nanorods or more slender nanowires/nanoneedles (A–C and H–K), rectangular prismatic bars (H and I), plates (E, F, H, and I), some down to 10 nm thick that are electron transparent in the SEM, polyhedra (G), and a few isolated instances of hollow tubes (D) which appear to have had their growth templated on a cluster of nanowires (e.g., the clusters in Fig. 13B). The larger crystallites appear very smooth and they have a very high degree of symmetry, including rectangular FeGa₃ bars (Fig. 13H and I) which even have sharp pyramidal caps. The smaller diameter rods and nanowires appear more rounded than the larger rods. The rounding is probably due to the crystal being so small that additional surface facets away from the principal crystal planes can be energetically favorable (per the Wulff construction).[50] Crystals formed at higher temperatures (Fig. 13A and H) produce thicker crystals than at lower temperatures (Fig. 13B and F) shown for Ag₂Ga and Ga₄Pt, respectively.[49] The increased thickness is expected due to the increased lateral diffusion lengths of the solute at higher temperatures.[51] Fig. 13C shows the early growth of Ag₂Ga nanowires at room temperature. A few rods protrude past the gallium droplet. The wire grows from the tip, and more

![Fig. 13](image_url) Nanocrystals that formed at a Ga–M interface (where M=Ag, Pt, Pd, Co) resulting in the alloys (A–D) Ag₂Ga, (E, F) Ga₄Pt, (G) Ga₄Pd, (H, I) FeGa₃, and (J) CoGa₃. All crystals formed at ~25°C, except (A) and (E), which formed at 200°C and 160°C, respectively.

Source: (A), (B), and (D) through (J) from Yazdanpanah, Dobrokhotov, et al.[49] © NSTI, (C) from Yazdanpanah, Harfenist, et al.[49] © AIP.
wires become exposed as gallium continues to react with and penetrate into the metal substrate. Eventually, gallium completely recedes into the metal leaving behind a dense cluster of nanowires (Fig. 13B).

The nest-like appearance of the bundles appears to be due to surface tension driven clustering of the nanowires as gallium recedes. While the smaller nanowires appear cylindrical, faceting is somewhat noticeable on higher magnification images (presented below). The tips, however, often take on a nearly rounded or spherical shape, typical of diffusion-limited growth.[52]

Gallium and mercury are by no means the only room temperature liquid metal solvents that could be considered for forming ordered phase nanostructures with melting points well above room temperatures. Ternary or quaternary alloys could also be formed from solvents such as Ga–In–Sn and Ga–Sn–Zn, which have eutectic melting temperatures of 11°C and 17°C, respectively.[53]

Conceptual Growth Models at Interfaces

It is well known from studies of alloy solidification and diffusional transformations of solids that fronts can be planar, cellular, or dendritic, based in a large part on the solute and temperature distributions across the solid-liquid or solid–solid interface. Fig. 14 reviews these concepts as presented in standard texts on the subject.[52,54]

The upper left panel shows a typical geometry of non-planar growth of a plate or a rod of the β phase. The small radius r of the tip locally raises the free energy over that of the bulk solid (through the Gibbs–Thomson effect) which serves to maximize diffusion currents near the tip, producing the concentration distribution shown in the α phase. The radius r and its size compared to the critical radius for nucleation r* is a critical factor in determining the growth velocity

\[ V = \frac{D(X_0 - X_r)}{k(X_β - X_r)} \cdot \frac{1}{r} \left( 1 - \frac{r^*}{r} \right) \]

where k is a factor ~1, D is the diffusion constant, and the percent concentrations X_i are indicated on the schematic in Fig. 14A. The equation shows that the growth velocity is maximized for r = 2r*. Similar dependencies on r and r* are developed for metal solidification[56] and lamellar eutectics.[57]

Temperature gradients also can have a profound effect on the morphology, where the eutectic Sn–Pb alloy shows (specifically, tin–lead solder) changes from planar, to ordered hexagonal cells with decreasing temperature gradient. Fig. 14C also shows the evolution of cellular fronts.

Directed Self-Assembly of Metal Alloy Nanowires

The above interfacial bulk processes can be conscripted or “directed” to form individual nanostructures at selected locations on a surface. Most of the reported activities have involved the Ga–Ag alloy system, for which specified locations on AFM tips, tungsten tips, quartz microtuning forks, and arrays of sharp silicon tips have been decorated with individual freestanding Ag2Ga nanowires in a matter of seconds, and at room temperature.

The procedure is shown schematically and in practice in Fig. 15A. As illustrated, the substrate is observed in the SEM and moved using a nanomanipulator under joystick control. Also, nanowires have been grown in air while observing the substrate–gallium interaction through a microscope. The initial substrate, which in the figure is represented by an AFM cantilever, is sputter-coated with around 50–200 nm of silver. The tip is dipped into the melted droplet of gallium. Immediately upon insertion, the substrate is retracted upward a small distance forming a gallium meniscus. After nanowire growth begins, the meniscus recedes, making the nanowire visible. At this point, the nanowire is growing at a constant rate. To avoid collision of the end of the wire with the substrate on which the droplet rests, the nanowire is retracted from gallium at a
constant rate, usually less than 200 nm/S. Faster retraction can be used to stop further growth. Fig. 15B shows a needle of 67 μm grown by this procedure. The schematic shows that several nanowires might form on the sidewalls of the tip (that do not extend off the surface of the tip). This occurs when there is extreme oversaturation of gallium. Reducing the thickness of the silver coating and inserting the tip only a small amount into the gallium can eliminate oversaturation, and result in the nucleation and growth of a single nanowire (Fig. 16A).

