36 Nanofabrication Technologies

Chapter Contents

The trend in miniaturization is continuing beyond the micrometer range into the nanometer (nm) scale. ***Nanotechnology*** refers to the fabrication and application of entities whose feature sizes range from less than 1 nm to 100 nm $(1 \text{ nm} = 10^{-3} \mu\text{m} = 10^{-6} \text{ mm} = 10^{-9} \text{ m})$.[1] The entities include films, coatings, dots, lines, wires, tubes, structures, and systems. The prefix "nano" is used for these items; thus, new words such as nanotube, nanostructure, nanoscale, and nanoscience have entered the vocabulary. ***Nanoscience*** is the field of scientific study that is concerned with objects in the same size range. ***Nanoscale*** refers to dimensions within this range and slightly below, which overlaps on the lower end with the sizes of atoms and molecules. For example, the smallest atom is hydrogen with a diameter close to 0.1 nm, whereas the largest of the naturally occurring atoms is uranium with a diameter of about 0.4 nm [4]. Molecules tend to be larger because they consist of multiple atoms. Molecules made up of about 30 atoms are roughly 1 nm in size, depending on the elements involved. Thus, nanoscience involves the behavior of individual molecules and the principles that explain this behavior, and nanotechnology involves the application of these principles to create useful products.

In the previous chapter, an overview of the products and devices in microsystem technology was provided. This chapter gives the same type of overview for nanotechnology. What are the currently available and potential future products and materials? Nanotechnology involves not just a reduction in scale by three orders of magnitude. The science is different when the sizes of the entities approach the molecular and atomic levels. Some of these differences are discussed in Section 36.2. Finally, in Section 36.3, the two major categories of fabrication processes used in nanotechnology are described.

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[1] The dividing line between nanotechnology and microsystem technology (Chapter 35) is considered to be $100 \text{ nm} = 0.1 \mu\text{m}$ [7]. This is illustrated in Figure 35.1.

36.1   Nanotechnology Products and Applications

Most products in nanotechnology are not just smaller versions of microsystem technology (MST) products; they also include new materials, coatings, and unique entities that are not included within the scope of MST. Nanoscale products and processes that have been around for a while include the following:

➢ The colorful stained-glass windows of churches built during the Middle Ages were based on gold particles of nanometer scale imbedded in the glass. Depending on their size, the particles can take on a variety of different colors.

➢ Chemical photography dates back more than 150 years and depends on the formation of silver halide nanoparticles to create the image in the photograph.

➢ Nanoscale particles of carbon are used as reinforcing fillers in automobile tires.

➢ Catalytic converters in the exhaust systems of modern automobiles use nanoscale coatings of platinum and palladium on a ceramic honeycomb structure. The metal coatings act as catalysts to convert harmful emission gases into harmless gases.

It should also be mentioned that the fabrication technology for integrated circuits now includes feature sizes that are in the nanotech range. Of course, integrated circuits have been produced since the 1960s, but only in recent years have nanoscale features been achieved.

Other more recent products and applications of nanotechnology include cosmetics, sun lotions, car polishes and waxes, coatings for eyeglass lenses, and scratch-resistant paints. All of these categories contain nanoscale particles (nanoparticles), which qualifies them as products of nanotechnology. A more complete list of examples of present and future products and materials based on nanotechnology is presented in Table 36.1.

36.1.1   CLASSIFICATION OF PRODUCTS AND APPLICATIONS

Nanotechnology products and applications can be organized into three categories: (1) incremental, (2) evolutionary, and (3) radical [4].[2] ***Incremental nanotechnology*** refers to products and applications in which nanoscale particles are used in great numbers to produce materials with unique and worthwhile properties or characteristics that could not be achieved as well by using larger particles. It is the presence of the nanoparticles functioning in aggregate that distinguishes incremental nanotechnology. All of the examples listed above are in this category, except chemical photography and integrated circuits.

Evolutionary nanotechnology involves the use of nanoparticles in great numbers that each accomplishes some unique and worthwhile purpose. The presence of nanoparticles functioning individually is what distinguished this category of nanotechnology. It could be argued that chemical photography is an example of evolutionary nanotechnology because of the individual responses of different regions of the film to the projected light from the image. Other examples are difficult to identify. One might imagine an array of trillions of nanoparticles being used in a data storage device or an

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[2]The classification scheme is attributed to R. A. L. Jones, ***Soft Machines Nanotechnology and Life***, Oxford University Press, Oxford, 2004.

TABLE • 36.1 Examples of present and future products and materials that are based on nanotechnology.

Computers. Carbon nanotubes (Section 36.1.2) are strong candidates to substitute for silicon-based electronics as the limits of size reduction are approached in the lithography-based processes used to make integrated circuits on silicon wafers. These limits are expected to be reached around the year 2015.

Materials. Nanoscale particles (nanodots) and fibers (nanowires) may prove to be useful reinforcing agents for composite materials. For example, the truck bed for one of General Motors' Hummer vehicles is made with nanocomposites. Entirely new material systems, not known today, may be possible with nanotechnology.

Nanoparticle catalysts. Metal nanoparticles and coatings of noble metals (e.g., gold, platinum) on ceramic substrates act as catalysts for certain chemical reactions. Catalytic converters in automobiles are an important example.

Cancer drugs. Nanoscale drugs are being developed that will be designed to match the specific genetic profile of the cancer cells of a patient and to attack and destroy the cells. For example, Abraxine is a nanoscale protein-based medicine produced by American Pharmaceutical that is used to treat metastatic breast cancer.

Solar energy. Nanoscale surface films have the potential to absorb more of the sun's electromagnetic energy than existing photovoltaic receptacles. Developments in this area may reduce reliance on fossil fuels for power generation.

Coatings. Nanoscale coatings and ultra-thin films are being developed that will increase scratch resistance of surfaces (eyeglass lenses with such coatings are already available), stain resistance of fabrics, and self-cleaning capabilities for windows and other surfaces (the "lotus effect").

Flat screen displays for television and computer monitors. TV screens based on carbon nanotubes are being developed for introduction in 2006. They are expected to be brighter, less expensive, and more energy efficient than current displays. They will be produced by Samsung Electronics of South Korea.

