

**TABLE 4.1*****Top-Down Mechanical-Energy Fabrication Methods***

<b>Method</b>	<b>Comments</b>
Ball milling	Production of nanoparticles by mechanical attrition to produce grain size <5 nm [3] High-energy ball milling uses steel balls to transfer kinetic energy by impact to the sample. Highly polydisperse products and contamination are problems.
Rolling/beating	Traditional mechanical methods to minimize material thickness and refine structure. Gold can be beat into a 50-nm thick film [4].
Extrusion; drawing	High-pressure processes of forcing materials in a plastic phase through a die to form high-aspect ratio parts like wires. Bi metal forced through nanopore alumina is an analogous process at the nanoscale and can be considered a thermal–mechanical process.
Mechanical Machining, polishing, grinding, and ultramicrotome	Also known as conventional machining; resolution limit: 5 $\mu\text{m}$ [5] Other techniques analogous to mechanical machining perform the same function with laser beams, focused ion beams, and plasmas. Mechanical grinders/cutters are used to thin TEM samples. These include dimple grinders, diamond saws, ultrasonic disc cutters, and ultramicrotomes (<100 nm sections).
Compaction; consolidation	Metal powder ball milled and compacted. Powders are considered to be bulk materials; therefore, compaction of powders to form bulk material is not considered to be a bottom-up method.
Atomization	Conversion of a liquid into aerosol particles by forcing through a nozzle at high pressure

TABLE 4.2

Top-Down Thermal Fabrication Methods

Method	Comments
Annealing	There are two applications of annealing: (1) anneal of bulk materials to form nanocrystallites, and (2) transformation of nanomaterials into another physical phase [6]. Microphase separation to form nanoscopic structures occurs in copolymer bulk materials upon application of thermal anneal above the glass transition temperature.
Chill block melt spinning	Metal is melted with RF coil and forced through nozzle on rotating drum, where it solidifies; strips formed with nanostructure [7].
Electrohydrodynamic atomization (EHDA)	Production of monodisperse droplets; melt or liquid materials at nozzle with electric field between nozzle and surface: cone → thin jet → droplets EDHA + pyrolysis to produce 10-nm Pt nanoparticles [8]
Electrospinning	A high voltage is applied to a polymer melt solution to induce charging. Polymer solutions at room temperature are also used routinely. At an acquired threshold, an electrospun fluid jet emerges from a needle tip to form a Taylor cone. The substrate, held at a lower potential, is covered by the charged polymeric solution
Liquid dynamic compaction (LDC)	Molten stream of metal is atomized by high-velocity pulses of an inert gas and the semisolidified droplets are collected on a chilled, metallic substrate [9].
Gas atomization	Molten metal is subjected to high-velocity inert gas impact that forms metal droplets [7,10]. Kinetic energy is transferred to metal, resulting in small droplets upon solidification to form powders. Powders are then compacted to form high-strength bulk materials.
Evaporation	Evaporation of solid metal or other material samples to form thin films; usually performed under high vacuum ( $10^{-6}$ torr). Heat is produced by electrical resistance. If nanoclusters are formed during the evaporation process, it is top down. If atoms or molecules are formed during the evaporation process that recombine to form a thin layer without any chemical reaction, it is a crossover technique.
Electrospinning	The process of electrospinning utilizes electricity to form thin layers of filaments from bulk polymer, composite, or ceramic solutions; fibers with nanoscale diameter can be fabricated [11].
Extrusion	Nanowires by extrusion of bismuth melt by pressure injection into porous template material such as alumina [12]. Parallel Bi nanowires with diameter ~13 nm
Template synthesis + evaporation	Formation of single-crystal Bi nanowires by a vapor-phase technique into porous alumina template—7-nm Bi nanowires [13]; 400–500°C with $N_2$ trap. Only phase changes are involved in this process.
Sublimation	The physical process of sublimation involves a phase change from a solid into gaseous form without a liquid intermediate phase. If nanoclusters are formed by this process, it is considered to be a top-down process. If atoms or molecules are formed first and then agglomeration into nanoparticles occurs, it is considered to be a crossover technique in which both top-down and bottom-up processes occur nearly simultaneously. Sublimation does not involve a chemical change of the material.
Thermolysis; pyrolysis	Decomposition of bulk solids at high temperature (top-down). These terms are also applied to the decomposition of molecules—nanomaterials are formed after decomposition in a bottom-up way by agglomeration. Because of this crossover, it is hard to place pyrolysis/thermolysis into one category or the other. The most common sense of the terms implies that molecules are simply converted into other molecules. In this sense, pyrolysis and thermolysis are neither top-down nor bottom-up methods. In such reactions (like decomposition), chemical change does occur.
Combustion	Chemical combustion is a top-down process in which there is chemical conversion of bulk organic materials + impurities into molecules like $CO_2$ , $H_2O$ , and nanomaterials such as ash with micron to submicron dimensions. The process of combustion involves oxygen.
Carbonization of copolymers	Spun fibers from polymethylmethacrylate (PMMA)—polyacrylonitrile (PAN) microspheres in PMMA matrix (top down? or bottom up?). Temperature treatment at 900°C removes PMMA and converts PAN into MWNTs [14]. Carbonization is another example of the difficulty encountered in cataloging such processes.