Fig. 15  Selective growth of individual nanowires onto the silver-coated AFM tips. (A) Schematic (above) and actual growth (below) of nanowires precipitated from a gallium melt; (B) Image of a 110 nm × 67 μm nanowire just prior to removing it from the gallium droplet.


Examination of the AFM tip region shows that silver is completely dissolved away from the end of AFM tip, and there is a band just above this region that is roughened due to a substantial fraction of gallium diffused into and reactively spread through the silver matrix. This roughening, due to interdiffusion of gallium into silver, is illustrated in the schematic of Fig. 15A by the raised and roughened area along the cantilever. In the schematic, a large amount of gallium remains adhered to the tip, and therefore, reaction of gallium with silver can eventually extend through the entire film. On the other hand, for the single needles, the gallium meniscus eventually loses adhesion at the edge of the silver film, leaving little gallium behind, and the remaining gallium is diluted before it can diffuse beyond the tip region, and materially change silver in the cantilever region.

The Ag₂Ga nanowires often have constant diameters over much of their length (as can be seen in Fig. 16A). Fig. 17 shows close-ups of the ends of nanowires that demonstrate (A) a single diameter, (B) two nanowires that have reached the same length, and (C) two nanowires, where one slightly extends past the other.[49] The models of growth described in the previous section (see Fig. 15A) suggest that there is a competition between nanowires for the solute. If a single wire of radius \( r = 2r^* \) forms, then once it grows slightly past a surrounding bundle of nanowires, it achieves the maximum growth rate and can then rapidly grow past the bundle. It has been argued[49] that the small diameter also tends to increase the diffusive flow of the solute toward the tip of this wire, and away from the bundle,

Fig. 16  Silver–gallium (Ag₂Ga) nanowires that have been selectively grown onto AFM tips. (A) A 157 nm × 16 μm nanowire that has been grown on a silicon probe tip. The inset shows the end of the constant diameter probe. (B) The nanowire from (A) being used to deflect a polymer nanofiber suspended between two rigid supports (as shown in inset). The buckled shape (white) is fit to an analytic mechanical model of buckling (dashed blue line) from which the force applied to the fiber is determined. (C) A 130 nm × 33 μm nanowire that is torsionally buckled. The nanowires are resilient, immediately recovering their unbent shape upon release of the applied forces.

Source: (A) and (B) Dobrokhotov, Yazdanpanah, et al.[60] © 2008 IOP. (C) From Yazdanpanah, Harfenist, et al.[49] © 2005 AIP.

Fig. 17  Metal nanoneedles. (A) A needle attached to the tip of an AFM cantilever. It is coated with a 10 nm thick coating of parafflene, which does not appreciably increase its nominal thickness of 200 nm. (B) Close-ups of the ends of three needles. The smallest one shown is ~50 nm wide.

which has a larger radius, further slowing the growth of the bundle.

The nanowire fabrication procedure can be compared to several other selective growth methods for nanowires. Like vapor–liquid–solid (VLS) growth, the solid needle precipitates from a liquid melt, but supersaturation is reached by dissolution of silver into the gallium melt, rather than through transport of solutes from the vapor phase. The VLS methods are usually performed with metal catalysts that melt well above room temperature, while gallium (which melts at 29°C) can be reacted under ambient conditions of temperature in room air (as well as in vacuum). Precipitation from micropipette-delivered aqueous solutions, as they dry near the orifice of the pipette, has been used to draw freestanding nanowires of the ionic salt copper sulfate, and, with simultaneous electrochemical reduction of salts, elemental metals of copper and platinum. Water is removed by evaporation from the meniscus, though salt residues were often found to be present. The silver–gallium nanowires were shown to be single crystals, while the aqueous-deposited wires were shown to be polycrystalline. The micropipette method also has some resemblance to the tip-directed and capillary-delivered polymer fiber methods described in the previous section. One physical similarity with polymer fiber assembly is that capillary force and evaporation rates are crucial in the formation of stably solidified salt fibers.

Directed Assembly of Freestanding Plates

There have been a few attempts at directed growth of other freestanding nanostructures. In a few trials, using a Pt coating instead of Ag on the tip of an AFM cantilever resulted in the formation of freestanding plates that resembled blades. Plates, having the appearance of scalpels, formed on the edges of the AFM tip (Fig. 18). Plates can be seen on the sidewalls of the tip, with one larger plate growing slightly past the edge of the pyramidal tip. In Fig. 18B, the plate had grown a few hundred nanometers past the tip. An edge view of the same plate in Fig. 18C shows this plate to be about 50 nm thick.

Parallel Growth of Ag₂Ga Nanowires

The directed self-assembly of nanowires appears to have the potential to be performed in parallel. For example, if applied to a wafer of AFM probes, it would add a batch fabrication step for the addition or functionalization of AFM probes with individual nanowires. Parallel fabrication is shown in a recent study, in which a flat film of gallium is contacted by an array of silver-coated tips, as illustrated in the schematic in Fig. 19. For several test runs under a variety of process conditions, Ag₂Ga nanowires were formed with diameters in the 40–400 nm range, lengths of 4–80 μm, growth rates of 80–170 nm/s, and most significantly, with yields of up to 97% in an array of 422 tip-like growth sites (Fig. 20A). The tip-array is a silicon substrate that was sputter-coated with 200 nm of silver. It was parallel contacted with a near planar thin film of gallium on a silicon substrate. The film has a bow of less than 5 μm across the 1 × 1 mm substrate. The gallium film was formed by squeeze coating liquid gallium (similar to brush-on in Fig. 1) at a speed of 5 mm/s over an array of silicon substrates. The film was flatter than could be predicted by rounding due to surface tension and is attributed to liquid pinning at the edge of the substrate, together with stiffening of the film by thin gallium oxides forming on the surface of the liquid.