Portable medical laboratories. Instruments based on nanotechnology will provide fast analysis of a variety of ailments such as diabetes and HIV.

Batteries. Carbon nanotubes may be future components in high-powered batteries and storage devices for hydrogen. Hydrogen storage will no doubt play a role in converting from fossil-fuel motors to hydrogen-based engines.

Light sources. Lamps are being developed based on nanotechnology that use a fraction of the energy of an incandescent light bulb and never burn out.

Based mostly on [1] and [24].

ultrahigh-resolution imaging device. As a storage device, each particle stores one bit of data that is individually addressable. As an imaging device, each particle emits its own color and brightness that are individually controllable; taken together, an image is formed.

Radical nanotechnology is concerned with the construction of microscopic machines that consist of nanoscale features and mechanisms. This nanotechnology category subdivides into two branches: molecular manufacturing and nanorobots. *Molecular manufacturing* envisions the possibility of constructing some macroscopic entity by assembling the atoms that comprise it. One way of doing this is by moving atoms or molecules one by one to controlled locations to accomplish the assembly. This approach involves the use of scanning probe techniques, discussed in Section 36.3.2. It is of scientific interest but not a practical production process. An alternative and more realistic approach, also discussed in Section 36.3.2, involves self-assembly, in which the atoms and/or molecules are guided by physical or chemical laws to build the macroscopic entity.

The other branch of radical nanotechnology is more futuristic. It conceives of nanoscale robots (i.e., *nanorobots* or *nanobots*) that are equipped with some form of intelligence and a gripper with which they could assemble atoms and molecules. Such devices could be used to perform molecular manufacturing, if there were a sufficient number of nanorobots on the job. The scary aspect of the nanobot concept is that these molecular machines could also self-replicate, perhaps increasing their numbers at an exponential rate to wreak havoc on earth.

The notion of nanoscale machines, which is the basis of radical nanotechnology, is reminiscent of microelectromechanical systems (MEMS), an important product category in microsystem technology. MEMS have found many applications in the computer, medical, and automotive industries (Section 35.1.2). With the advent of nanotechnology, there is growing interest in extending the development of these kinds of devices into the nanoscale range. The term for this is ***nanoelectromechanical systems*** (NEMS), which are the sub-micron sized counterparts of MEMS devices, only their smaller sizes would result in even greater potential advantages. An important NEMS structural product currently produced is the probe used in atomic force microscopes (Section 36.2.2). The sharp point on the probe is of nanoscale size. Nanosensors are another developing application. Nanosensors would be more accurate, faster responding, and operate with lower power requirements than larger sensors. Current NEMS sensor applications include accelerometers and chemical sensors. It has been suggested that multiple nanosensors could be distributed throughout the subject area to collect data, thus providing the benefit of multiple readings of the variable of interest, rather than using a single larger sensor at one location.

Formidable technical problems arise in attempting to build nanorobots and other ***nanomachines***, defined as nanosystems that consist of movable parts and at least two different materials [8]. The problems result from the fact that the part surfaces cannot be made smooth and part edges and corners cannot be made sharp at the atomic and molecular sizes. Other surface characteristics also come into play, as discussed in Section 36.2.1.

36.1.2 CARBON NANOSTRUCTURES

Two structures of significant scientific and commercial interest in nanotechnology are carbon bucky balls and nanotubes. They are basically graphite layers that have been formed into spheres and tubes, respectively.

Fullerenes (Bucky Balls) The name "bucky ball" refers to the molecule C_{60}, which contains exactly 60 carbon atoms and is shaped like a soccer ball, as in Figure 36.1.
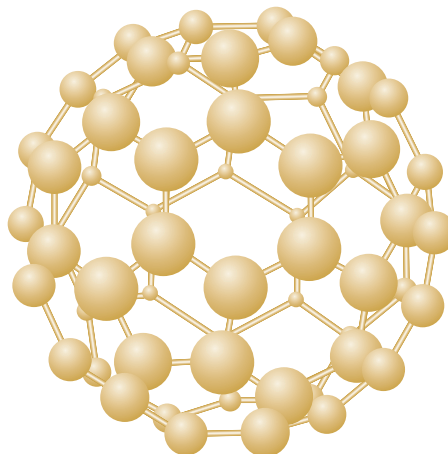

FIGURE 36.1 Fullerine structure of the C_{60} molecule. (Reprinted by permission from [18].)

The original name of the molecule was ***buckministerfullerene***, after the architect/ inventor R. Buckminister Fuller, who designed the geodesic dome that resembles the C_{60} structure. Today, C_{60} is simply called a ***fullerene***, which refers to any closed hollow carbon molecules that consist of 12 pentagonal and various numbers of hexagonal faces. In the case of C_{60}, the 60 atoms are arranged symmetrically into 12 pentagonal faces and 20 hexagonal faces to form a ball. These molecular balls can be bonded together by van der Waals forces (Section 2.2) to form crystals whose lattice structure is face-centered cubic (Figure 2.8(b), Section 2.3.1). The separation between any molecule and its closest neighbor in the C_{60} lattice structure is 1 nm. The bonded assembly of multiple fullerenes is called a fullerite.

Fullerenes and fullerites are of interest for a number of reasons. One is their electrical properties and the capability to alter these properties. A C_{60} crystal has the properties of an insulator. However, when doped with an alkaline metal such as potassium (forming K_3C_{60}), it is transformed into an electrical conductor. Moreover, it exhibits properties of a superconductor at temperatures of around 18°K. Another potential application area for the C_{60} fullerenes is in the medical field. The C_{60} molecule has many possible attachment points for focused drug treatments. Other possible medical applications for bucky balls include antioxidants, burn creams, and diagnostic imaging.