**TABLE 4.3** *Top-Down High-Energy and Particle Fabrication Methods*

Method	Comments
Arc discharge	High-intensity electrical arc discharge directed on a graphite target (anode) + catalyst to produce single-walled carbon nanotubes that accumulate on the cathode Temperature ~4000 K [15,16]
Laser ablation	High-intensity laser beam directed on a graphite target + catalyst to produce single-walled carbon nanotubes; sample warmed to 1200–1500°C by furnace, laser Sample is collected on water-cooled copper collector [17]. This process can be considered to be a thermal and a high-energy method.
Solar energy vaporization	Solar energy focused on graphite target + catalyst to produce single-walled carbon nanotubes Temperature ~3000+K [18]
RF sputtering	Ion bombardment of metal, oxide, or other material targets to form thin film coatings Usually performed under moderate vacuum ( $10^{-3}$ torr). Atoms, molecules, and clusters are formed by this process.
Ion milling	Argon ion plasma is used to subtract material from a surface. The purpose is to clean surface or remove (thin) materials for TEM. No change in the chemical nature of the sample happens during this process.
Electron beam evaporation	This is similar to evaporation in <b>Table 4.2</b> but uses an electron beam source to heat material. Evaporated material condenses on target substrate. High vacuum is required. Thin-layer antireflection, scratch-resistant coatings are formed by this technique.
Reactive ion etching	Sensitive materials are etched by reactive chemical species in charged plasma. Chemical change of the etched material takes place during this process. The etching process is guided by maskant materials.
Pyrolysis	Pyrolysis can also be considered a high-energy method. Application of high-energy source like fire to bulk hydrocarbon materials (like a steak) in the absence of oxygen creates polyaromatic hydrocarbons (PAHs)—a top-down process (or if considering intermediates—for example, carbon atoms—it can be considered to be a bottom-up process). Pyrolysis of solid refractory nanoscale materials like Si–C–N substrate to form nanotubes at 1500–2200°C is a crossover technique [19]. Large-scale synthesis of multiwalled carbon nanotubes occurs in flame environments by burning carbon sources such as methane, ethylene, or benzene.
Combustion	Combustion can be considered to be a high-energy, thermal, or chemical fabrication method.
High-energy sonication	Ultrasonication uses high-energy sound waves to make nanomaterials from bulk materials. The technique is also used to disperse carbon nanotubes in a suitable solvent. The dispersion of bundles of nanotubes into individual tubes is top down. Probe tips are made of titanium, vanadium, and other metals and alloys. Micron- to nanosized residual tip metal is introduced into solutions during the sonication process.