The nanowires in this run are from 35 to 43 μm long and 150–250 nm in diameter. There is evidence in Fig. 20B of partial dissolution of silver from the tips, and diffusion of gallium into silver. In a few runs, some nanowires formed

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**Fig. 18** Plates of Ga₆Pt and (A, B) selectively grown plates on AFM probes. (C) Edge view of the same plate as in (B).

**Source:** (A) From Yazdanpanah, Dobrokhotov, et al. © 2008 IEEE.

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**Fig. 19** Method of selective growth of Ag₂Ga nanowires. Comparison of the steps for growing (A) a single nanowire, and (B) nanowires in parallel on an array of tips. (row 1) Dip silver-coated tips into gallium, and retract somewhat to form a meniscus. At ~2 minutes, retract tips at constant velocity to the desired nanowire length (rows 2 and 3). Retraction at a high speed to remove the nanowires from the gallium (not shown).

**Source:** From Jalilian, Rivera, et al. © 2011 IOP.
that are remarkable for their high aspect ratio and constant diameter (75 nm) over their entire length (Fig. 21C, D). There are slight contrast changes on the silicon tips in Fig. 20C that again suggest diffusion of gallium into silver. The very rough region is likely where the gallium meniscus had been attached. The amount of silver dissolved and the small dimensions of the meniscus apparently led to the growth of single, constant diameter nanowires, whereas the greater insertion depth of the tip in Fig. 20A and B led to bundles of nanowires fusing together forming tapered bases on the nanowires.

The method of growing nanoneedles in parallel does not necessarily require that the substrate be prepatterned with tips. In an earlier experiment, a very rough substrate of gallium with a few drops protruding past the others was contacted to a planar array of 1 μm diameter, 200-nm-thick silver dots (that were patterned by liftoff). While nanowires only formed at a few percent of the locations, the two sub-100 nm nanowires shown in Fig. 21 (which were found widely separated from each other on the substrate) are remarkably similar in diameter (81 and 86 nm), length (1.9 and 2.2 μm), and shape—including their tapered bases. A tighter confinement of the gallium meniscus (as in Fig. 20A) and a reduction of nanowire tapering should be expected for patterning of smaller silver dots (and, as required to provide enough solute, making the silver thicker).

The philosophy of simplified and rapid fabrication is one of the major themes that has arisen from nanotechnology research. The leading proponent of simplified fabrication and low cost of materials and facilities is George Whitesides.\cite{67,68} Rather than depending on major semiconductor front-end facilities that involve large costs and time delays,\cite{69} Whitesides and other advocates of this theme have developed fabrication processes that work remarkably well in standard chemistry wet labs. It is significant that these new processes work with a much wider range of inorganic, organic, and soft materials, including biological materials and living cells, than is usually possible or even allowed in most front-ends. In addition to soft lithography, many other recent fabrication approaches have been demonstrated, quickly accepted by the research community, and in many cases, commercialized. These include nanoimprint lithography,\cite{70} voltage lithography with the atomic force microscope (AFM),\cite{71} dip pen lithography,\cite{72} electrostatically driven self-assembled texturing of melted polymers,\cite{73} and many groups’ self-assembly of colloids into (photonic) crystal structures.\cite{74} These new methods are especially important in them enabling the researchers simpler ways to develop and study new device concepts. The self-assembly methods in this entry, together with subsequent processing of the nanostructures, fit the above nanotechnology theme.

Compared to traditional microfabrication and micromachining methods, the directed polymeric and metallic self-assembly methods provide simple and fast ways to produce suspended or freestanding nanostructures. These structures provide a natural starting point for the fabrication of 3-D NEMS and MEMS devices, where the structures are used as the resolution-defining features in a device. By using self-assembled structures as nanoscale templates in many cases, it may be possible to avoid the use of extremely expensive nanometer resolution lithography tools. This section provides a few examples of using the nanostructures from the...
sections above to fabricate structures of increased complexity. These additional processes, taken as a whole, provide quite a wide range of opportunities for rapid and simplified fabrication of nanodevices.

**Templated Fabrication on Nanostructures**

Once a nanostructure is formed, there are many simple, yet well controlled, non-lithographic methods to template and develop structures, and devices of greater complexity. Numerous materials can be deposited conformally or directionally with thicknesses and precision of a few nanometers or less. Fig. 22 illustrates this concept for developing a disk nano electrode (possibly for electrochemical detection) around a Ag₂Ga nanowire. After coating the needle, the end can be exposed using a broad directional ion beam, and then the end can be electrochemically exchanged to produce an electrochemically stable platinum electrode. None of the processes require lithographic patterning. Fig. 23 shows two needles coated, in one case with a parylene insulator and in the other with CVD deposited silicon nitride.

The original nanostructure can also serve as a temporary or sacrificial template. Capillaries can be templated following the schematic in Fig. 24A and B. The large reservoirs at each end can be formed by first depositing large drops of polymer and then the fiber is formed by direct drawing of liquid from one drop to the second, followed by capillary thinning and solidification. Examples of capillaries templated on sacrificial fibers are shown for polymer fibers resting on the surface (Fig. 24C), or suspended as air-bridges (Fig. 24D and E) are converted to capillaries by overcoating them with various metallic or dielectric coatings, followed by dissolution of the polymer fiber. Similar results were demonstrated using electrospray polymer fibers to template capillary flow channels on the substrate, and as suspended beams whose mechanical resonance frequencies were measured. The structure in Fig. 24B was generalized with multiple coatings to fabricate a device that eletrokinetically drives the flow of particles from one reservoir to the other. Fig. 24F shows the result of sacrificing two crossing fibers to form a junction for combining or splitting fluid flows. A serial fiber direct-write tool has been used to produce capillary junctions of this form for evaluating tissue regeneration of microvasculature. In the later study, a confluent monolayer of endothelial cells was successfully grown over the polymer junctions. Endothelial cells are known to be the first cells to define and template capillaries during the tissue regeneration process known as angiogenesis. Many polymers used in regeneration, in addition to being biocompatible, are

**Fig. 22** Steps in fabricating an insulated nanoelectrode from a self-assembled nanoneedle.

**Source:** From Safir, Yazdanpanah, et al. © 2006 IEEE.

**Fig. 23** (A) Parylene-insulated nanoneedle and (B) 200 nm recessed semihollow needle with a 20 nm silicon nitride sidewall insulation.

