Chapter 1

1- Introduction the Canvas of Nano

Nanoscience and nanotechnology refer to the control and manipulation of matter at nanometer dimensions. This control has made it possible to have life, which is a collection of most efficient nanoscale processes. The best eco-friendly and efficient processes must learn from nature. When we explore life around us, it is found that organization of nanomaterials is central to biology. Architectures made by organisms are all based on nanoassemblies. Today we know that it is possible to use biological processes to make artificial nanostructures. Chemically synthesized nanostructures have been used at various stages of civilization.

Why nanotechnology?

What are the connections between nanotechnology and biology?

What are wet and dry nanotechnologies?

What are the historical landmarks in this area?

What are the historical milestones in the saga of nano?

Many nano forms of matter exist around us. One of the earliest nano-sized objects known to us was made of gold. Faraday prepared colloidal gold in 1856 and called it 'divided metals'. In his diary dated 2 April 1856, Faraday called the particles he made the 'divided state of gold. Metallic gold, when divided into fine particles ranging from sizes of 10–500 nm particles, can be suspended in water. In 1890, the German bacteriologist Robert Koch found that compounds made with gold inhibited the growth of bacteria. He won the Nobel prize for medicine in 1905. The use of gold in medicinal preparations is not new. In the Indian medical system called *Ayurveda,* gold is used in several preparations. One popular preparation is called '*Saraswatharishtam*', prescribed for memory enhancement. Gold is also added in certain medicinal preparations for babies, in order to enhance their mental capability.

All these preparations use finely ground gold. The metal was also used for medical purposes in ancient Egypt. Over 5,000 years ago, the Egyptians used gold in dentistry. In Alexandria, alchemists developed a powerful colloidal elixir known as 'liquid gold', a preparation that was meant to restore youth. The great alchemist and founder of modern medicine, Paracelsus, developed many highly successful treatments from metallic minerals including gold. In China, people cook their rice with a gold coin in order to help replenish gold in their bodies. Colloidal gold has been incorporated in glasses and vases to give them colour. The oldest of these is the fourth Century AD. Lycurgus cup made by the Romans, see Fig. 1.2 (Plate 1). The cup appears red in transmitted light (if a light source is kept within the cup) and appears green in reflected light (if the light source is outside). Modern chemical analysis shows that the glass is not much different from that used today. The compositions are given in Table 1.2.

Table 1.2: *Compositions of Lycurgus cup and modern glass*

Constituent	Lycurgus Cup	Modern Glass
Silicon dioxide	73%	70%
Sodium oxide	14%	15%
Calcium oxide	7%	10%

So what helps to impart colour to the glass? It contains very small amounts of gold (about 40 parts per million) and silver (about 300 parts per million) in the form of nanoparticles.

Nature makes nano objects of varying kind. Magnetite (Fe_3O_4) particles of nanometer size are made by the bacteria, *Magnetosperillum magnetotacticum*. These bacteria make particles of specific morphology. For a bacterium, the magnetism caused by the particles helps in finding a direction favourable for its growth. There are several bacteria like the familiar *Lactobacillus* which can take up metal ions added into buttermilk, and reduce them inside the cell and make nanoparticles. In Fig. 1.3, we see the transmission electron microscopic picture of a single *Lactobacillus* bacterium after incubation with gold ions for several hours. Fungi and

viruses are known to make nanoparticles. However, the science of nanometer scale objects was not discussed until much later. On December 29, 1959, the Nobel prize winning physicist, Richard Feynman gave a talk at the annual meeting of the American Physical Society entitled "There's plenty of room at the bottom'. In this talk, he stated, "The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom." He, in a way, suggested the bottom up approach, "...it is interesting that it would be, in principle, possible (I think) for a physicist to synthesize any chemical substance that the chemist writes down. Give the orders and the physicist synthesizes it. How? Put the atoms down where the chemist says, and so you make the substance. The problems of chemistry and biology can be greatly helpedif our ability to see what we are doing, and to do things on an atomic level, is ultimately developed—a development which I think cannot be avoided.

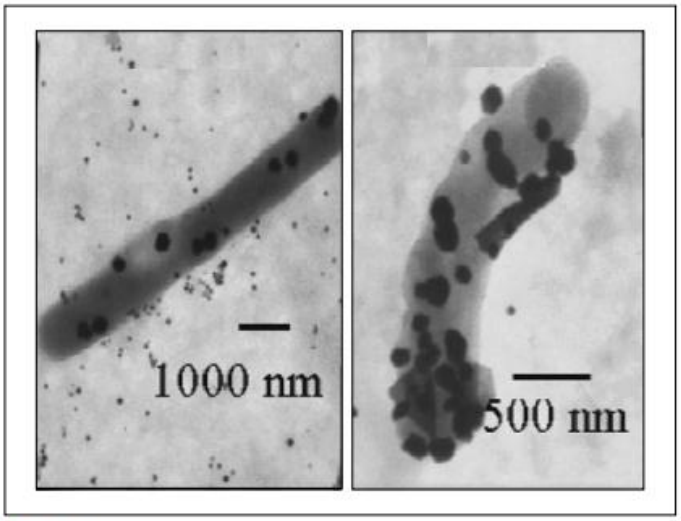


Fig. 1.3: *Gold nanoparticles within the Lactobacillus contour. This transmission electron microscopic image shows large particles of more than 200 nm diameter. However, smaller particles are also made (from the Author's work).*