**TABLE 4.4*****Top-Down Chemical Fabrication Methods***

<b>Method</b>	<b>Comments</b>
Chemical etching	Standard acid or base solution etching of silicon and other materials, usually guided by maskant materials. Materials with nanometer pore channels are produced by this method. Etching of a metal surface without substantial oxide growth results in nanofacets.
Chemical–mechanical polishing (CMP)	CMP utilizes abrasives with or without a corrosive chemical slurry. Purpose is to thin and flatten samples. Surface roughness depends on size of abrasive. Mirror finishes with nanometer-scale roughness are produced by CMP methods.
Electropolishing	Electropolishing is an anodic method for brightening and smoothing the surface of a metal, primarily used for aluminum. The purpose of electropolishing is to reduce the surface roughness of a metal to nanometer scale. Conditions are extreme: concentrated acids (or bases), elevated temperature, and elevated current.
Anodizing	Anodizing is considered to be a crossover method in that nanofacets are formed on a bulk aluminum surface from the top down that in turn direct the formation of an anodic oxide from the bottom up. Anodizing operates under the same principle as electropolishing except that film growth is favored instead of film dissolution. Conditions are mild in comparison: dilute polyprotic acids, low temperatures (ca. 0°C), and low current.
Combustion	Combustion is an irreversible and dynamic chemical process that is catalyzed by high-temperature flames. Trees burning in a forest fire is a top-down way to form nanoaerosols.

**TABLE 4.5** *Top-Down Lithographic Fabrication Methods*

Method	Comments
LIGA techniques	LIGA is a German acronym for "Lithographie Galvanoformung Abformung," a microlithographic method developed in the 1980s. It was one of the first major techniques to demonstrate the fabrication of high-aspect ratio structures. Beam sources include x-ray, ultraviolet, and reactive ion etching. MEMS devices are fabricated using LIGA techniques.
Photolithography	Light is used to transfer patterns onto light-sensitive photoresist substrates. Photolithography is primarily used in the manufacture of integrated circuits and MEMS devices. The wavelength range of optical lithography techniques ranges from the visible to the near ultraviolet—ca. 300 nm. The resolution of photolithography techniques is ~100 nm [20].
Immersion lithography	Just like with immersion optical microscopy, resolution can be enhanced by 30–40% with application of a liquid medium between the aperture and the sample with higher refractive index. The medium needs to conform to the following criteria: (1) refractive index $n > 1$ , (2) low optical absorption at 193 nm $\lambda$ , (3) immersion fluid compatible with the photoresist and the lens, and (4) be noncontaminating.
Deep ultraviolet lithography (DUV)	Resolution with deep ultraviolet with $\lambda = 248\text{--}193$ nm, resulting in features on the order of 50 nm
Extreme ultraviolet lithography (EUVL)	Short wavelength ultraviolet, $\lambda = 13.5$ nm. EUVL resolution: ~30 nm [20]. The major problem with EUVL is that all matter absorbs EUV and damage to substrates is very likely. High vacuum is required and mask must be made of Mo-Si.
X-ray lithography (XRL)	X-rays are produced by synchrotron sources. XRL is capable of producing features down to 10 nm. Problems include damage to substrate materials.
Electron beam lithography (EBL)	An electron beam source is used instead of light to generate patterns. Although e-beams can be generated below a few nanometers, the practical resolution is determined by the electron scattering of the photoresist material. Just like in SEM, electron interaction volumes are generated during exposure. Line width <20 nm and electron energy: 10–50 keV
Electron beam writing (EBW)	EBW is a direct-writing procedure and, therefore, no pattern masters are required. Direct-write e-beam resolution is ca. 20 nm with lateral dimensions <10 nm [20]. Operation of electron beam parameters and patterning are computer controlled.
Electron beam projection lithography (EPL)	This technique is similar to TEM in that electrons are focused through a lens and projected onto a surface. In this case, however, a pattern is placed near the aperture. EPL is a high-throughput technique. A diamond membrane is used as stencil mask material. The process is not limited by diffraction as are the photolithographic techniques [21].
Focused ion beam lithography (FIBL)	Utilizes a liquid metal ion source (LMIS) with beam size of 10+ nm. FIBL resolution is 30 nm [20]. There is less backscattering than EBL and FIBL resists are more sensitive. FIBL, however, is restricted by limitations in reliable ion sources, difficulty in focusing, shorter penetration depth, swelling of resist, and whimsical ion implantation episodes. FIBL is also more expensive and slower than optical methods.
Microcontact printing methods	The George Whitesides group at Harvard University invented the lithographic method of microcontact printing. A topographical master is created by standard lithographic techniques that employ electron, ion, or electromagnetic beams. A negative replica of the master is made by pouring an elastomeric polymer, usually polydimethylsiloxane (PDMS), over the master. Upon curing, the elastomer is removed and coated with a self-assembled monolayer such as hexadecanethiol. Application of gold then reproduces the master pattern. Sub-100 nm features are possible by this technique [20].
Nano-imprint lithography (NIL)	Nano-imprint lithography is used to fabricate nanometer-scale patterns. It is a straightforward economical process with high throughput and high resolution. Patterns are created by stamping a resist material with a prefabricated stamp. The stamp can be used over and over. There are two types: thermoplastic (TNIL) [22,23] and photo (PNIL) [22,23]

