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NANOMATERIALS

Background

It is important to separate fact from fiction when it comes to nanotechnology. According to the popular media, nanotechnology will soon deliver everything from genetic engineering to injectable “nanobots,” inserted into the body to repair diseased or damaged tissue. And what if these nanobots become self-replicating and even sentient—the stuff of science fiction? We find out later in this chapter why such nanobots are highly unlikely.

The reality of nanotechnology is far less “fantastic.” There are many examples of ways nanomaterials are being used to advantage in products that affect our lives. For example, tennis racquets are being made with carbon nanotubes to improve their mechanical properties. Stain-repellent fabrics are being made with hydrophobic (water-repelling) nanoparticles, making use of their unique chemical properties. And skin creams are being produced with ultraviolet-absorbing nanoparticles for UV-protection, taking advantage of their unique optical properties. New applications are emerging on a regular basis.

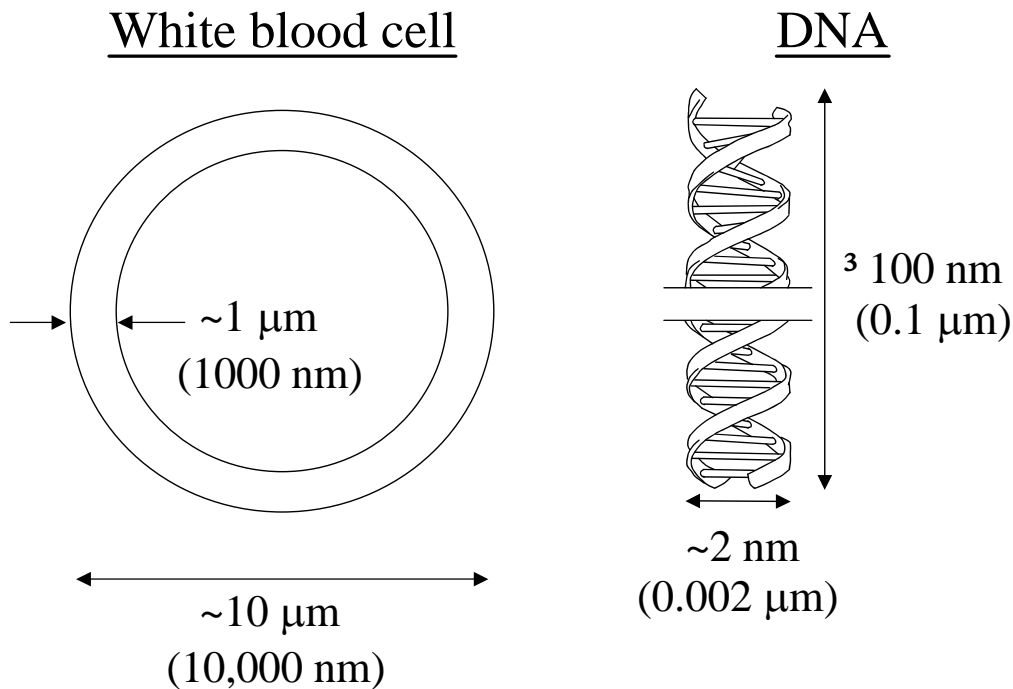
But the real potential for nanomaterials is still on the horizon. As early as 1959, in a now famous lecture entitled, “There’s Plenty of Room at the Bottom,” Nobel laureate Richard Feynman envisaged being able to write the 24 volumes of Encyclopaedia Britannica on the head of a pin. This would require patterning on the scale of tens of nanometers. Such “nano-writing” is now possible, as we will see. Actually, we store

larger amounts of information on pin head-sized spaces in the current generation integrated circuits or “chips.” But the reign of “Moore’s Law,” where the memory capacity of IC chips has doubled approximately every 18 months since 1970, may soon come to an end. In this chapter and the case study to follow, we’ll find out why and how further miniaturization of electronic devices will require the development of reliable “nanoelectronics.”

How Small is a Nanometer?

In the 1966 movie, “Fantastic Voyage,” a medical team was miniaturized and injected into the body of an ailing scientist to repair damaged tissue. Let’s follow the lead of “Fantastic Voyage” and take a journey into a human hand. If you look at the palm of your hand, it is something like 10 centimeters across. The lines in my palm are spaced approximately 1 centimeter apart. Under a microscope, you would see skin cracks spaced on the order of 1 millimeter apart, and approximately one-tenth of a millimeter wide. This is about the thickness of human hair (50-100 micrometers, or 0.05-0.1 millimeter). But we have a long way to go, size-wise, to reach nanometer scale.