However, the world had to wait a long time to put down atoms at the required place. In 1981, the scanning tunneling microscope was made and later a number of tools collectively called scanning probe microscopes were developed. The team associated with these developments got the 1986 Nobel prize for physics. The tools they developed can help see and place atoms and

molecules wherever needed. An exhaustive summary of the historical development in the area of nanoscience and technology is listed separately. The current growth of technology suggests that reductions are needed in the dimensions of devices and active materials. This is evident in the case of computer technology. The number of transistors used in an integrated circuit has increased phenomenally in the past 40 years. In 1965, Gordon Moore, the cofounder of Intel, observed that the number of transistors per square inch on integrated circuits doubled every year since the integrated circuit was invented. Moore predicted that this trend would continue in the foreseeable future. In the subsequent years, this pace slowed down, but the data density doubled approximately every 18 months. This is the current definition of Moore's Law. Most experts, including Moore himself, expect Moore's Law to hold for some more time. For this to happen the device dimension must shrink, touching the nanometer regime very soon. The Pentium 4 of 2000 (see Table 1.3), used a 130 nm technology, i.e. the device structure drawn on silicon was as small as this dimension. In 2004, the technology graduated to 90 nm, well into the nanotechnology domain (under 100 nm) and 45 nm technology is being discussed currently.

Table 1.3: *The complexity of integrated circuits as seen in the evolution of Intel microprocessors*

Name	Year	Transistors	Microns	Clock speed
8080	1974	6,000	6	2 MHz
8088	1979	29,000	3	5 MHz
80286	1982	134,000	1.5	6 MHz
80386	1985	275,000	1.5	16 MHz
80486	1989	1,200,000	1	25 MHz
Pentium	1993	3,100,000	0.8	60 MHz
Pentium II	1997	7,500,000	0.35	233 MHz
Pentium III	1999	9,500,000	0.25	450 MHz
Pentium 4	2000	42,000,000	0.18	1.5 GHz
Pentium 4 "Prescott"	2004	125,000,000	0.09	3.6 GHz

2- Ancient Nanotechnology

- Lycurgus Cup

Nanotechnology has been used in sculptures, paintings, and other artifacts since the fourth century AD. For example, the Lycurgus cup is an artifact

containing dichroic glass, which is a material that changes color depending on the nature of light exposure (Horikoshi and Serpone 2013). When light is reflected off the surface of the cup, the cup appears green, however, when light passes through the cup it appears red (Freestone et al. 2007). This unusual optical effect is a direct result of the presence of a small quantity of 70 nm diameter particles of silver and gold in the glass (Horikoshi and Serpone 2013). The gold component is responsible for the red color and the silver component is responsible for the green color .

- Damascus Swords

Damascus swords are ancient artifacts that, according to reports, can cut a piece of silk in half as it falls to the ground. These swords possess high mechanical strength, flexibility, and sharpness. It is claimed that the blades can be bent at angles up to 90 °. To explain the high mechanical properties and flexibility of the swords, a specimen was taken from one of the swords and dissolved in hydrochloric acid. The remnants were examined by highresolution transmission electron microscopy, and the images revealed the presence of carbon nanotubes that were not dissolved by the acid.

- Stained Glass Windows

There is also evidence of nanotechnology in the Middle Ages, particularly in the stained-glass windows used in churches during that time. During the Middle Ages, it was common to use a ruby red color in stained glass windows. Beautiful examples of this application can be seen in the windows of the Cathedral Notre-Dame de Chartres in France (Figure 1.1)