**TABLE 4.5** *Top-Down Lithographic Fabrication Methods*  
(CONTD.)

Method	Comments
Nanosphere lithography (NSL)	NSL is used to fabricate nanometer-scale patterns. It is a straightforward economical process with high throughput and high resolution. It is difficult to categorize this technique as top down or bottom up. Micron-scale latex spheres are often used as the template material. The interstices are nanoscale in size. NSL utilizes nanospherical materials in close-packed configuration as a mask to aid in the fabrication of periodic particle arrays (PPAs). Polymer nanospheres (diameter <300 nm) are in a single or double layer over insulator, semiconductor, metal, inorganic ion insulator, or organic $\pi$ -electron semiconductor materials. Depending on the sphere diameter, nanoscale facets on the order of 22 nm are easily formed [24].
Scanning AFM nanostencil	An evaporated particle beam source is focused through a hole in an AFM cantilever. The procedure is good for metal deposition. This technique combines the ability to pattern a surface simultaneously with the ability to image the surface with the same cantilever. It is difficult to classify this technique as top down or bottom up (e.g., as it is for the thermal evaporation technique discussed before).
Scanning probe nanolithographies	There exist several forms of scanning probe nanolithographies. Some impart mechanical stress via the probe tip to a sensitized surface, followed by a chemical treatment; others apply an STM current to a substrate to create dangling bonds that react further to produce nanofeatures. These methods can be considered as top down in that nanofacets and features are produced from a solid bulk substrate.
2-Photon polymerization	Photopolymerization causes polymer to solidify to form three-dimensional image. Resolution of ~120 nm, although the laser $\lambda$ is 780 nm [25]. This is, in the clearest sense of the term, a top-down process.

**TABLE 4.6** *Top-Down Natural Fabrication Methods*

Method	Comments
Erosion	Conversion of macroscopic mineral-based materials into micro- and nanoparticles.
Etching	Etching of silicate rocks by carbonic acid from the environment contributes to erosion.
Hydrolysis	The decomposition of organic (and inorganic) matter by hydrolysis is a common way to make nanomaterials in the natural world.
Volcanic activity	Formation of fly ash and other materials by volcanic activity. The dispersion of volcanic byproducts is mostly airborne. Volcanic by-products contribute to the formation of clays like <i>montmorillonite</i> (a nanostructured material discussed in chapter 13).
Forest and brush fires	Formation of combustion gases, nanometer scale PAHs, amorphous carbons, and particulates
Solar activity	Radiation degradation of bulk synthetic, inorganic, and organic materials
Pressure and temperature	Formation of diamond crystallites from pressure and temperature processes applied to bulk materials; application to bulk carbon deposits (coal)
Biological decomposition	Decomposition is a process that begins at the bulk, micro-, or nanoscale level and terminates at the nano, molecular, or atomic level. Biological decomposition is mitigated by bacterial and other life forms in addition to inorganic natural processes.
Digestion	Reduction of bulk biological materials into nanometer and subnanometer scale components by the action of acids and hydrolysis; the formation of nitrogenous wastes is a bottom-up procedure, so to speak.