**Source:** From Safir, Yazdanpanah, et al. © 2006 IEEE.

**Fig. 24** Sacrificial formation of capillaries and capillary networks. (A) Deposition of capillary templated on a polymer fiber. (B) Decomposition of polymer. (C) Chrome capillary formed with fiber on substrate. (D) Parylene capillary template away from the surface. (E) Gold capillary with 20 nm sidewalls. (F) Suspended glass capillary network.

**Source:** From Harfenist, Cambron, et al. © 2004 ACS.
biodegradable. This study demonstrates the concept of templated fabrication of microvasculature, where biological processes themselves perform templated assembly, including sacrificing of the polymer fibers.

A variation on sacrificial patterning is to use the polymer as a carrier for the nanomaterial of interest. Nanotubes (Fig. 25B), nanowires (Fig. 25C), graphene sheets, and scrolls have been directed to form air-bridges by first brushing or electrospinning nanomaterial-loaded polymers over micropillar arrays, followed by thermal decomposition of the polymer. The polymers used (PMMA) tend to leave carbon contamination behind, by the time most of the material is removed. Many linear polymers can be decomposed at much lower temperatures and into their constituent monomers (which are volatile) if the standard final step, adding a capping end group, is omitted during synthesis. Use of these types of polymers could enable residue-free decomposition of the fibers. Structures as narrow as a 10 nm thick bundle of single wall carbon nanotubes were suspended in this way.

**Adding Porosity**

There are several methods to induce a nanoporous structure in polymers and metals. A non-exhaustive set of ways to make polymers porous include: (1) Forming fibers from block copolymers and then selectively decomposing one of the blocks. This can be particularly effective when the polymer is microphase separated into ordered domains (such as spheres, lamellae, rods, and gyroids). For instance, with PMMA-polystyrene, UV irradiation can be used to degrade the PMMA domains, while cross-linking the polystyrene domains. (2) Drawing or electrospinning a polymer in a highly volatile solvent. This has been observed to produce highly ordered arrays of pores that are attributed to rapidly crossing the phase boundary between solvated and solid polymer, that drives phase separation by spinodal decomposition. (3) Using a block copolymer that consists of hydrophobic and hydrophilic blocks, e.g., polystyrene-PEO. Immersing the polymer in water can lead to restructuring of polymers including the formation of nanopores. Fig. 26A presents two views of a 14 μm diameter fiber that is composed of the triblock copolymer PLLA–PEO–PLLA. It has been converted from smooth to porous by soaking the fiber in water by this third method.

De-alloying is the refinement of an alloy into its elemental constituents. Spinodal decomposition is often observed when de-alloying intermetallics, resulting in a nanoporous material. Gallium-metal nanocrystals, such as the Ga–Pt crystals in Fig. 13 and others have been de-alloyed by etching with HCl, which selectively removes gallium. Fig. 26B shows the results after etching polyhedral Ga–Pd and Ga–Pt, including 10 nm plates similar to those in Fig. 13F. Pores of 10 nm and less are evident in the images. The percentage of the elemental metal was measured by EDS and is listed on the two images. These numbers show that the elemental metal is considerably enriched compared to the intermetallic alloy. For a gold–gallium alloy, following extended etching, the nanoporous film was measured to be at least 99% gold.

**SUGGESTED APPLICATIONS AND DEVICES BASED ON THE POLYMERIC AND METALLIC SELF-ASSEMBLED NANOSTRUCTURES**

The structures produced by the self-assembly methods, together with templated fabrication, as described above, present novel forms that suggest new devices and integrated systems of devices. The forms that arise may challenge convention and obscure the possible uses. We cannot completely envision the new forms and functions, and the novel types of integration that might be developed from these structures. The flexible, high aspect ratio structures by
themselves appear to be directly useful for demonstrating electronic, optical, and mechanical functions. Using the fibers as a 3-D substrate, it is also possible to build up more advanced structures including networks of interconnected capillaries (as mentioned in the previous section).\cite{5,78} The ability to rapidly create 3-D substrates suggests a route to rapidly and economically build experimental prototypes of nanoscale mechanical, optical, electronic, and fluidic devices—though of potentially different forms than produced by top-down microfabrication. This section presents a few microsystem concepts that should be possible to realize by suspending nanostructures in a 3-D format.