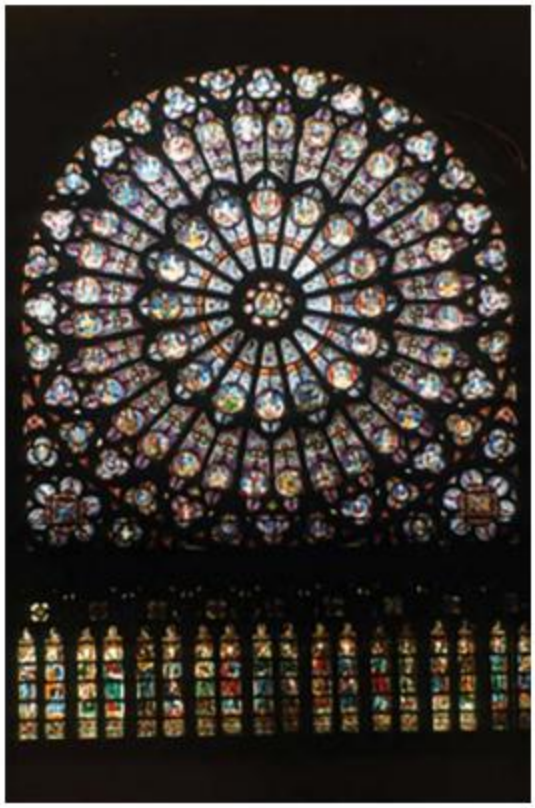


FIGURE 1.1
Notre Dame Cathedral North Rose window. The Rev. Paul Cioffi, S.J. Photographs Collection, Georgetown University.

the colors of the glass; they were simply aware of the color produced by mixing gold chloride into molten glass. This resulted in the creation of tiny gold spheres, which absorbed and reflected sunlight in a way that produced a ruby-red color. The gold nanoparticles were 25 nm in diameter (Chang 2005). When the nanoparticles in stained glass interact with light, certain wavelengths of light are absorbed via a surface plasmon resonance mechanism , while other wavelengths of light are reflected.

3- Early Nanotechnologists

- **Michael Faraday**

In 1857, Michael Faraday reported the production of ruby red mixtures containing gold nanoparticles; he referred to these mixtures as colloidal gold. A colloidal mixture, or colloid, is a mixture of two phases of matter. These mixtures are usually solid particles dispersed in a liquid or gas. The suspended particles can absorb or scatter visible light. When Faraday added

a reducing material to sodium tetrachloroaurate ($NaAuCl_4$), he observed that the yellow color of $NaAuCl_4$ changed over a course of a few minutes to a deep ruby red color. Faraday suggested the ruby-red mixture contained very fine metallic gold not visible with any of the microscopes available during his time. Nearly 100 years later, electron microscopy was used to reveal that ruby-red colloids contain particles of gold with diameters approximately 6 nm in size.

- **Richard Feynman**

Richard Feynman was a Nobel prize-winning physicist who presented a now famous lecture on atom-by-atom assembly. This lecture is often credited with kick-starting nanotechnology (Ball 2009). The lecture Feynman presented to the American Physical Society on December 29th, 1959 was entitled ***"There's plenty of room at the bottom".*** Among the things he discussed, was the possibility of small devices. He states, "I don't know how to do this on a small scale in a practical way, but I do know that computing machines are very large; they fill rooms. Why can't we make them very small, make them of little wires, little elements and by little I mean little. For instance, the wires should be 10 or 100 atoms in diameter, and the circuits should be a few thousand angstroms across. There is plenty of room to make them smaller. There is nothing that I can see in the laws of physics that says the computer elements cannot be made enormously smaller than they are now.". Additionally, in this speech Feynman discussed the amount of space required to store written material on the nanoscale, ***"For each bit I allow 100 atoms. And it turns out that all of the information that man has carefully accumulated in all the books in the world can be written in this form in a cube of material one two-hundredth of an inch wide–which is the barest piece of dust that can be made out by the human eye. So there is plenty of room at the bottom! Don't tell me about microfilm!. Feynman's vision was realized 30 years later.***

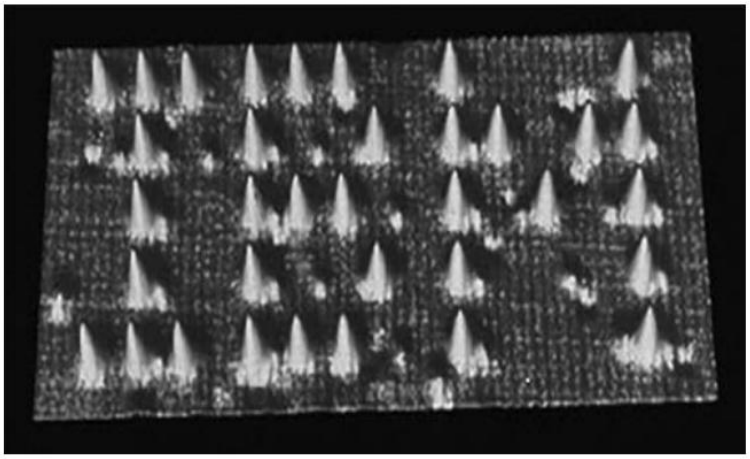
- **Eric Drexler**

A few decades after Richard Feynman's speech regarding atomic-level manipulation, K. Eric Drexler published a book entitled, Engines of Creation

(1986). Drexler described “molecular technology,” which involves creating structures using atoms and molecules. he believed molecular assembly would be driven by ordinary chemical reactions (guided by other nanomachines). In his book, Drexler also predicted biochemists would use protein molecules as motors, bearings, and moving parts to build robot arms capable of handling individual molecules (Drexler 1986). Drexler also suggested that bonded atoms resemble bearings mounted by single chemical bonds allowing atoms to turn freely and smoothly (Drexler 1986).