Carbon Nanotubes   Carbon nanotubes (CNTs) are another molecular structure consisting of carbon atoms bonded together in the shape of a long tube. The atoms can be arranged into a number of alternative configurations, three of which are illustrated in Figure 36.2. The nanotubes shown in the figure are all
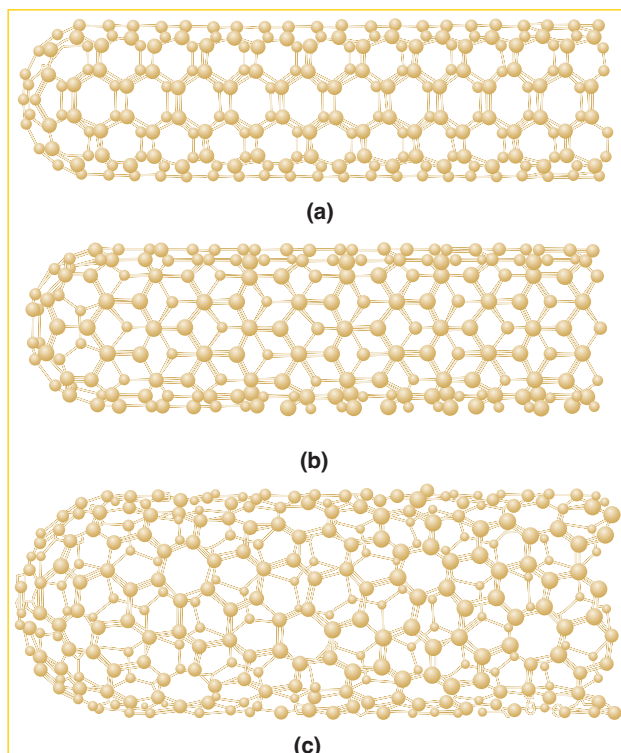

(a)

(b)

(c)

FIGURE 36.2   Several possible structures of carbon nanotubes: (a) armchair, (b) zigzag, and (c) chiral. (Reprinted by permission from [18].)

single-walled nanotubes (SWNT), but multi-walled structures (MWNT) can also be fabricated, which are tubes within a tube. A SWNT has a typical diameter of a few nanometers (down to ~ 1 nm) and a length of ~ 100 nm, and it is closed at both ends. Much larger SWNTs are possible, and the longest one on record is 18 mm (~ 3/4 in) long and 20 nm in diameter [4]. That is a length–to–diameter ratio of 900,000:1.

The electrical properties of nanotubes are unusual. Depending on the structure and diameter, nanotubes can have metallic (conducting) or semiconducting properties. Conductivity of metallic nanotubes can be superior to that of copper by six orders of magnitude [8]. The explanation for this is that nanotubes contain few of the defects existing in metals that tend to scatter electrons, thus increasing electrical resistance. Because nanotubes have such low resistance, high currents do not increase their temperature the way metals heat up under the same electrical loads. Thermal conductivity of metallic nanotubes is also very high. These electrical and thermal properties are of significant interest to manufacturers of computers and integrated circuits because they may allow higher clock speeds of processors without the heat buildup problems currently encountered as the density of components on a silicon chip increases. Clock speeds 10^4 times faster than current-day processors may be possible [18], along with much higher densities.

Another electrical property of carbon nanotubes is field emission, in which electrons are emitted from the ends of the tubes at very high rates when an electrical field is applied parallel to the axis of a nanotube. The possible commercial applications of field emission properties of nanotubes include flat panel displays for televisions and computer monitors.

Mechanical properties are another reason for the interest in single-walled nanotubes. Compared with steel, density is only 1/6, modulus of elasticity is five times higher, and tensile strength is ~ 100 times greater [8]. Yet, when SWNTs are bent, they exhibit great resilience to return to their previous shape without damage. These mechanical properties present opportunities for using them in applications ranging from reinforcing materials in polymer matrix composites (Section 9.4) to fiber cloths in bulletproof vests. Ironically, multiwalled nanotubes are not as strong.

36.1.3 THE NATIONAL NANOTECHNOLOGY INITIATIVE

In the year 2000, a national initiative on nanotechnology was enacted by the U.S. Congress at a funding level of $400 million starting in 2001. Funding levels have increased in what is now called the National Nanotechnology Initiative (NNI). A total of $3.7 billion was allocated over the 4-year period starting in 2005, making it the largest federally funded R&D program since the Apollo Space Program. The NNI Act mandated the coordination of nanotechnology research and development activities in the various federal agencies that are involved in this technology, including the Departments of Defense and Energy, the National Science Foundation, National Institutes of Health, National Institute of Standards and Technology, and the National Aeronautics and Space Administration. In addition, the Act defined nine areas of nanotechnology development (referred to as the NNI Grand Challenges) that will affect the lives of virtually all U.S. citizens. Table 36.2 briefly describes the nine areas of nanotechnology development to provide an overview of the future opportunities envisioned for this technology.

TABLE • 36.2 Nine areas of nanotechnology development identified in the National Nanotechnology Initiative (NNI).

Nanostructured materials by design. The objective is to develop materials that are stronger, harder, lighter, safer, and smarter; and to also devise materials that possess self-repairing characteristics. The research will focus on (1) understanding the relationships between a material's nanostructure and its macroscopic properties and (2) development of new methods of fabrication and measurement.

Nanoelectronics, optoelectronics, and magnetics. The objectives include developing new devices and fabrication technologies in these areas for integration into existing systems and new architectures (e.g., new circuit architectures to address the limits of present trends in silicon-based integrated circuit fabrication technologies).

Advanced health care, therapeutics, and diagnosis. The objectives are to (1) improve health of humans by the development of new biosensors and medical imaging technologies, (2) develop nano-based devices that can be used to direct the delivery of medications to targeted sites in the human body, (3) improve biological implants by means of nanoscale processing of the implant interface with the bone, (4) develop nanoscale-based devices to enable sight and hearing, and (5) devise improved diagnostic techniques using gene sequencing methods.

Nanoscaled processes for environmental improvement. The objectives are to (1) find new methods to measure pollutants based on nanotechnology, (2) develop new ways of removing submicroscopic pollutants from the air and water, and (3) extend scientific knowledge about nanoscale phenomena that are important to maintaining environmental quality and reducing undesirable emissions.

Efficient energy conversion and storage. The objectives include developing (1) more efficient energy sources using nanocrystal catalysts, (2) more efficient solar cells, (3) efficient photoactive materials for solar conversion of materials into fuels, and (4) high-efficiency light sources. Additional activities include exploring the use of carbon nanotubes for high-density storage of hydrogen and improving the efficiency of heat exchangers using fluids with suspended nanocrystalline particles.