**TABLE 4.7** Bottom-Up Gas-Phase Fabrication Methods

Method	Comments
Chemical vapor deposition (CVD)	CVD involves the formation of nanomaterials from the gas phase, usually at elevated temperatures, onto a solid substrate or catalyst. Carbon nanotubes are formed by catalytic decomposition of carbon feedstock gas in inert carrier gas at elevated temperature. Single-walled carbon nanotube production by CVD requires nanoscale Fe, Co, or Ni catalyst plus Mo activator on high surface area support (alumina) at >650°C. Methane gas serves as the carbon source [26].
Atomic layer deposition (ALD)	ALD is an incredibly precise sequential surface chemistry layer deposition method to form thin films on conductors, insulators, and ceramics. The layer formed by ALD conforms to surface topography. Precursor materials are kept separate until required. Atomic scale control pinhole-free layers are formed. Al <sub>2</sub> O <sub>3</sub> layers are generated from hydroxylated Si substrate + Al(CH <sub>3</sub> ) <sub>3(g)</sub> , then H <sub>2</sub> O vapor is applied to remove methyl groups. The process is repeated until a target thickness is attained. Layer thickness: 1–500 nm
Combustion	The formation of Si nanoparticles from the combustion of SiH <sub>4</sub> (silane gas) and other silicon-containing gases like hexamethyldisiloxane under low-oxygen conditions produces Si nanoparticles as small as 2 nm. Al <sub>2</sub> O <sub>3</sub> and TiO <sub>2</sub> can also be formed by combustion.
Thermolysis; pyrolysis	Solid Si nanoparticles can also be formed by the thermal decomposition of silane gas in the absence of oxygen. The bottom-up decomposition of ferrocene to form Fe nanoparticles is one of the best examples of a bottom-up gas-phase fabrication method.
Metal oxide (MOCVD) Organometallic vapor phase epitaxy (OMVPE)	Chemical characteristics of precursor materials utilize reactive gas-phase-organometallic compounds that decompose to form nanometer-scale thin films or nanoparticles. H <sub>2</sub> carrier gas, group III metal–organic compounds + group V hydrides 500–1500°C at 15- to 750-torr pressure are representative conditions under which MOCVD is performed.
Molecular beam epitaxy (MBE)	MBE is a thin film growth process conducted under high vacuum. A heated Knudsen cell or effusion cell is used to introduce reactants by molecular beams. MBE is able to deposit one atomic layer per application. Examples include alternate layers of GaAs and AlGaAs with each layer of 1.13 nm in thickness and InGaAs quantum dots [27]. The temperature used in MBE is commonly 750–1050°C in H <sub>2</sub> carrier gas.
Ion implantation	This is a tough method to categorize. Nanovoids, for example, can be created by ion implantation of Cu ions into silica and subsequent annealing [28]. It is bottom-up action performed on a bulk material. If the ions come from a bulk source, it has a bottom up component. Once the ions are formed, ion implantation is bottom up.
Gas phase condensation; thermolysis	Formation of Fe nanoparticles by decomposition of ferrocene at 200°C is an example of gas-phase process to form nanoscale Fe. Formation of lithium nanoclusters by decomposition of LiN <sub>3</sub> is another example [7]. Temperature at decomposition depends on the material.
Solid template synthesis	Provides a solid template substrate for gas-phase deposition of materials on the solid substrate. This is considered to be a mixed bottom-up system. Final nanomaterial size, shape, and orientation are predetermined by template parameters.