- **Donald M. Eigler (IBM)**

The predictions of Richard Feynman and K. Eric Drexler regarding atomic and molecular scale manipulation were realized in 1989. In thatyear, Dr. Donald M. Eigler of IBM’s Almaden Research Center in San Jose, California, positioned individual xenon atoms spelling out “IBM” (Figure 1.2).



4 -Nanotechnology in Nature

- Insect Colors

The wings of morpho butterflies contain a combination of multilayer optical gratings and other unique structures (Figure 1.3).

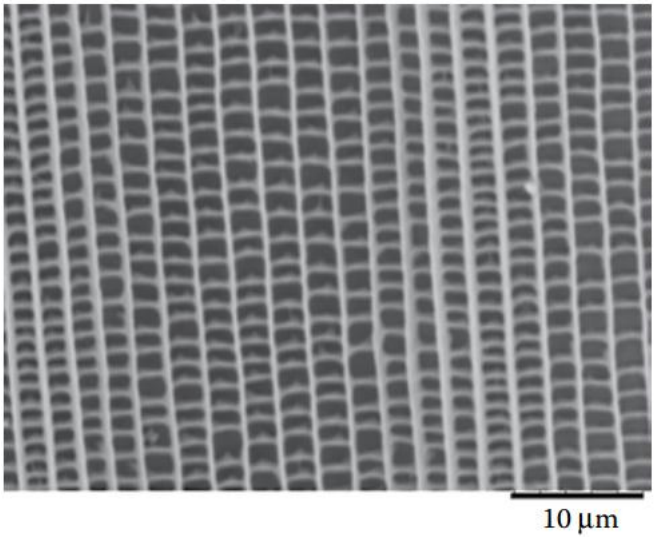


Figure 1.3 Scanning electron microscope image of a butterfly wing.

- Geckos

Geckos can climb and run on wet, dry, smooth, or rough surfaces with extremely high maneuverability and efficiency. Gecko feet (Figure 1.4a and b) contain compliant micro and nanoscale beta-keratin structures, known as foot-hairs, which allow geckos to adhere to any surface.

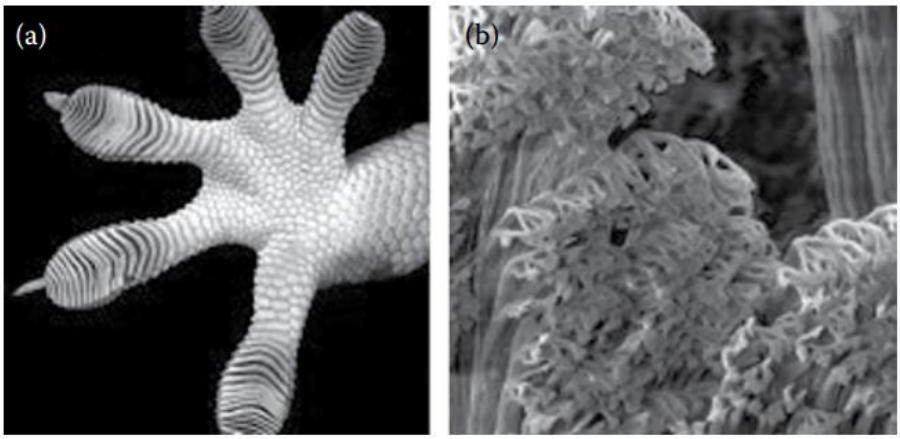
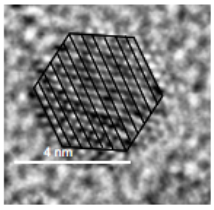


FIGURE 1.4 Gecko foot (a) and microscale foot-hairs (b). Images originally created by Dr. Autumn Kellar.

Chapter 2

Investigating and Manipulating Materials in the Nanoscale



The observation of materials in the nanoscale can be done using electrons, photons, scanning probes, ions, atoms, etc. A wide range of techniques is available in each of these areas and a systematic application of several tools leads to a complete understanding of the system. In addition, in-situ nano measurements become a reality with these tools. The properties of individual nano objects can be studied with precision and some examples of this are illustrated. It is also possible to adapt the techniques mentioned for nanomanipulation, which becomes the basis of nanotechnology.