Microcraft space exploration and industrialization. The objectives are to (1) reduce the size of spacecraft by an order of magnitude, (2) utilize the light weight and high strength of nanostructured materials to reduce fuel consumption, (3) enable autonomous decision making and increased data storage by means of nanoelectronics and nanomagnetics, and (4) utilize self-repairing materials to extend the reach of space exploration.

Bionanosensor devices for communicable disease and biological threat detection. The objectives include (1) improving detection of and response to threats from chemical and biological warfare and from human disease, (2) increasing human capabilities and improving health by means of nanoscale devices, and (3) performing research on the compatibility between nanoscale materials and living tissue.

Application to economical and safe transportation. The objectives include developing (1) more efficient transportation modes using nanomaterials that are lighter and have lower failure rates, (2) more durable materials for roads and bridges, (3) smart materials and devices capable of detecting imminent failure and performing self-repair processes, (4) nanoscale coatings with low friction and low corrosion properties, and (5) nanoscale performance sensors.

National security. The general objective is to achieve military dominance at lower cost and manpower, and to reduce the risks of personnel engaged in combat. Proposed research and development activities include (1) improving knowledge superiority by increasing processor speed, storage capacity, access speed, display technology, and communications capability, (2) use of materials with better properties for military systems, and (3) sensor technologies to protect combat personnel and enhance their fighting capabilities.

Compiled from [14].

36.2 Introduction to Nanoscience

The fields of nanoscience and nanotechnology are interdisciplinary. They rely on the synergistic contributions of chemistry, physics, various engineering disciplines, and computer science. The fields of biology and medical science are also involved. Biology operates in the nanoscale range. Proteins, basic substances in living organisms, are large molecules ranging in size between about 4 nm and 50 nm. Proteins are made up of amino acids (organic acids containing the amino group NH_2), whose molecular size is about 0.5 nm. Each protein molecule consists of combinations of various

amino acid molecules[3] connected together to form a long chain (call it a nanowire). This long macromolecule twists and turns to compact itself into a mass with a cross section in the 4- to 50-nm range. Other biological entities of nanoscale size include chlorophyll molecules in plants (about 1 nm), hemoglobin in blood (7 nm), and flu viruses (60 nm). Biological cells are orders of magnitude larger. For example, a red blood cell is disk-shaped with diameter of about 8000 nm (8 μm) and thickness of about 1500 nm (1.5 μm). The diameter of the human hair shown in Figure 35.3 is approximately 100,000 nm (0.1 mm).

The focus in this chapter is on nanoscale entities that are nonbiological. As in biology, nanotechnology deals with objects that are not much bigger than the atoms and molecules that comprise them. Section 36.2.1 discusses these "size effects" and how material properties are affected when the dimensions of an entity are measured in nanometers. The inability to "see" nanoscale objects has inhibited developments in nanotechnology until recently. The advent of scanning probe microscopes in the 1980s has allowed objects at the molecular level to be visualized and measured. These types of microscopes are described in Section 36.2.2.

36.2.1   SIZE MATTERS

One of the physical effects that occurs with very small objects is that their surface properties become much more important relative to their bulk properties. Consider the surface-to-volume ratio of a given amount of material as its dimensions are changed. Starting with a cubic block of material that is one meter on each side, its total surface area is 6 m^2, and its volume is 1 m^3, giving it a surface-to-volume ratio of 6–to–1. If that same volume of material were now compressed into a flat square plate that is 1 μm thick (0.00004 in, or about 1/100 the diameter of a human hair), its dimensions would be 1000 m on each side, and its total surface area (top, bottom, and edges) would be 2,000,000.004 m^2 (1,000 $\times$ 1,000 m^2 on each of two sides, plus 0.001 m^2 on each of the four edges). This would give it a surface–to–volume ratio of slightly greater than 2,000,000-to-1.

Next, suppose the flat plate were sliced in two directions to create cubes that are 1 μm $\times$ 1 μm $\times$ 1 μm. The total number of cubes would be 10^{18}, and the surface area of each cube would be 6 μm^2 or $6(10^{-12})$ m^2. Multiplying the surface area of each cube by the number of cubes gives a total surface area of 6,000,000 m^2, or a surface–to–volume ratio of 6,000,000–to–1 for the original amount of material.

A cube that is 1 μm on each side is surely small, but in nanometers, it is 1000 nm on each edge. Suppose the molecules of this material are cube-shaped, and from the earlier discussion, each molecule measures 1 nm on a side (admittedly, the molecular cube shape is a stretch, but the 1-nm size is plausible). This means that the 1-μm cube contains 10^9 molecules, of which $6(10^6)$ are on the surface of the cube. This leaves $10^9 - 6(10^6) = 994(10^6)$ molecules that are internal (beneath the surface). The ratio of internal to surface molecules is 994–to–6 or 165.667–to–1. By comparison, the same ratio for a cube with 1 m on a side is about 10^{27}–to–1. As the size of the cube decreases, the ratio of internal–to–surface molecules continues to get smaller and smaller, until finally, there is a cube that is 1 nm on a side (the size of the molecule itself), and there are no internal molecules.

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[3]There are more than 100 different amino acids that occur naturally, but most of the proteins found in living organisms consist of only 20 of these amino acid types.

What this numerical exercise demonstrates is that as the size of an object decreases, approaching nanometer dimensions, the surface molecules become increasingly important relative to the internal molecules simply because of their increasing numerical proportion. Thus, the surface properties of the materials out of which nanometer-sized objects are made become more influential in determining the behavior of the objects, and the relative influence of the bulk properties of the material is reduced.

Recall from Section 2.2 that there are two types of atomic bonding: (1) primary bonds that are generally associated with combining atoms into molecules and (2) secondary bonds that attract molecules together to form bulk materials. One of the implications of the large surface-to-volume ratio of nanoscale objects is that the secondary bonds that exist between molecules assume greater importance because the shape and properties of an object not much bigger than the molecules comprising it tend to depend on these secondary bonding forces. Accordingly, the material properties and behaviors of nanoscale structures are different from those of structures with dimensions in the macroscale or even microscale. These differences can sometimes be exploited to create materials and products with improved electronic, magnetic, and/or optical properties. Two examples of recently developed materials in this category are (1) carbon nanotubes (Section 36.1.2), and (2) magnetoresistive materials for use in high-density magnetic memories. Nanotechnology will enable the development of entirely new classes of materials.