A Multifunctional Integrated Opto-Fluidic Microsystem

The first illustrative example is described with the aid of the concept drawing in Fig. 27. The drawing shows a suspended set of capillaries connected to an array of sharp micromachined tips that are hollow and conductive through their centers. The suspended hollow fibers can be made by the processes in Figs. 1 and 24, and as demonstrated in Fig. 24. The solid support of the tip array could simplify the attachment of gas or liquid lines to the system. Applied voltage could be used to electrokinetically pump fluids through or to emit light from electroluminescent polymers inside the capillaries. Light is probably most easily introduced to the suspended fibers by placing single-mode polymer fibers of submicron diameters in contact with a suspended fiber. For instance, Tong et al. demonstrated low-loss evanescent single-mode coupling by adhering together glass fibers of \( \sim 170 \) nm diameter with van der Waals forces.\cite{82} For small diameter unclad fibers of moderate lengths, of say, 500 \( \mu \)m, evanescent coupling can be quite sensitive to nanometer displacements (Fig. 28), polymer swelling, or changes in the refractive index. Applying a voltage potential difference between two fibers to stimulate deflection, provides a mechanism to deduce the elastic modulus of the fibers, or a voltage-controlled optical switch. Under a liquid medium, the fiber separation could be varied by using salts to vary the charge of the fibers.

Fig. 27 also presents the concept that microbeads in liquids could be trapped near a fiber, translated, and could simultaneously serve as very high \( Q > 10^7 \) whispering gallery mode\cite{84} optical resonators. With nearby crossing fibers, it would be possible to translate beads in three dimensions. The possibility for trapping on the side of a fiber is suggested by the result that the evanescent fields from total internal reflection at a plane dielectric interface can trap particles.\cite{85} Given the high \( Q \) of microsphere resonators, the change in coupled intensity could be quite dramatic due to changing surface adsorption, fluid viscosity, and Brownian motion, making a very rich and interesting physical system.

High Aspect Ratio Probes for Advanced Scanning Probe Microscopies

Several applications are suggested (and in several cases already demonstrated) that take advantage of the well-defined shape of nanowire-tipped AFM probes, including quantitative measurements of surface tension, viscosity, evaporation rate,\cite{59} force measurements inferred from images of the buckled shape of a long nanowire (Fig. 1B),\cite{60} topographic profiling of objects in deep recesses, and access to objects immersed inside liquids or gels (e.g., small organelles within the body of a live cell). Electrochemical probing and dielectrophoretic manipulations in confined areas are also possible if the sidewalls of a conductive nanowire are coated with a thin insulating layer.\cite{61}

The bending modulus of the silver–gallium nanowires has been measured in several studies to be between 17–96 GPa,\cite{47,60,86} and the tensile strength is around 660 MPa based on the breaking of a 130 nm diameter wire at 3 \( \mu \)m radius of curvature.\cite{47} The wires are resilient and
immediately recover their unbent shape even after being elastically buckled. Even with an aspect ratio of 100:1, a 157-nm diameter wire did not buckle below 160 nN—a considerably high force for most AFM studies.

Visual Force Detection in SEMs and Optical Microscopes

In addition to demonstrating nanowire-tipped AFM cantilevers in topographic and force–distance spectroscopy measurements, the nanowires have been applied to evaluate force by visual examination of the buckled shape of the nanowires in compression. Fig. 16B shows a SEM image in side view of a nanowire as it is pressed against and deflects a polymer nanofiber. The blue line shows the best fit according to an elastica model of buckling with the applied force being a variable. Once the force is determined, the loading of the fiber is also determined from which the elastic modulus of the fiber was deduced. The opaque and reflective nanowires produce strong Mie scattering and detectable levels of optical modulation, which enables them to be directly used as cantilevers for sub-picoNewton force measurement. The SEM imaging method depends on being able to align the needle deflection in the plane of observation. There are several optical methods (e.g., confocal scanning, structured light illumination, and deconvolution microscopy) that permit the 3-D reconstruction of an object at optical resolution. As long as the wire is microns long, the blurring of the suboptical-wavelength nanowires should not appreciably affect fits to the shape of the curves. Fig. 16C shows that very long nanowires can torsionally buckle, which further illustrates the importance of 3-D reconstruction of the shape for this type of force detection.

Constant Diameter Nanowires for Quantitative Measurements of Surface Wetting Force, Viscosity, and AFM of Submerged Objects

Since the diameter of Ag$_2$Ga nanowires can be constant over a considerable length, the contact line, and hence wetting force will be constant with insertion depth. Compared to a tapered tip, this result simplifies the interpretation of AFM force–distance measurements, enabling the quantitative determinations of viscosity, surface tension, contact angle, and evaporation rate.

A key advantage of constant diameter and high aspect ratio nanostructures can be appreciated by comparing the interaction of a tapered AFM tip with a constant diameter tip (Fig. 29). The left panel shows a schematic and a typical AFM force–distance $(F–D)$ curve for an AFM cantilever having a standard tapered tip. The forces on the AFM cantilever as the tip is inserted into the liquid are plotted as the red curve and the forces during the retraction of the probe are shown as the blue curve. When the tip just touches the liquid, there is a step change in the force as the liquid wets the tip. With further insertion, the wetting force increases in proportion to the increasing length of the contact line on the tapered tip. When using such a tapered probe as a nanomanipulating tool in liquids, the growing wetting force makes the cantilever increasingly unstable and difficult to control, to the point that the much larger cantilever can unstably snap-down and become stuck to the surface of the liquid. However, for a constant diameter tip (right panel of Fig. 29), the wetting force is constant with insertion depth. Therefore, it becomes possible to manipulate or sense objects underneath the surface while the liquid–air interfacial force remains constant. As shown in the schematic, this structure has a step change in diameter. (The structure is two-fused Ag$_2$Ga nanowires with one wire growing ~3 µm past the other.) Therefore, the $F–D$ curve shows two step changes in force, and two regions of constant force with insertion depth.

If the length of the contact line is known (see Fig. 29), surface tension can be determined from $F_c$ (wetting force with zero contact angle), and then contact angle from $F_c$ (the force applied by the meniscus at its equilibrium height). For typical AFM tips which have a pyramidal taper, the length of the contact line varies with insertion depth, so it is not obvious. On a cylindrical tip or a constant diameter nanowire, the contact length is well known, enabling the direct measurement of surface tension and contact angle.