Learning Objectives

- What are the principal properties used to explore nanomaterials?
- What are the differences between photon, electron, and scanning probe techniques?
- What are the modern advances in these techniques?
- How do we manipulate objects in the nano dimension?

Observation is the key to making new discoveries, and this is especially true in the nanoscale. In fact, as far as nano objects are concerned, one cannot proceed further with the investigations without observing these objects. Observation is done with a probe which may consist of photons, electrons, neutrons, atoms, ions or even an atomically sharp pin. For nanomaterials, the probing light or particle often has varying frequencies, ranging from gamma to infrared rays or beyond in the case of photons or hyper thermal (<100 eV) to relativistic energies in the case of particles. The resulting

information can be processed to yield images or spectra which reveal the topographic, geometric, structural, chemical or physical details of the material. Several techniques are available under the broad umbrella of characterization of materials, which may be used to study nanomaterials in one way or the other. A partial list of these techniques is given in Table 2.1. Some of these techniques may be used in a spatially resolved fashion. In this chapter, we look at some of the more important tools used in the context of nanoscience and technology.

Table 2.1: *Common analytical tools used for characterization of materials*

AES	Aüger Electron Spectroscopy*
AFM	Atomic Force Microscopy*
APECS	Aüger Photoelectron Coincidence Spectroscopy
APFIM	Atom Probe Field Ion Microscopy*
APS	Appearance Potential Spectroscopy
ARPES	Angle Resolved Photoelectron Spectroscopy*
ARUPS	Angle Resolved Ultraviolet Photoelectron Spectroscopy*
ATR	Attenuated Total Reflection
BEEM	Ballistic Electron Emission Microscopy*
BIS	Bremsstrahlung Isochromat Spectroscopy
CFM	Chemical Force Microscopy*
CM	Confocal Microscopy (especially with fluorescence and Raman detection)*
DRIFTS	Diffuse Reflectance Infra-Red Fourier Transform Spectroscopy
EDX	Energy Dispersive X-ray Analysis
EELS	Electron Energy Loss Spectroscopy*
	Ellipsometry, see RDS
EMS	Electron Momentum Spectroscopy
EPMA	Electron Probe Micro-analysis*
ESCA	Electron Spectroscopy for Chemical Analysis, also XPS (X-ray photoemission spectroscopy)*
ESD	Electron Stimulated Desorption
ESDIAD	Electron Stimulated Desorption Ion Angle Distributions
EXAFS	Extended X-ray Absorption Fine Structure
FEM	Field Emission Microscopy*
FIM	Field Ion Microscopy*
FRET	Fluorescence Resonance Energy Transfer*
FTIR	Fourier Transform Infra-red Spectroscopy*
FT RA-IR	Fourier Transform Reflectance-Absorption Infra-red

Contd.

Table 2.1 Contd.

HAS	Helium Atom Scattering
HEIS	High Energy Ion Scattering
HREELS	High Resolution Electron Energy Loss Spectroscopy
IETS	Inelastic Electron Tunneling Spectroscopy
KRIPES	k-Resolved Inverse Photoemission Spectroscopy
ILS	Ionization Loss Spectroscopy
INS	Ion Neutralization Spectroscopy
IPES	Inverse Photoemission Spectroscopy
IRAS	Infra-red Absorption Spectroscopy
ISS	Ion Scattering Spectroscopy
LEED	Low Energy Electron Diffraction*
LEEM	Low Energy Electron Microscopy*
LEIS	Low Energy Ion Scattering
LFM	Lateral Force Microscopy*
MBS	Molecular Beam Scattering
MCXD	Magnetic Circular X-ray Dichroism
MEIS	Medium Energy Ion Scattering
MFM	Magnetic Force Microscopy*
MIES	Metastable Impact Electron Spectroscopy
MIR	Multiple Internal Reflection
NEXAFS	Near-Edge X-ray Absorption Fine Structure
NSOM	Near Field Scanning Optical Microscopy*
PAES	Positron Annihilation Aüger Electron Spectroscopy
PEEM	Photoemission Electron Microscopy*
PED	Photoelectron Diffraction
PIXE	Proton Induced X-ray Emission
PSD	Photon Stimulated Desorption
RAIRS	Reflection Absorption Infra-red Spectroscopy
RAS	Reflectance Anisotropy Spectroscopy
RBS	Rutherford Back Scattering
RDS	Reflectance Difference Spectroscopy

Contd.

Table 2.1 Contd.