Another difference that arises between nanoscale objects and their macroscopic counterparts is that material behavior tends to be influenced by quantum mechanics rather than bulk properties. *Quantum mechanics* is a branch of physics that is concerned with the notion that all forms of energy (e.g., electricity, light) occur in discrete units when observed on a small enough scale. The discrete units are called quanta (plural of quantum), which cannot be further subdivided. For example, electricity is conducted in units of electrons. An electrical charge of less than one electron is not possible. In light energy, the quanta are photons. In magnetic energy, they are called magnons. For every type of energy there are comparable units. All physical phenomena exhibit quantum behavior at the submicroscopic level. On a macroscopic level, the energy appears to be continuous because it is being released in very large quantities of quanta.

The movement of electrons in microelectronics is of particular interest because of the significant reductions in size that continue to be achieved in the fabrication of integrated circuits. The feature sizes of the devices in integrated circuits produced in 2009 were on the order of 50 nm. They are projected to decrease in size to about 20 nm by around 2015. At a feature size of around 10 nm, the effects of quantum mechanics become significant, changing the way a device operates. As feature size continues to be reduced toward just a few nanometers, the proportion of surface atoms in the device increases relative to those beneath the surface, which means that the electrical characteristics are no longer determined exclusively by the bulk properties of the material. As device size continues to decrease and density of components on a chip continues to increase, the electronics industry is approaching the limits of technological feasibility of the current fabrication processes described in Chapter 33.

36.2.2 SCANNING PROBE MICROSCOPES

Conventional optical microscopes use visible light focused through optical lenses to provide enlarged images of very small objects. However, the wavelength of visible light is 400–700 nm, which is greater than the dimensions of nanosized objects. Thus,

these objects cannot be seen with conventional optical microscopes. The most powerful optical microscopes provide magnifications of about 1000 times, allowing resolutions of about 0.0002 mm (200 nm). Electron microscopes, which allow specimens to be visualized utilizing a beam of electrons instead of light, were developed in the 1930s. The electron beam can be considered as a form of wave motion, but one that has a much shorter effective wavelength. (Today's electron microscopes permit magnifications of about 1,000,000 times and resolutions of about one nanometer). To obtain an image of a surface, the electron beam is scanned across the surface of an object in a raster pattern, similar to the way that a cathode ray scans the surface of a (tube-type or projection-type) television screen.

For making observations on the nanoscale level, an improvement over the electron microscope is the family of scanning probe instruments that date from the 1980s. They possess magnification capabilities approximately 10 times greater than an electron microscope. In a scanning probe microscope (SPM), the probe consists of a needle with a very sharp tip. The point size approaches the size of a single atom. In operation, the probe is moved along the surface of the specimen at a distance of only one nanometer or so, and any of several properties of the surface are measured, depending on the type of scanning probe device. The two scanning probe microscopes of greatest interest in nanotechnology are the scanning tunneling microscope and the atomic force microscope.

The *scanning tunneling microscope* (STM) was the first scanning probe instrument to be developed. It is called a tunneling microscope because its operation is based on the quantum mechanics phenomenon known as *tunneling*, in which individual electrons in a solid material can jump beyond the surface of the solid into space. The probability of electrons being in this space beyond the surface decreases exponentially in proportion to the distance from the surface. This sensitivity to distance is exploited in the STM by positioning the probe tip very close to the surface (i.e., 1 nm) and applying a small voltage between the two. This causes electrons of surface atoms to be attracted to the small positive charge of the tip, and they tunnel across the gap to the probe. As the probe is moved along the surface, variations in the resulting current occur due to the positions of individual atoms on the surface. Alternatively, if the elevation of the tip above the surface is allowed to float by maintaining a constant current, then the vertical deflection of the tip can be measured as it traverses the surface. These variations in current or deflection can be used to create images or topographical maps of the surface on an atomic or molecular scale.

A limitation of the scanning tunneling microscope is that it can only be used on surfaces of conducting materials. By comparison, the *atomic force microscope* (AFM) can be used on any material; it uses a probe attached to a delicate cantilever that deflects due to the force exerted by the surface on the probe as it traverses the specimen surface. The AFM responds to various types of forces, depending on the application. The forces include mechanical due to physical contact of the probe with the specimen surface, and noncontact, such as van der Waals forces (Section 2.2), capillary forces, magnetic forces,[4] and others. The vertical deflection of the probe is measured optically, based on the interference pattern of a light beam or the reflection of a laser beam from the cantilever. Figure 36.3 shows an image generated by an AFM.

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[4]The term *magnetic force microscope* (MFM) is used when the forces are magnetic. The principle of operation is similar to that of the reading head on a hard disk drive.

FIGURE 36.3 An atomic force microscope image of silicon dioxide letters on a silicon substrate. The oxide lines of the letters are about 20 nm wide. (Image courtesy of IBM Corporation.)

The discussion here has focused on the use of scanning probe microscopes for observing surfaces. Section 36.3.2 describes several applications of these instruments for manipulating individual atoms, molecules, and other nanoscale clusters of atoms or molecules.

36.3 Nanofabrication Processes

Creating products at least some of whose feature sizes are in the nanometer range requires fabrication techniques that are often quite different from those used to process bulk materials and macro-sized products. The fabrication processes for nanometer-scale materials and structures can be divided into two basic categories:

1. *Top-down approaches*, which adapt some of the lithography-based microfabrication techniques discussed in Chapters 33 and 35 to nanoscale object sizes. They involve mostly subtractive processes (material removal) to achieve the desired geometry.

2. *Bottom-up approaches*, in which atoms and molecules are manipulated and combined into larger structures. These might be described as additive processes because they construct the nanoscale entity from smaller components.

The organization in this section is based on these two approaches. Because the processing methods associated with the top-down approaches are discussed in two previous chapters, the coverage in Section 36.3.1 emphasizes how these processes must be modified for the nanoscale. Section 36.3.2 discusses the bottom-up approaches, which may be of greater interest because of their special relevance to nanotechnology.