Again under the microscope, the diameter of a white blood cell is approximately 10 micrometers, and its cell membrane is around 1 micrometer thick, as illustrated below. To “see” any smaller, we need to use electron microscopes instead of light microscopes. Also shown in the following illustration, DNA strands are at least 0.1 micrometers long (or 100 nanometers) and can be much longer. The famous double helix is on the order of 2 nanometers wide. At the finest scale there are individual atoms in DNA molecules. These are typically one-tenth of a nanometer in size.



The dimensions of a white blood cell and strand of DNA demonstrate the relative size of a nanometer.

So a nanometer-sized object is quite small. For the purpose of comparison, if we enlarged it to the size of a penny held in your palm, a foot would be large enough to extend from Miami to Seattle!

Everything Is Different at the Bottom!

Until now, the properties of the materials considered have not been size- or shape-dependent. For example, the properties of a cube of gold are the same whether it is a meter on a side or a micrometer on a side—the gold will have the same color and the same electrical conductivity. Furthermore, both cubes of gold will melt at the same temperature—you can look this up in a handbook as 1064°C . And it doesn't matter

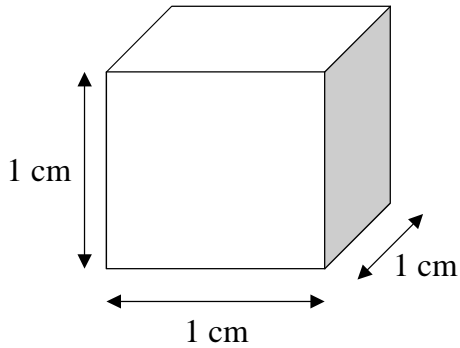
whether the gold is in the shape of a cube or a sphere, or some other shape. Properties are shape-independent.

Everything changes, however, in the nanorealm! For example, small nanoparticles of gold can melt as low as 300°C. And the color of gold changes from opaque yellow in micrometer or larger crystals, to transparent blue or crimson in the 30-500 nm range, to transparent red in the 3-30 nanometer range. Below 3 nanometers, gold appears transparent orange in color, and these particles are no longer metallic! But there is more to the strange behavior in the nanorealm. 100 nanometer silver spheres are pale blue in color, whereas triangular prisms of silver the same size are crimson. So the optical properties change with shape as well as size. Incidentally, one of the earliest uses of nanoparticles was in stained glass. Gold nanoparticles impart a rich crimson color to glass, whereas silver nanoparticles give a bright yellow color. Of course, medieval artisans did not know they were forming nanoparticles when they added gold or silver to their glasses.

Why do properties change so dramatically with size in the nanometer range? One reason has to do with something called the surface-to-volume ratio. Consider a cube of gold one centimeter on a side. There are approximately 10^{23} atoms per cubic centimeter in gold. (You may recall Avogadro's number, or 6.02×10^{23} atoms per mole. There is something like a tenth of a mole of atoms in a cubic centimeter of gold.) But how many atoms are on the surface of our cube? A shortcut is to take the two-thirds power of the number of atoms per cm^3 or approximately 10^{15} per cubic centimeter. Since there are six faces of area 1 cm^2 (1 cm by 1 cm), we have something like 6×10^{15} atoms on the surface. This gives a surface-to-volume ratio of 6×10^{15} divided by 10^{23} , or 6×10^{-8} . In

other words, only six atoms out of every 100 million atoms are on the surface. The surface will have very little influence on the properties.

Bulk Cube



Volume atoms:

$$\frac{10^{23} \text{ atoms}}{\text{cm}^3} \times (1 \text{ cm})^3 \sim 10^{23} \text{ atoms}$$

Surface atoms per area:

$$\sim \left[\frac{(10^{23} \text{ atoms})}{\text{cm}^3} \right]^{2/3} \sim \frac{10^{15}}{\text{cm}^2}$$