REFLEXAFS	Reflection Extended X-ray Absorption Fine Structure
RHEED	Reflection High Energy Electron Diffraction*
RIfS	Reflectometric Interference Spectroscopy
SAM	Scanning Aüger Microscopy* also Scanning Acoustical Microscope*
SCM	Scanning Confocal Microscope* also CM
SEM	Scanning Electron Microscopy*
SEMPA	Scanning Electron Microscopy with Polarization Analysis*
SERS	Surface Enhanced Raman Scattering*
SEXAFS	Surface Extended X-ray Absorption Spectroscopy
SFS	Sum Frequency Spectroscopy
SHG	Second Harmonic Generation
SH-MOKE	Second Harmonic Magneto-optic Kerr Effect
SIM	Scanning Ion Microscope*
SIMS	Secondary Ion Mass Spectrometry*
SKS	Scanning Kinetic Spectroscopy
SLM	Scanning Light Microscope*
SMOKE	Surface Magneto-optic Kerr Effect
SNMS	Sputtered Neutral Mass Spectrometry
SNOM	Scanning Near Field Optical Microscopy*
SPIPES	Spin Polarized Inverse Photoemission Spectroscopy*
SPEELS	Spin Polarized Electron Energy Loss Spectroscopy
SPLEED	Spin Polarized Low Energy Electron Diffraction*
SPM	Scanning Probe Microscopy*
SPR	Surface Plasmon Resonance
SPUPS	Spin Polarized Ultraviolet Photoelectron Spectroscopy
SPXPS	Spin Polarized X-ray Photoelectron Spectroscopy
STM	Scanning Tunneling Microscopy*
SXAPS	Soft X-ray Appearance Potential Spectroscopy
SXRD	Surface X-ray Diffraction
TDS	Thermal Desorption Spectroscopy
TEAS	Thermal Energy Atom Scattering
TIRF	Total Internal Reflectance Fluorescence

Contd.

Table 2.1 Contd.

TPD	Temperature Programmed Desorption
TPRS	Temperature Programmed Reaction Spectroscopy
TXRF	Total Reflection X-ray Fluorescence
UPS	Ultraviolet Photoemission Spectroscopy*
XANES	X-ray Absorption Near-Edge Structure
XPD	X-ray Photoelectron Diffraction*
XPS	X-ray Photoemission Spectroscopy*
XRR	X-ray Reflectometry
XSW	X-ray Standing Wave

We use microscopy in order to see objects in more detail. The best distance that one can resolve with optical instruments, disregarding all aberrations, is about 0.5 , λ or of the order of 250 nm with visible radiation. All forms of microscopy are aimed at improving our capacity to see. Under ideal conditions, the smallest object that the eye can resolve is about 0.07 mm. This limit is related to the size of the receptors in the retina of the eye.

Several forms of microscopy are available for studying nanomaterials. These can be broadly grouped under the following categories:

1. Optical microscopes.

2. Electron microscopes.

3. Scanning probe microscopes.

4. Others.

A microscope is an instrument used to form enlarged images. The word ‘microscope’ is derived from two Greek words, “micros” meaning ‘small’; and “skopos” meaning ‘to look at’. Microscopes developed by Antoni van Leeuwenhoek (1632–1723) were the state-of-the-art for about 200 years.
These single lens microscopes had to be held against the eyeball because of their short focal lengths. They helped in the discovery of bacteria. As his research was not appreciated, van Leeuwenhoek destroyed most of his 500 odd microscopes before his death at the age of 91. Only two or three microscopes developed by Leeuwenhoek are known to exist today. The following definitions must be listed before we discuss microscopies.

Resolution: A measure of the capacity of the instrument to distinguish two closely spaced points as separate points, given in terms of distance. *Resolving power*: The resolution achieved by a particular instrument under optimum conditions. While resolving power is a property of the instrument and is a quantity that may be estimated, resolution is equal to or poorer than the resolving power and has to be determined for the instrument.

The following two kinds of microscopes exist:

1. *Transmitting*—The probe beam passed through the specimen is differentially refracted and absorbed.
2. *Scanning*—The probe beam is scanned over the surface. The image is created point-by-point.

There are several kinds of scanning microscopes. These are listed below.

1. Scanning Electron Microscope (SEM)—In this, a monochromatic electron beam is passed over the surface of the specimen which induces various changes in the sample. The resulting particles from the sample are used to create an image of the specimen. The information is derived from the surface of the sample. The most important advantage of SEM is its large depth of field. Although the images appear to be three-dimensional, a true three-dimensional image is obtained only by using a combination of two pictures.
2. Scanning Ion Microscope (SIM)—In this, charged ions are used to obtain the image and the process etches away the top surface.
3. Scanning Acoustical Microscope (SAM)—This uses ultrasonic waves to form images. The best resolution achieved is of the order of 2.5 microns, which is limited by the wavelength of sound. Its advantage is that it allows one to look at live biological materials.
4. Scanning Light Microscope (SLM)—In this, a fine beam of visible light is passed over the surface to build up the image point-by-point. It facilitates increased depth of field and colour enhancement.
5. Scanning Confocal Microscope (SCM)—In this, a finely focused beam of white or monochromatic light is used to scan a specimen. It allows one to optically section through a sample. This technique is more commonly referred to as confocal microscopy.