36.3.1 TOP-DOWN PROCESSING APPROACHES

The top-down approaches for fabricating nanoscale objects involve the processing of bulk materials (e.g., silicon wafers) and thin films using lithographic techniques like those used in the processing of integrated circuits and microsystems.

The top-down approaches also include other precision machining techniques (Section 35.2.3) that have been adapted for making nanostructures. The term *nanomachining* is used for these processes that involve material removal when applied in the sub-micron scale. Nanostructures have been machined out of materials such as silicon, silicon carbide, diamond, and silicon nitride [24]. Nanomachining must often be coupled with thin-film deposition processes such as physical vapor deposition and chemical vapor deposition (Section 27.5) to achieve the desired structure and combination of materials.

As the feature sizes of the components in an integrated circuit (IC) become smaller and smaller, fabrication techniques based on optical lithography become limited because of the wavelengths of visible light. Ultraviolet light is currently used to fabricate ICs because its shorter wavelengths permit smaller features to be fabricated, thus allowing higher densities of components in the IC. The current technology being refined for IC fabrication is called extreme ultraviolet (EUV) lithography (Section 33.3.2). It uses UV light with a wavelength as short as 13 nm, which is certainly within the nanotechnology range. However, certain technical problems must be addressed when EUV lithography is used at these very short UV wavelengths. The problems include (1) new photoresists that are sensitive to this wavelength must be used, (2) focusing systems must be based on all reflective optics, and (3) plasma sources based on laser irradiation of the element xenon [15] must be used.

Other lithography techniques are available for use in fabricating nanoscale structures. These include electron-beam lithography, X-ray lithography, and micro- or nano-imprint lithography. Electron-beam and X-ray lithography are discussed in the context of integrated circuit processing (Section 33.3.2). *Electron-beam lithography* (EBL) operates by directing a highly focused beam of electrons along the desired pattern across the surface of a material, thus exposing the surface areas using a sequential process without the need for a mask. Although EBL is capable of resolutions on the order of 10 nm, its sequential operation makes it relatively slow compared to masking techniques and thus unsuited to mass production. *X-ray lithography* can produce patterns with resolutions around 20 nm, and it uses masking techniques, which makes high production possible. However, X-rays are difficult to focus and require contact or proximity printing (Section 33.3.1). In addition, the equipment is expensive for production applications, and X-rays are hazardous to humans.

Two of the processes known as soft lithography are described in Section 35.2.3. The processes are *micro-imprint lithography*, in which a patterned flat mold (similar to a rubber stamp) is used to mechanically deform a thermoplastic resist on the surface of a substrate in preparation for etching, and *micro-contact printing*, in which the stamp is dipped into a substance and then pressed against a substrate. This transfers a very thin layer of the substance onto the substrate surface in the pattern defined by the stamp. These same processes can be applied to nanofabrication, in which case they are called *nano-imprint lithography* and *nano-contact printing*. Nano-imprint lithography can produce pattern resolutions of approximately 5 nm [24]. One of the original applications of nano-contact printing was to transfer a thin film of thiols (a family of organic compounds derived from hydrogen sulfide) onto a gold surface. The uniqueness of the application was that the film was only one molecule thick (called a monolayer, Section 36.3.2), which certainly qualifies as nanoscale.

36.3.2   BOTTOM-UP PROCESSING APPROACHES

In the bottom-up approaches, the starting materials are atoms, molecules, and ions. The processes bring these basic building blocks together, in some cases one at a time, to fabricate the desired nanoscale entity. The coverage consists of four approaches that are of considerable interest in nanotechnology: (1) production of fullerenes, (2) production of carbon nanotubes, (3) nanofabrication by scanning probe techniques, and (4) self-assembly.

Production of Fullerenes   The starting material for the manufacture of fullerenes is carbon black produced from an electric arc between two graphite electrodes. The resulting product contains 20% or less carbon fullerenes mixed in with other forms of carbon and hydrocarbons. Around 75% of the fullerene content is C_{60} with the rest being fullerenes of higher molecular weight. The problem is to separate the C_{60} and other fullerenes from the mixture. It turns out that fullerenes are soluble in certain organic solvents whereas the other carbon products are not. Thus, the entire output is subjected to the solvent process and the insoluble carbon solids are filtered out, leaving the fullerenes in solution. These are classified into different sizes using a chromatographic technique that distinguishes among molecules by their molecular weight.

Production of Carbon Nanotubes   The remarkable properties and potential applications of carbon nanotubes are discussed in Section 36.1.2. Carbon nanotubes can be produced by several techniques. In the following paragraphs three are discussed: (1) laser evaporation, (2) carbon arc techniques, and (3) chemical vapor deposition.

In the *laser evaporation method*, the starting raw material is a graphite workpiece containing small amounts of cobalt and nickel. These metal traces perform the role of catalyst, acting as nucleation sites for the subsequent formation of the nanotubes. The graphite is placed in a quartz tube filled with argon gas and heated to 1200°C (2200°F). A pulsed laser beam is focused on the workpiece, causing the carbon atoms to evaporate from the bulk graphite. The argon moves the carbon atoms out of the high-temperature region of the tube and into an area in which a water-cooled copper apparatus is located. The carbon atoms condense on the cold copper, and as they do, they form nanotubes with diameters of 10 to 20 nm and lengths of about 100 μm.

The *carbon arc technique* uses two carbon electrodes that are 5 to 20 μm in diameter and separated by 1 mm. The electrodes are located in a partially evacuated container (about 2/3 of 1 atmospheric pressure) with helium flowing in it. To start the process, a voltage of about 25 V is applied across the two electrodes, causing carbon atoms to be ejected from the positive electrode and carried to the negative electrode where they form nanotubes. The structure of the nanotubes depends on whether a catalyst is used. If no catalyst is used, then multiwalled nanotubes are produced. If trace amounts of cobalt, iron, or nickel are placed in the interior of the positive electrode, then the process creates single-walled nanotubes that are 1 to 5 nm in diameter and about 1 μm long.