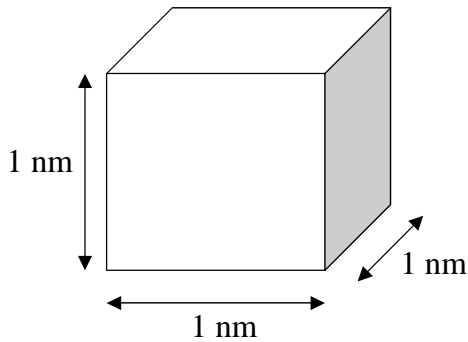
Surface atoms:

$$\frac{10^{15} \text{ atoms}}{\text{cm}^2} \times 6 \times (1 \text{ cm})^2 \sim 6 \times 10^{15} \text{ atoms}$$

$$\text{S/V ratio of atoms} \sim 6 \times 10^{-8}$$

On the other hand, consider a cube 1 nanometer on a side. A nanometer is 10^{-7} of a centimeter, so our nanocube is 10^{-21} cubic centimeters in volume. Multiplying this value by 10^{23} atoms per cubic centimeter gives us 100 atoms in this small cube. How many atoms are on the surface? Each face will be 10^{-14} cm^2 (10^{-7} cm squared) and there are 6 faces. Using the 10^{15} atom per cm^2 figure (above) we arrive at approximately 60 atoms. Now 60 of the atoms are on the surface, or 60% of the atoms in our nanocube!

Nano Cube



Volume atoms:

$$\frac{10^{23} \text{ atoms}}{\text{cm}^3} \times (10^{-7} \text{ cm})^3 \sim 100 \text{ atoms}$$

Surface atoms per area:

$$\sim \left[\frac{(10^{23} \text{ atoms})}{\text{cm}^3} \right]^{2/3} \sim \frac{10^{15}}{\text{cm}^2}$$

Surface atoms:

$$\frac{10^{15} \text{ atoms}}{\text{cm}^2} \times 6 \times (10^{-7} \text{ cm})^2 \sim 60 \text{ atoms}$$

S/V ratio of atoms ~ 0.6

This proves that nanocrystals have much higher surface-to-volume ratios than larger crystals, but they also have much higher energies. This has to do with bonding. In the interior of a crystal, atoms are bonded to other atoms in all directions, but on the surface the bonds facing outward are “unsatisfied,” meaning that they don’t have other atoms to bond to. As a result, surfaces have higher energies. So do nanoparticles, which are almost “all surface,” so to speak. This explains why nanocrystals melt at temperatures far lower than their bulk melting points. Nanocrystals are also much more reactive, which is used to advantage in chemical catalysis. For example, large gold crystals are chemically inert, whereas nanocrystalline gold particles are capable of catalyzing (promoting, speeding up) many chemical reactions.

Surface forces also increase as size decreases into the nanometer range. One such force is adhesion, which describes the “stickiness” of a surface. With so many

unsatisfied bonds, nanoparticles tend to be very “sticky.” Another surface property is surface “tension,” which describes the tendency of water to form beads (to minimize its surface energy by decreasing its surface area) or to rise against gravity in a small diameter “capillary” tube. Such forces are referred to as “capillary” forces, and can be quite strong at the nanoscale. For example, an insect like an ant can pick up objects several times its mass, but cannot escape from a drop of water. The capillary forces are just too strong. Now we know why functioning nanobots for the human body are highly unlikely. Surface forces such as adhesion and capillary action are just too strong at the nanoscale. A nanotool like a tweezers might be made to close on a nano-object, but getting it to open again might be difficult or even impossible. A more recent Nobel laureate, Richard E. Smalley, concluded, “Such a nanobot will never become more than a futurist’s dream.” (Scientific American, Sept., 2001, pp. 76-77)

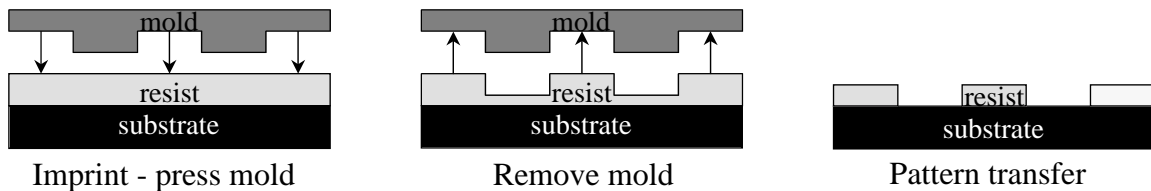
How Do You Make Nanoscale Materials?

As with all materials, there are two approaches—so-called “top-down” approaches and “bottom-up” approaches. In top-down approaches we remove material much like a sculptor chisels material away from a block of marble to produce his sculpture. Bottom-up approaches are more like working with Legos® to build up a comparable sculpture.