TABLE 4.8

## Nonbiological Bottom-Up Liquid-Phase Fabrication Methods

Method	Comments
Molecular self-assembly	This generic process is supported in liquid media. From some perspectives, supramolecular chemistry is a subset of molecular self-assembly. Almost all molecular self-assembly takes place in liquids. The liquid plays a major role in supporting intermolecular interactions and intermediate metastable species.
Supramolecular chemistry	Supramolecular chemistry, for reasons to be explained in chapter 11, is conducted in liquid media. Weak intermolecular forces are supported in liquids that allow many kinds of intermolecular interactions to take place. All significant biological metabolic processes occur in a liquid medium.
Nucleation and sol-gel processes	Precursor chemicals in a supersaturated state combine by self-assembly or chemical reaction to form seed particles. Thermodynamics drives a nucleation process that forms nanoparticles. The nucleation process depends on prevailing conditions of pH, temperature, ionic strength, and time [5]. Due to van der Waals attractions, colloids are formed. Sol-gel methods are irreversible chemical reactions of homogeneous solutions that result in a three-dimensional polymer. Sol-gel methods yield nanostructured materials of high purity and uniform nanostructures formed at low temperatures [5]. Negative replicas of colloidal hierarchical structures, upon drying, yield aerogels or xerogels. Such gels can be back-filled to produce nanocomposites or hybrid materials [5]. These are all pure bottom-up processes.
Reduction of metal salts	Noble metal clusters and colloids are formed by the reduction of metal salts like $\text{HAuCl}_4$ and $\text{H}_2\text{PtCl}_6$ . Common reducing agents come in the form of organic salts like sodium citrate— $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ . By means of phase transfer reactions (consisting of an interface between two immiscible liquids), metal clusters and colloids are stabilized by the addition of organic ligands. For example, phosphine or thiols are adsorbed onto gold-55 to produce a stable cluster [29].
Single-crystal growth	Nucleation process to form single crystals in liquid media
Electrodeposition	Electrodeposition is direct deposition of metals from metal salt solutions to form thin layers or films on a solid conducting substrate. Electrodeposition is an electrolytic process that forms thin metal films on the cathode of the cell. The process conforms to Faraday's law.
Electroplating	Electroless deposition is the autocatalytic deposition of metals without electrical assistance. It requires metal cation + catalytic (activated) surface + reducing agents like formaldehyde, alkali diboranes, alkali borohydrides, or hypophosphorous acid. Pt, Ni, Co, Au, and numerous other metals can be deposited on many kinds of substrates, including plastics. Electroless deposition has been used to create negative or positive replicas of porous nanostructures [30].
Electroless deposition	We have already characterized anodizing as a top-down process. We mentioned earlier that anodizing method contains a top-down component (formation of scalloped structure). Here, we focus on the bottom-up formation of the porous alumina. Aluminum metal is made the anode in an electrolytic cell consisting of a polyprotic acid (usually sulfuric, phosphoric, or oxalic). Pore diameter of $<5 \text{ nm} \rightarrow >200 \text{ nm}$ ; with pore density: 20–80% and film thickness: $<1 \mu\text{m} \rightarrow >100 \mu\text{m}$ . Anodized titanium several nanometers thick generates bright interference colors $\rightarrow >100 \mu\text{m}$ . Anodized titanium several nanometers thick generates bright interference colors $\rightarrow >100 \mu\text{m}$ . Anodized titanium several nanometers thick generates bright interference colors [31].
Anodizing	Utilization of molten alkali halide salts with graphite electrodes with 3- to 5-A current [31]
Electrolysis in molten salt solutions	Erosion at the cathode to form tubes. The product is transferred to toluene.
Solid template synthesis	Provides a solid template substrate for electrochemical, chemical, polymerization, and other liquid-phase reactions. Most methods are accomplished in a liquid medium. Final nanomaterial size, shape, and orientation predetermined by template parameters.
Liquid template synthesis	Liquid templates (micelles and reverse micelles) are commonly used to make quantum dots from the bottom up.
Supercritical fluid	Solvent removal under hypercritical conditions forms aerogels and xerogels that contain water-sized voids. Supercritical conditions imply that the medium is in neither liquid