Chemical vapor deposition (Section 27.5.2) can be used to produce carbon nanotubes. In one variation of CVD, the starting work material is a hydrocarbon gas such as methane (CH_4). The gas is heated to 1100°C (2000°F), causing it to decompose and release carbon atoms. The atoms then condense on a cool substrate to form nanotubes with open ends rather than the closed ends characteristic of the other

FIGURE 36.4 Manipulation of individual atoms by means of scanning tunneling microscopy techniques: (a) Probe tip is maintained a distance from the surface that is sufficient to avoid disturbance of adsorbed atom and (b) probe tip is moved closer to the surface so that the adsorbed atom is attracted to the tip.
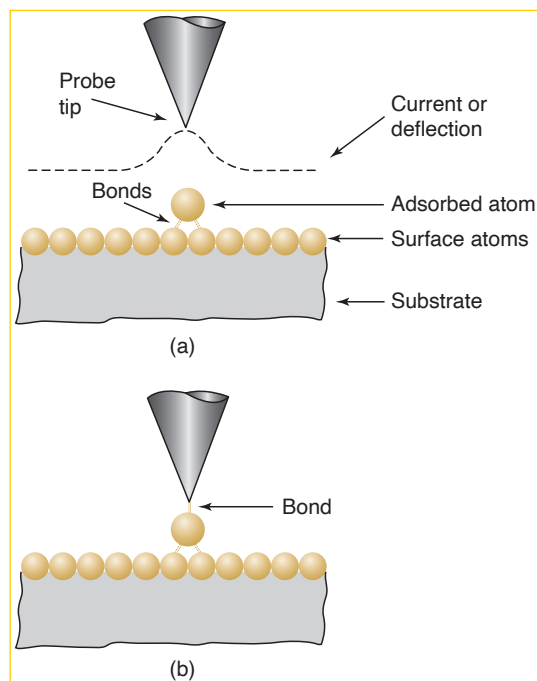
fabrication techniques. The substrate may contain iron or other metals that act as catalysts for the process. The metal catalyst acts as a nucleation site for creation of the nanotube, and it also controls the orientation of the structure. An alternative CVD process called HiPCO[5] starts with carbon monoxide (CO) and uses carbon pentacarbonyl $(Fe(CO)_5)$ as the catalyst to produce high-purity, single-walled nanotubes at 900 to 1100°C (1700–2000°F) and 30 to 50 atm [8]. Production of nanotubes by CVD has the advantage that it can be operated continuously, which makes it economically attractive for mass production.

Nanofabrication by Scanning Probe Techniques Scanning probe microscopy (SPM) techniques are described in Section 36.2.2 in the context of measuring and observing nanometer-scale features and objects. In addition to viewing a surface, the scanning tunneling microscope (STM) and atomic force microscope (AFM) can also be used to manipulate individual atoms, molecules, or clusters of atoms or molecules that adhere to a substrate surface by the forces of adsorption (weak chemical bonds). Clusters of atoms or molecules are called *nanoclusters*, and their size is just a few nanometers. Figure 36.4(a) illustrates the variation in either current or deflection of the STM probe tip as it is moved across a surface upon which is located an adsorbed atom. As the tip moves over the surface immediately above the adsorbed atom, there is an increase in the signal. Although the bonding force that attracts the atom to the surface is weak, it is significantly greater than the force of attraction created by the tip, simply because the distance is greater. However, if the probe tip is moved close enough to the adsorbed atom so that its force of attraction is greater than the adsorption force, the atom will be dragged along the surface, as suggested in Figure 36.4(b). In this way, individual atoms or molecules

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[5]HiPCO stands for high-pressure carbon monoxide decomposition process.

can be manipulated to create various nanoscale structures. A notable STM example accomplished at the IBM Research Labs was the fabrication of the company logo out of xenon atoms adsorbed onto a nickel surface in an area 5 nm by 16 nm. This scale is considerably smaller than the lettering in Figure 36.3 (which is also nanoscale, as noted in the caption).

The manipulation of individual atoms or molecules by scanning tunneling microscopy techniques can be classified as lateral manipulation and vertical manipulation. In lateral manipulation, atoms or molecules are transferred horizontally along the surface by the attractive or repulsive forces exerted by the STM tip, as in Figure 36.4(b). In vertical manipulation, the atoms or molecules are lifted from the surface and deposited at a different location to form a structure. Although this kind of STM manipulation of atoms and molecules is of scientific interest, there are technological limitations that inhibit its commercial application, at least in high production of nanotech products. One of the limitations is that it must be carried out in a very high vacuum environment to prevent stray atoms or molecules from interfering with the process. Another limitation is that the surface of the substrate must be cooled to temperatures approaching absolute zero ($-273°C$ or $-460°F$) to reduce thermal diffusion that would gradually distort the atomic structure being formed. These limitations make it a very slow and expensive process.

The atomic force microscope is also used for similar nanoscale manipulations. In comparing the AFM and STM applications, the AFM is more versatile because it is not restricted to conductive surfaces as is the STM and it can be used under normal room conditions. On the other hand, the AFM has a lower resolution than the STM. Consequently, the STM can be used to manipulate single atoms, while the AFM is better suited to the manipulation of larger molecules and nanoclusters [24].

Another scanning probe technique, one that shows promise for practical applications, is called dip-pen nanolithography. In ***dip-pen nanolithography*** (DPN), the tip of an atomic force microscope is used to transfer molecules to a substrate surface by means of a solvent meniscus, as shown in Figure 36.5. The process is somewhat analogous to using an old-fashioned quill pen to transfer ink to a paper surface via capillary forces. In DPN, the AFM tip serves as the nib of the pen, and the substrate becomes the surface onto which the dissolved molecules (i.e., the ink) are deposited. The deposited molecules must have a chemical affinity for the substrate material, just as wet ink adheres to paper. DPN can be used to "write" patterns of molecules onto a surface, in which the patterns are of submicron dimension. Line widths as small as 10 to 15 nm are reported [27]. In addition, DPN can be used to deposit different types of molecules at different locations on the substrate surface.