As described in the Semiconductor Device chapter, photolithography is a means of top-down patterning. A light-sensitive polymer or photoresist is coated on the surface of silicon and then exposed to light through a “mask.” These regions of the photoresist can then be etched away, exposing the underlying semiconductor surface for further

treatments such n-type or p-type doping in selected areas by ion implantation. The problem with light is that its wavelength is on the order of 0.5 micrometers. (Visible light is 0.4 to 0.7 microns, or 400 to 700 nanometers.) Of course, ultraviolet light can be used, but the “minimum feature size” will still be limited to on the order of 0.1 micrometer (100 nm). How can we make smaller features?

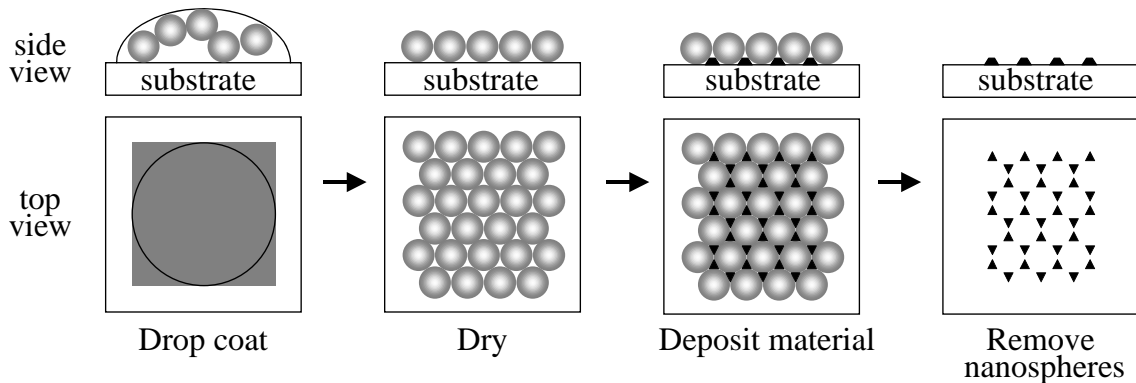
Two “top-down” methods are nano-imprint lithography and nanosphere lithography. In nano-imprint lithography, a special mold is made with features as small as 40 nm. One way to “carve” such a mold is with a carefully guided electron beam. Think of this mold as being like a stamp from a child’s stamp set. As shown in the diagram below, this mold can be pressed against photoresist layers on a suitably prepared surface to emboss or “punch out” resist-free areas for subsequent lithography, just as in conventional photolithography. The mold can be moved from spot to spot to build up a much larger pattern, just as with a stamp in a stamp set.



Nano-imprint lithography uses a mold that can be “stamped” across a photoresist. To complete pattern transfer, the remaining resist is etched away with a beam of reactive ions.

Nanosphere lithography takes advantage of the ability to produce small spheres of various materials in the 100 nanometer range, and to make them of identical size. These can then be deposited on surfaces in close-packed layers, not unlike the close-packed planes in CCP and HCP crystal structures. But the spheres are only temporary. They serve as a template through which the real “nano” material gets deposited from above. The key here is that the interstice size (the holes between the spheres) is much smaller

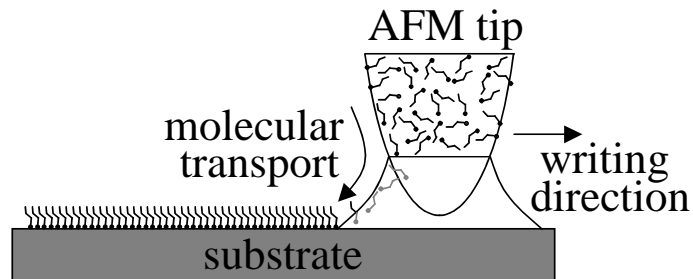
than the spheres themselves. Once a small quantity of material is deposited in the interstices, the spheres are dissolved away, leaving the interstice pattern behind. The diagram below illustrates the process. With 100 nanometer spheres, it is possible to get nano-dots in the 10 nanometer range.



Nanosphere lithography uses the interstices between close-packed nanospheres to deposit material. The nanospheres can be dissolved away or lifted off to produce the desired pattern.

The other way to pattern nanomaterials is from the bottom up, much the way that nature builds materials. The key to many “bottom-up” approaches is molecular self-assembly. This refers to the tendency of molecules to self-assemble into nanometer-scale layers or clusters, largely due to secondary bonds (e.g., hydrogen and van der Waals), which we have discussed previously. Certain techniques make use of delivering “inks” containing such molecules to selected areas of a surface in the desired pattern. One such technique uses a mold, just like in nano-imprint lithography, only this time the mold is “inked” with molecule-containing ink. This is really like the child’s stamp and ink set. As it is pressed against a surface, it leaves behind its pattern of ink marks. The process is referred to as microcontact printing. It is easy to imagine going from a “stamp” to a “paint roller” to accomplish mass fabrication of nanostructured layers.