A more detailed examination of the $F–D$ curves of single- and dual-diameter nanowires is presented. Fig. 30 presents an idealized model of the $F–D$ curve for a dual-diameter nanowire. It relates the geometry of the needle and liquid meniscus to the features on the $F–D$ curve. Several features are different from those seen in $F–D$ curves with macroscopic probes. In macroscopic $F–D$ curves, the portions of the curves between $ii$ and $iii$, and to the right of $iv$ are not level due to the buoyant displacement of the probe and viscous drag forces. With the nanoscale probes, the buoyant force (due to liquid displacement) is negligible compared to wetting force, and for the low scan speeds of the AFM
For lower viscosity liquids (less than 100 μm/s), and for lower viscosity liquids (less than 1000 cP), the drag force is not evident.

The idealized $F$–$D$ curve in Fig. 30 also includes differences in the advancing and receding contact angles and approximately in the same order of decreasing surface tensions.

**Source:** From Yazdanpanah, Hosseini, et al. [59] © 2008 ACS.

(under 100 μm/s), and for lower viscosity liquids (less than 1000 cP), the drag force is not evident.

The idealized $F$–$D$ curve in Fig. 30 also includes differences in the advancing and receding contact angle. This corresponds to a vertical separation between the horizontal portions of the insertion and retraction curves. Current theories attribute these differences in contact angle to "defects" in local composition or shape variations of the solid surface. [91] Defects pin the (liquid, air, solid) triple line causing the hysteresis in contact angle. However, for defects that are small in physical dimension or differ in a small amount in surface energy, thermal fluctuations greater than $\sim 20 k_B T$ can surmount the defects and attain the equilibrium contact angle. An estimate of the maximum defect size that can be overcome has a square root dependence on the surface tension, which is about 20 nm for a liquid of surface tension 20 mN/m (about the same surface tension as for dibasic ester) and 10 nm for 74 mN/m (water).

The $F$–$D$ curves (measured with the same nanowire-tipped AFM probe) on the right of Fig. 30 are from liquids that span this range of surface tensions. As surface tension decreases, the advancing and receding forces (and hence, contact angles) come closer together and nearly vanish. These subtle transitions between surfaces that wet as smooth and homogenous surfaces, to surfaces that wet as rough or inhomogeneous surfaces would be extremely difficult to observe using force curves from tapered tips (like the $F$–$D$ curve in Fig. 29A).

The constant diameter of the nanowires has proved useful in determining viscosity by either (a) drag force vs. retraction velocity for higher viscosity liquids, and for lower viscosity liquids, or (b) resonance or "Q" damping of thermal fluctuations of the AFM cantilever vs. insertion depth into a liquid. [59]

It is notable that the nanowires proved to be very robustly attached and resistant to breakage. Probes were dipped in acetone for cleaning after each measurement, removed from the AFM, viewed in the SEM, and remounted in the AFM, sometimes up to 60 times without breaking.

**Ultracompliant Force Sensors and Actuators**

It is truly remarkable that the brush-on method redirects the same capillary and wetting forces (that normally cause overly flexible, suspended micromechanical structures to undesirably snap down during fabrication) to form liquid polymers into delicately suspended nanofibers. The BOS structures, such as in Fig. 7, have been formed by brush-on (as in Fig. 31A) with aspect ratios of up to 20,000:1 (1 mm long by 50 nm in diameter), as illustrated schematically in Fig. 31B and shown under the microscope (Fig. 31C) and SEM (Fig. 31D).

Fibers of such high aspect ratios can have stiffnesses of around 1 μN/m, which can be compared with the softest commercial AFM cantilevers at around 10 mN/m. As summarized in Table 2, the sensitivity of current commercial AFMs for force–distance measurements is around 10 pN (to put this level of force into perspective, ~10 pN and below correspond to the forces exerted by many single molecules and biomolecular events, such as those produced by flagellar motors, growth of single actin filaments, bonding forces

**Fig. 30** $F$–$D$ curves for a dual diameter probe tip in a simple low molecular weight liquid. (A) Idealized model of $F$–$D$ curves for (B) the geometric parameters of the nanowire, the surface of the liquid, and the meniscus. (C) Measured $F$–$D$ curves. The curves are arranged in order of decreasing difference between advancing and receding contact angles and approximately in the same order of decreasing surface tensions.

**Source:** From Yazdanpanah, Hosseini, et al. [59] © 2008 ACS.

**Fig. 31** Magnetic BOS nanofibers. (A) The brush-on method, specifically showing the formation of BOS air-bridges and magnetic alignment of polymer-dispersed iron oxide nanowires. (B) Schematic of typical BOS fibers and (C) the optical image in which the fiber portion is barely visible in the light microscope. (D) SEM image showing a 60 nm fiber. Lateral deflections are produced by (E) blowing a stream of air over the bead from a tapered pipette, as shown, or by magnetic fields from a similarly tapered electromagnet near the bead.

**Source:** From Rathfon, Yan, et al. [22] © 2012 Elsevier.
between pairs of DNA nucleotides, hydrogen bonds, etc.), using quad photodetection schemes. However, for the BOS fibers at 1 μN/m (or equivalently 1 pN/μm), forces at the limiting sensitivity of the AFM could be visually observed under optical microscopes. Specifically, with microscope resolution, generally much higher than 1 μm (~half the wavelength of light divided by the numerical aperture of the microscope objective) deflections corresponding to pN levels of force could be visually detected. Visual detection is enhanced by the presence of the large bead, which can be more easily seen than the subwavelength fiber (as in Fig. 31C and E).