2.1.Nanoscale Characterization

Key Objectives

• Understand the basic operation of the following scanning probe microscopes:

• Scanning tunneling microscope (STM)

• Atomic force microscope (AFM)

• Become familiar with the key components of scanning probe microscopes

• Understand the operation of the feedback loop

• Understand the basic operation of the scanning electron microscope

• Become familiar with the signals produced in the scanning electron microscope, and the information provided by each signal

• Understand the basic operation of a transmission electron microscope

2.2. Introduction

Methods used to visualize and manipulate nanomaterials have been a significant factor in the emergence of nanoscience and nanotechnology. Normal light microscopes are limited by the fact that they cannot see anything much smaller than the wavelengths of visible light. The smallest features observed with light microscopes are dependent upon the smallest wavelength of visible light utilized by the lenses. Two terms used to describe the power of a microscope are resolution and resolving power. Resolution refers to the smallest distinguishable distance between two objects. The human eye can see as small as 0.07 mm. The reported resolution limit of optical microscopes is 200 nanometers. However, the resolving power of a microscope involves the best resolution achieved under optimum conditions; this is a property inherent to the instrument used. The Abbe criterion describes the smallest resolvable distance between closely spaced objects. There are several forms of microscopy 124 Basic Principles of Nanotechnology available for the study of nanoscale matter, including specialized forms of optical microscopies, electron microscopies, and scanning probe microscopies. This chapter will describe scanning probe and electron microscopes frequently used to characterize nanomaterials with at least one dimension between 1 and 100 nanometers. Scanning probe

microscopy is a collective term encompassing technologies such as scanning tunneling microscopy and atomic force microscopy.

2.3 Scanning Tunneling Microscopy

In the mid-twentieth century, the possibility to image or to see an atom was a matter of great debate. However, the STM was the first instrument to generate real-time images of surface features with an atomic resolution. The STM was invented in the early 1980s by Gerd Binnig and Heinrich Rohrer of IBM; they were awarded the Nobel prize in 1986 for their invention of the STM .

2.3.1 Tunneling

STMs have a metal tip which scans back and forth across the surface of a sample while never touching it. During imaging the tip is approximately 1 nm from the sample's surface. STM operation is based on a quantum mechanical phenomenon known as "tunneling". When a voltage is applied between the tip and sample, electrons can tunnel though the gap. The space between the tip and sample is an electrical barrier. However, due to the small distance between the tip and sample, the wave nature of electrons allows them to hit the barrier and reappear on the other side (Figure 7.1). Miniscule changes in the distance—less than a fraction of the atomic length—can thus be detected. Bringing a conductive tip and a conductive sample in very close proximity, while a small bias voltage is being applied, makes it possible for tunneling to occur. The movement of Fermi Level electrons travelling between the tip and sample via quantum mechanical tunneling produces a measurable current and occurs among a few atoms. The sample must be conductive; STMs in principle cannot image insulating materials. By monitoring the tunneling current, the STM can track a surface's topography with picometer (10^{-12}) resolution. The measured tunneling current is very sensitive to the distance between the tip and the surface. Small tip-sample separation results in higher current.

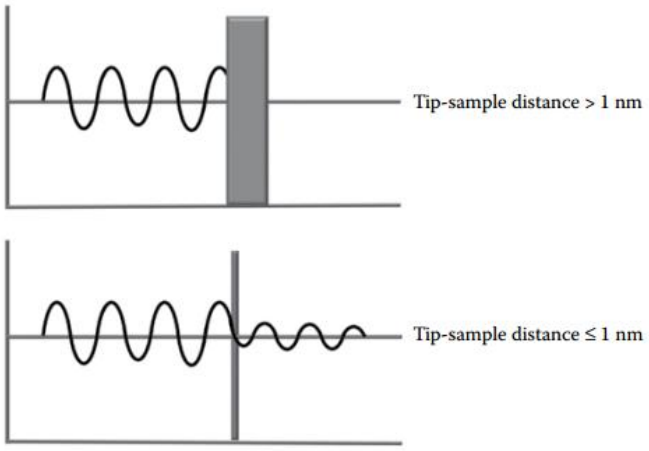


FIGURE 7.1
Effect to tip-sample distance on tunneling between the tip and sample.

2.2.2 STM Operation

A probe tip, usually made of tungsten (W) or platinum-iridium (Pt–Ir) alloy, is attached to a scanner consisting of three piezoelectric transducers, one each for x, y, and z tip motion. Upon applying a voltage, a piezoelectric transducer expands or contracts. Applying voltages to the x and y piezo allows the tip to scan the x-y plane . The horizontal resolution of the STM is 200 pm. The vertical resolution of the STM can be good as 1 pm or 1/100th of an atom's diameter . The result is an image of the electron cloud of the surface atoms.