Another “molecular ink” technique takes advantage of the ability to produce very sharp tips. Such tips are routinely used in the atomic force microscope (see below). An AFM measures attractive or repulsive forces between the tip and the surface of a sample. The tip is located on the end of a leaf spring or cantilever. As the tip is moved back and forth across the surface of a specimen, the cantilever records nano-deflections of the tip (in response to small changes in surface height). These tips can also be used much like quill pen tips in what is called dip-pen nanolithography, which is illustrated below. When dipped in molecule-containing ink and then carefully moved across a surface of a substrate, they can “write” nanofeatures in ink as thin as 50 nanometers.



Dip-pen nanolithography uses a very sharp tip to deposit “molecular ink” onto a substrate. The sharp tip is often used in atomic force microscopy (AFM).

Sufficiently fine lines can now be written to literally fulfill Richard Feynman’s vision of writing the Encyclopaedia Britannica on the head of a pin! In both microcontact printing and dip-pen nanolithography, subsequent processing steps such as heating are required to complete the molecular self-assembly process.

Are still finer features possible? Can we manipulate individual atoms? The scanning tunneling microscope (STM) also makes use of a very sharp tip and highly precise x-y-z positioning of that tip above a surface. It can be brought so close to the surface of a material that quantum mechanical tunneling takes place. You don’t need to

know the complicated physics behind tunneling, but with such tunneling the current becomes very sensitive to distance. In fact, the STM is sensitive to height differences of 0.1 nanometer on the surface of a material. By moving the tip back and forth across a surface, the STM is capable of resolving individual rows of atoms. That's the "microscope" mode, but voltage pulses can also be applied to blast "lines" or groups of atoms off the surface of specially prepared monolayers (single layers). For example, hydrogen monolayers can be laid down on silicon surfaces, and then blasted away in controlled patterns. The unsatisfied bonds along such rows or at such sites are then quite attractive for the selective deposition of yet other molecules. In this way lines or dots of molecules can be deposited in predefined nano-patterns.

What Can You Do with Nanotechnology?

It would be impossible to cover all of the current, emerging and potential applications of nanotechnology. Furthermore, this field is moving so quickly that any specific application might be obsolete by the time you get to read this chapter. But we can at least consider some of the fields in which nanotechnology will have major impact. The following table lists some key areas, including the properties being exploited and some example applications. Some of these have been around for a long time (e.g., catalysis), others are just now emerging (e.g., sensors), and still others have yet to be fully developed (e.g., spintronics).

Examples of Nanotechnology

Area	Properties	Example Applications
Nanochemical	chemically active surfaces	catalysis, propulsion
Nano-optical	color, absorption	UV skin protection, chemical sensors
NEMS	mechanical, electrical	accelerometers, sensors
Nanomagnetism	spin, (GMR) giant magnetoresistance	spintronics, hard disks
Nanoelectronics	tunneling, junctions	nano-transistors, computer processors

It should be stressed that the unique properties of nanomaterials enable each of the current and pending applications. For example, high surface area/reactivity underlies the use of nanoparticles in catalysis, thereby speeding up technologically important chemical reactions. The unusual color vs. size/shape relationships of nanoparticles can be used in chemical sensing. As a chemical species to be sensed interacts with nanoparticles, adsorption on their surfaces and/or aggregation of particles can lead to readily detectable color changes. The field of MEMS or Micro-electro-mechanical systems is the integration of mechanical elements, sensors, actuators and electronics on silicon substrates by microfabrication methods. Similarly, NEMS, or nano-electro-mechanical systems will be the integration of nano-sized elements (sensors, actuators, electronics) via nanofabrication. An example of a NEMS sensor might be a cantilever (a nanoscale “leaf spring”), which can bend as a chemical species to be sensed is adsorbed on it, resulting in a change in electrical signal. Yet another area of interest is nanomagnetism. Scientists are learning how information can be stored in the spins of

electrons (as opposed to its storage as charge) and also how really thin nanolayers can exhibit big changes in resistance with changes in magnetic field, so-called giant magnetoresistance or GMR. This exciting new area is referred to as “spintronics,” i.e., spin-based electronics. The last area of nanoelectronics deals with how we might perpetuate Moore’s law, stuffing more and more transistors into smaller and smaller spaces. This exciting area is more fully addressed in the following case study.