FIGURE 36.5 Dip-pen nanolithography, in which the tip of an atomic force microscope is used to deposit molecules through the water meniscus that forms naturally between the tip and the substrate.
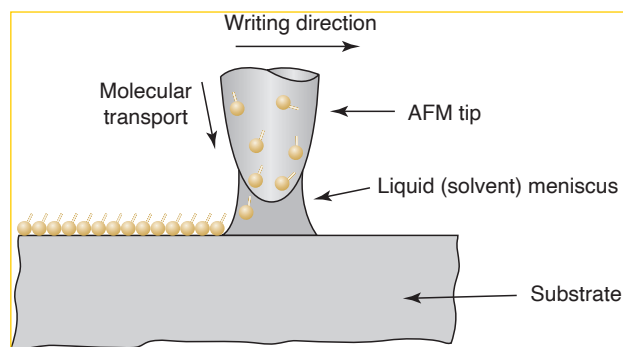
Self-Assembly   Self-assembly is a fundamental process in nature. The natural formation of a crystalline structure during the slow cooling of molten minerals is an example of nonliving self-assembly. The growth of living organisms is an example of biological self-assembly. In both instances, entities at the atomic and molecular level combine on their own into larger entities, proceeding in a constructive manner toward the creation of some deliberate thing. If the thing is a living organism, the intermediate entities are biological cells, and the organism is grown through an additive process that exhibits massive replication of individual cell formations, yet the final result is often remarkably intricate and complex (e.g., a human being).

One of the promising bottom-up approaches in nanotechnology involves the emulation of nature's self-assembly process to produce materials and systems that have nanometer-scale features or building blocks, but the final product may be larger than nanoscale. It may be of micro- or macro-scale size, at least in some of its dimensions. The term *biomimetics* describes this process of building artificial, nonbiological entities by imitating nature's methods. Desirable attributes of atomic or molecular self-assembly processes in nanotechnology include the following: (1) they can be carried out rapidly; (2) they occur automatically and do not require any central control; (3) they exhibit massive replication; and (4) they can be performed under mild environmental conditions (at or near atmospheric pressure and room temperature). Self-assembly is likely to be the most important of the nanofabrication processes because of its low cost, its capacity for producing structures over a range of sizes (from nanoscale to macroscale), and its general applicability to a wide variety of products [19].

An underlying principle behind self-assembly is the principle of minimum energy. Physical entities such as atoms and molecules seek out a state that minimizes the total energy of the system of which they are components. This principle has the following implications for self-assembly:

1. There must be some mechanism for the movement of the entities (e.g., atoms, molecules, ions) in the system, thus causing the entities to come into close proximity with one another. Possible mechanisms for this movement include diffusion, convection in a fluid, and electric fields.

2. There must be some form of molecular recognition among the entities. Molecular recognition refers to the tendency of one molecule (or atom or ion) to be attracted to and bind with another molecule (or atom or ion), for example, the way sodium and chlorine are attracted to each other to form table salt.

3. The molecular recognition among the entities causes them to join in such a way that the resulting physical arrangement of the entities achieves a state of minimum energy. The joining process involves chemical bonding, usually the weaker secondary types (e.g., van der Waals bonds).

At least two instances of molecular-level self-assembly have previously been encountered in this book: (1) crystal formation and (2) polymerization. Crystal formation in metals, ceramics, and certain polymers is a form of self-assembly. Growing silicon boules in the Czochralski process (Section 33.2.2) for fabrication of integrated circuits is a good illustration. Using a starting seed crystal, very pure molten silicon is formed into a large cylindrical solid whose repeating lattice structure matches that of the seed throughout its volume. The lattice spacing in the crystal structure is of nanometer proportions, but the replication exhibits long-range order.

It can be argued that polymers are products of nanometer-scale self-assembly. The process of polymerization (Section 8.1.1) involves the joining of individual monomers (individual molecules such as ethylene C_2H_4) to form very large molecules (macro-molecules such as polyethylene), often in the form of a long chain with thousands of repeating units. Copolymers (Section 8.1.2) represent a more complex self-assembly process, in which two different types of starting monomers are joined in a regular repeating structure. An example is the copolymer synthesized from ethylene and propylene (C_3H_6). In these polymer examples, the repeating units are of nanometer size, and they form by a massive self-assembly process into bulk materials that have significant commercial value.

The technologies for producing silicon boules and polymers precede the current scientific interest in nanotechnology. Of greater relevance in this chapter are self-assembly fabrication techniques that have been developed under the nanotechnology banner. These self-assembly processes, most of which are still in the research stage, include the following categories: (1) fabrication of nanoscale objects, including molecules, macromolecules, clusters of molecules, nanotubes, and crystals; and (2) formation of two-dimensional arrays such as self-assembled monolayers (surface films that are one molecule thick) and three-dimensional networks of molecules.

Some of the processes in category 1 have already been discussed (e.g., fullerenes and nanotubes). The self-assembly of surface films is an important example of category 2. Surface films are two-dimensional coatings formed on a solid (three-dimensional) substrate. Most surface films are inherently thin, yet the thickness is typically measured in micrometers or even millimeters (or fractions thereof), well above the nanometer scale. Of interest here are surface films whose thicknesses are measured in nanometers. Of particular interest in nanotechnology are surface films that self-assemble, are only one molecule thick, and where the molecules are organized in some orderly fashion. These types of films are called self-assembled monolayers (SAMs). Multilayered structures are also possible that possess order and are two or more molecules thick.

The substrate materials for self-assembled monolayers and multilayers include a variety of metallic and other inorganic materials. The list includes gold, silver, copper, silicon, and silicon dioxide. Noble metals have the advantage of not forming an oxide surface film that would interfere with the reactions that generate the desired layer of interest. Layering materials include thiols, sulfides, and disulfides. The layering material must be capable of being adsorbed onto the surface material. The typical process sequence in the formation of the monolayer of a thiol on gold is illustrated in Figure 36.6.[6] Layering molecules move freely above the substrate surface and are adsorbed onto the surface. Contact occurs between adsorbed molecules on the surface, and they form stable islands. The islands become larger and gradually join together through the addition of more molecules laterally on the surface, until the substrate is completely covered. Bonding to the gold surface is provided by the sulfur atom in the thiol, sulfide, or disulfide layer. In some applications, self-assembled monolayers can be formed into desired patterns or regions on the substrate surface using techniques such as nano-contact printing and dip-pen nanolithography.

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[6]This combination of thiol on a gold surface was mentioned in Section 36.3.1 in the context of nano-contact printing.