By blowing air at a low velocity (i.e., Reynolds number less than unity, Stokes regime) as in Fig. 31E, the drag force on the sphere was calculated and plotted against displacement (Fig. 32A and B). The 1 mm long by 270 nm diameter fiber deflects 1 μm for the 10 pN drag force. Since the bending stiffness of the slender structure (modeled as an elastic string rather than a beam) is proportional to cross-sectional area, sub-100 nm fibers should reach 1 pN/μm sensitivity through direct visual observation.

Quad photodetection, as used in AFM, has been modified and applied to position sensing of microbeads in laser and magnetic tweezers. Quad detection has even been demonstrated to work well with non-spherical and sub-wavelength objects and with position sensitivity well below the visual limit of detection. The quad detection method is sensitive enough to detect the thermal vibration noise \( \langle x^2 \rangle = k_B T/k \) (as based on the equipartition theorem), where \( x \) is the position noise and \( k \) is the stiffness of the structure. As compared with AFM cantilevers, the nanofibers with 10,000X smaller stiffness should have 100X greater thermal displacements, thereby greatly increasing detectability of the thermal spectra. This enhanced sensitivity would enhance real-time spectrum analysis of the structure, providing a complete spectrum with vibrational bandwidth, resonance frequency, and \( Q \) of structure. This capability could be applied to continuous in situ monitoring of instantaneous changes in the material properties of the polymer nanostructure or perturbations produced by outside forces. Therefore, the quad detection method can provide intimate details of changing physical states of the BOS structure.

As simple as adding a fiber to a bead may seem, it nonetheless adds many new features, capabilities, and complexities to the structure. As described above, a microbead simplifies optical sighting of deflection and optical scattering for quad detection. The large size of the bead, compared to the fiber, also was used to concentrate loading due to Stokes drag at the center of the fiber, thereby approximating point loading of the fiber.

Yet another feature of the bead is that it has an enormous volume compared to the fiber (typically much greater than 100X more volume than the fiber). This has been used to advantage in making magnetically deflectable BOS structures. Filling the fiber alone with a magnetic material would require enormous magnetic fields to produce any observable deflection. However, the bead can contain orders of magnitude more material, enabling deflections with modest fields (Fig. 32C). These structures were formed
from an aqueous PEO solution containing 0.03 vol.% of superparamagnetic iron oxide nanoparticles (γ-Fe₂O₃). The addition of the material at these small concentrations (either as nanoparticle or nanowires) does not noticeably affect the dimensions of the BOS structures. After drying, the bead contains about 1 vol.% (~5 wt.%) iron oxide.

Also recently, magnetic nanoparticles have been included in elastomeric polymers (specifically PDMS) in order to enable various types of magnetic actuation. The shape anisotropy of the rods enables strong torques to be applied to the structures with modest magnetic fields. Fig. 31A shows an idea for magnetically aligning nanorods prior to solidification. Aligned nanorods would maximize the magnetic torque possible with a fixed amount of magnetic material. Even with randomly oriented nanorods, it is possible to magnetically produce torque and rotation of a bead. This may be due to the non-uniform distribution of the nanorods or to a preference for paramagnetic nanorods aligned parallel with the magnetic field to become magnetized faster than nanorods that are perpendicular to the field.

The addition of a bead to a fiber also makes additional vibrational modes and mechanical manipulations evident. Fig. 33 summarizes the deflections that have been observed for the BOS structures. These have been laterally deflected with laminar air streams and magnetic fields (Fig. 33ii) with the deflections measured under a light microscope.

There are several distinct modes of motion that have been observed under a light microscope due to applied air flows, magnetic fields, or a combination of both. The modes should differ dramatically in stiffness, with rotation around the fiber axis being the least stiff (Fig. 33iii), followed by lateral deflection (Fig. 33ii). Fig. 33iii is drawn to suggest that the fiber could be rotated several turns, which was indeed observed (as in Fig. 33iv) when there was an unequal flow of air between the top and bottom of the bead. After removing the air flow the bead returned to its undeflected position while continuing to unwind. This deflection with rotation was repeated, and then the electromagnet was turned on, which stopped the rotation. The bead was deflected further without additional rotation. One could gradually lower the magnetic field to the rotational holding limit and then determine the torque caused by the unequal drag over the bead. By winding the fiber using different amounts, one could study the effect of different degrees of tensioning on the force deflection curve. The stiffest modes are v and vi in Fig. 33, and are hard to discern under a light microscope, but evident in an SEM (where deflection is probably induced by charging from and attraction to the nearby beam at a distance of a few microns with a 100 pA current, rather than due to the magnetic field induced by the beam).

One can envision using individual BOS fibers as probes in place of AFMs. Probes could be batch fabricated and then individual probes consisting of a yoke and a single BOS fiber could be cleaved from a wafer. For example, the most simply fabricated micropillar arrays are made using a wafer-dicing saw to cut pillars. The C-shaped yokes in Fig. 34 can be defined, prior to brush-on, by making saw cuts at a shallow depth between pairs of pillars that define yokes, and cuts to a greater depth to permit cleaving of yokes after the nanofiber air-bridges are formed. The complete probe can be mounted on a nanomanipulator arm (as is common in many biophysical studies) and brought to the sample under test on the inverted microscope (Fig. 34). Inserting a small probe in this way takes up much less space on microscopes than an AFM head, enabling much greater mechanical and optical access to samples of interest.