**TABLE 4.9** Bottom-Up Lithographic Fabrication Methods

Method	Comments
Nanolithography: Dip-pen methods (DPNL)	Nanoprobe lithography in the form of dip-pen nanolithography was invented by Chad Mirkin's group at Northwestern University in Chicago [32]. DPNL is considered as an AFM-based soft-lithography technique. The operation of this method is quite simple. A water meniscus is formed between an AFM tip and a substrate. The AFM tip, in conjunction with the water meniscus conduit, is able to transfer molecules to the surface. The method has high spatial resolution (<10 nm), has high registration capability (probe can both read and write), and is able to deliver complex molecules such as DNA to a surface [20]. The major disadvantage, like that of STM writing, is low throughput.
Nanosphere template methods	Nanosphere lithography is a template method for fabrication of nanomaterials. Latex spheres are arranged on a substrate surface in various configurations: hexagonal close packed, or into a square array. The interstitial spaces between latex spheres serve as sites through which deposition can occur—a very straightforward, simple process. Although the distribution and placement of the spheres can be considered to be a top-down process, the deposition of material through the interstices definitely occurs from the bottom up.
Nanopore template methods (shadow mask evaporation)	Use of porous alumina membrane templates as templates to form arrays of nanoparticles. The size of the nanoparticles can be controlled from 5 nm to >200 nm. The space between nanoparticles can also be adjusted. Nanoparticle aspects are adjusted by the height of the mask, the pore size, and the direction of evaporation [33]. This technique is good for direct patterning without the need for additional steps such as etching or lift-off. The combinations of masks, materials, and substrates are enormous, and the process allows for straightforward upscale. Arrays have been used in the secondary fabrication of memory devices and carbon nanotubes.
Block copolymer lithography (BCPL)	BCPs applied by spin-coating (top down) self-assemble into an ordered array of nanoscopic domains on a surface. Selective removal of one component yields an etch mask. The substrate pattern is formed by plasma etching. In a specific example: a 35-nm thick polystyrene-PMMA copolymer layer is applied to a $\text{Si}_3\text{Ni}_4$ -coated Si wafer. Removal of the PMMA leaves an ordered array of polystyrene nanodots. Reactive ion etching (REI) with $\text{CHF}_3$ transfers the pattern to the $\text{Si}_3\text{Ni}_4$ layer. The $\text{Si}_3\text{Ni}_4$ -formed pattern is etched again by REI with HBr. The result is an ordered array of silicon pillars (wires) [34]. Block copolymer lithography was able to produce periodic arrays of $10^{11}$ holes per $\text{cm}^{-2}$ [35]. One problem that faces this procedure is long-range order.
Local oxidation nanolithography	A scanning probe tip (a dynamic AFM tip) is placed a few nanometers above a substrate surface. The environment consists of saturated water vapor. A bias voltage is applied between the tip and the surface. Oxidation of the surface, if silicon, produces lines of silicon oxide. The breadth of the meniscus and the distribution of the electric field within determine the size of the feature [36]. Features as small as 7 nm were produced. One-nanometer projections were formed in the z-direction.
STM writing	The IBM logo pictured in chapter 1 was fabricated by a bottom-up method. Starting with xenon atoms, each atom was manipulated by the scanning probe tip into its final position. Other examples of this technique include the <i>quantum corral</i> —a circular array of Fe atoms placed on a Cu surface [37]. All scanning probe fabrication methods are hindered by low throughput.

**TABLE 4.10** *Bottom-Up Biological and Inorganic Fabrication Methods*

<b>Method</b>	<b>Comments</b>
Protein synthesis	Formation of proteins from precursor amino acids by elaborate process of protein synthesis Transfer RNA transports amino acids to ribosomal RNA and link with peptide bonds.
Nucleic acid synthesis	Synthesis of nucleic material (RNA, DNA) from sugars, phosphate, and nuclides (adenosine, guanine, cytosine, and thymine) from the bottom up The processes of mitosis and meiosis are template (replication) methods.
Membrane synthesis	Bottom-up agglomeration of lipids, phospholipids to form organized membrane structures that make life possible
Inorganic biological structures	Mother of pearl (nacre) 95% Inorganic aragonite (platelets 200–500 nm thick) + organic biopolymer Deformable nanograins [38]
Crystal formation methods	Nucleation depends on P, T, concentration, and composition. Flaws reduce surface energy by nucleation. Direction of growth depends on nanostructure.