**CONCLUDING REMARKS**

The methods of self-assembly presented above result in the formation of suspended or freestanding nanomechanical...
structures. These form specified locations, with relatively crude directions from the operator that then spontaneously evolve into precise nanoscale structures. These methods can be made to work at room temperature with relatively crude fixtureing, resulting in a low cost for fabricating individual devices and arrays of devices. While the structures can regularly produce nanoscale features, the ability to repeatedly and precisely achieve a designed feature size has not been explored, and is probably challenging. On the other hand, very good uniformity of size can be achieved in the single run of an array of devices. Starting from this point of having a good array, a manufacturing method could be based on the selection of arrays that have the desired dimensions. Such an approach may not prove to be economically feasible. On the other hand, the ability to rapidly make nanomechanical structures out of a variety of materials (e.g., polymers including functionalized polymers, metals, nanomaterial composites, etc.) could prove immediately useful for the rapid exploration and prototyping of complex NEMS and microsystems concepts. Following the prototype evaluation phase, one could commit to the extreme precision top-down nanofabrication of a functionally equivalent system. Such a commitment would require an extensive phase of process development. In order to maximize the potential of these directed self-assembly methods for the prototyping of device concepts, templated fabrication to increase device complexity was reviewed, together with the consideration of possible microsystems that could be constructed by these methods and which could exhibit a rich range of functionalities and multiphysical properties.

ACKNOWLEDGMENTS

This entry represents for the most part, the thoughts, investigations, discoveries, and results of my colleagues and collaborators who are cited as coauthors on the referenced papers. I am truly grateful for their interest, enthusiasm, encouragement, and creativity on these studies. Of special note are Prof. Gareth McKinley’s contributions to identifying key dimensionless groups in understanding the capillary force driven thinning of polymeric liquids. Table 1 is a modified and extended version of a table originally developed by McKinley in discussions with me. Prof. Doo Jin Cho, Ajou University, during his time as a Visiting Professor in my lab, performed the simulation of evanescent coupling between parallel fibers that is summarized in Fig. 28. Dr. B.H. Fasciotto (listed as B.H.F. Totten by Lin, Guan, et al.\cite{10}) provided extensive assistance in manuscript proofreading and formatting. I sincerely appreciate Prof. David Quéré and ESPCI ParisTech for hosting me on my sabbatical in 2009. The many ESPCI faculty, staff, and students introduced me to a myriad of soft matter problems that have strongly shaped and broadened my view of what self-assembly is, and how it might be applied to the fabrication and manufacture of nanodevices.

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Freestanding Metallic and Polymeric Nanostructures: Directed Self-Assembly


Table 1. Important time scales in elasto-capillary thinning of liquid fibers. Here $\eta$, $\rho$, $\gamma$ are the viscosity (of the Newtonian solvent alone or for a viscoelastic fluid at infinitesimally slow disturbance), density and interfacial/surface tension of the fluid. $R$ is the initial diameter of a liquid thread, $\lambda$ is the relaxation time of the polymer molecules in solution, and $h$ is the mass transfer coefficient (in m/s) characterizing evaporation of the volatile solvent.

<table>
<thead>
<tr>
<th>Time Scale</th>
<th>Dimensionless Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscous time scale</td>
<td>$t_v = \eta R / \gamma$</td>
</tr>
<tr>
<td>Inertial time scale</td>
<td>$t_R = \sqrt{\rho R^3 / \gamma}$</td>
</tr>
<tr>
<td>Ohnesorge number</td>
<td>$Oh = \frac{t_v}{t_R} = \frac{\eta}{\sqrt{\rho \gamma R}}$</td>
</tr>
<tr>
<td>Polymer relaxation time</td>
<td>$\lambda$</td>
</tr>
<tr>
<td>Deborah number</td>
<td>$De = \frac{\lambda}{t_R} = \frac{\lambda}{\sqrt{\rho R^3 / \gamma}}$</td>
</tr>
<tr>
<td>Elastocapillary number</td>
<td>$Ec = \frac{\lambda}{t_v} = \frac{\lambda \gamma}{\eta R} = \frac{De}{Oh}$</td>
</tr>
<tr>
<td>Mass transfer time scale</td>
<td>$t_m = R / h$</td>
</tr>
<tr>
<td>Processability parameter</td>
<td>$P = \frac{t_v}{t_m} = \frac{\eta h}{\gamma}$</td>
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</tbody>
</table>
Table 2. BOS sensing compared with other low force probes

<table>
<thead>
<tr>
<th>Method</th>
<th>Force range (pN)</th>
<th>Resolution (nm)</th>
<th>Stiffness (mN/m)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>$10^{-4}$</td>
<td>0.5-1</td>
<td>$10^{-5}$</td>
<td>Force-Distance</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Scanned stiffness maps</td>
</tr>
<tr>
<td>Magnetic tweezers</td>
<td>$10^{-3}$-$10^{-2}$</td>
<td>5-10</td>
<td>$10^{-3}$-$10^{-6}$</td>
<td>Force-Distance</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Apply small torques</td>
</tr>
<tr>
<td>Optical tweezers</td>
<td>0.1-100</td>
<td>0.1-2</td>
<td>0.005-1</td>
<td>Force-Distance</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3D manipulation</td>
</tr>
<tr>
<td>BOS device with visible detection*</td>
<td>$0.1-10^{-3}$</td>
<td>$10^{2}$</td>
<td>$10^{-3}$-$1$</td>
<td>Force-Distance</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Apply large torques</td>
</tr>
</tbody>
</table>

* Sub-nm position resolution, as in laser trapping, is possible by using quadrature detection instead of visible detection to locate bead position.
Figure 1. Self-assembly of nanofiber air-bridges by brushing polymeric liquids over micropillar arrays. The process can yield uniform arrays of structures even when the liquids are brushed over the array by hand.105
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