Additionally, STM allows the study of layer growth in the semiconductor industry . STM tips are able to move atoms around, which is accomplished by varying tip-sample distance and using a voltage bias to pick up and carry, or drag a surface atom to a new position .

2.2.3 Feedback Loop

In constant-current mode, STMs use feedback to keep the tunneling current constant by adjusting the height of the scanner at each measurement point . The feedback loop moves the tip up or down to keep the tunneling current at a constant value (Figure 7.2) . If the current starts to go down, the needle is moved towards the atoms to bring the current back up, and vice versa. Recording tip distance moved up or down allows a topographic image of the

surface to be produced with the aid of computer imaging software (Figure 7.3).

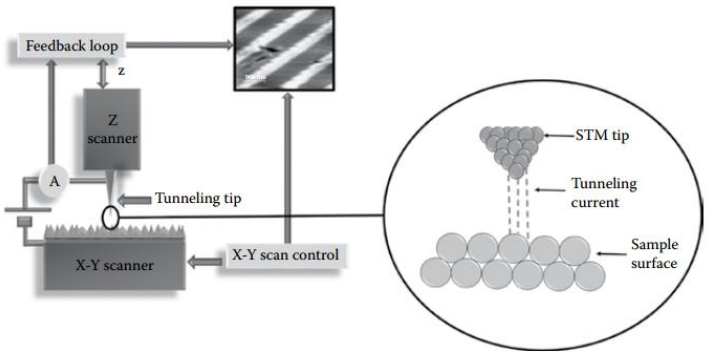


FIGURE 7.2
Operation of the STM feedback loop.

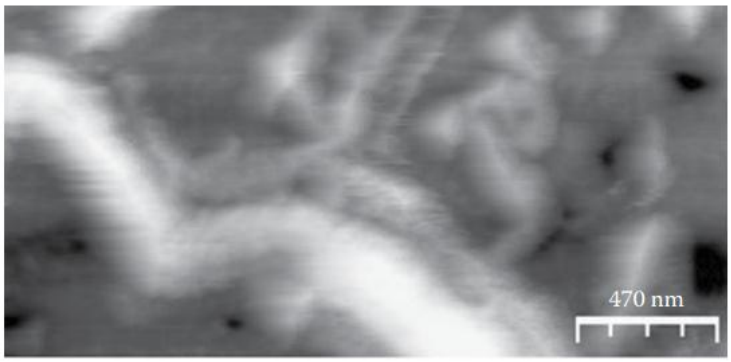


FIGURE 7.3
STM image of silver nanowire.

2.3 AFM

The AFM was invented in 1986. Unlike STM, AFMs can investigate the surfaces of conductors and insulators. The basis of AFM, as a microscopic technique, is it measures the topography of the sample by generating maps of height measurements.

2.3.1 AFM Components

AFMs consist of a piezoelectric scanner moving a tip across the surface of a sample. A detector is used to monitor tip–sample interaction (Figure 7.4). A control station, which includes a computer and an AFM controller–electronics unit, controls the AFM's operation and generates digital images.
AFMs measure atomic forces on a surface by scanning a sharp tip attached to a flexible cantilever across the sample (Figure 7.5a,b). AFM tips are sharp enough and force sensitivity is good enough to feel forces between atoms.

The tip diameter can be as small as 5 nm. AFM tips are moved across a sample surface using a scanner containing piezoelectric materials. Piezoelectric materials convert electrical signals into mechanical motion. Typically, the expansion coefficient for a single piezoelectric device is on the order of 0.1 nm per applied volt. This means if the voltage applied to the piezoelectric device is 2 volts, then the material will expand approximately 0.2 nm, which is approximately the diameter of a single atom.

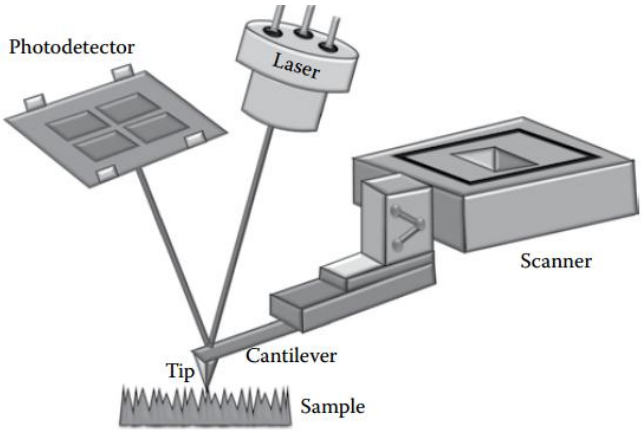


FIGURE 7.4
Diagram of AFM operation.

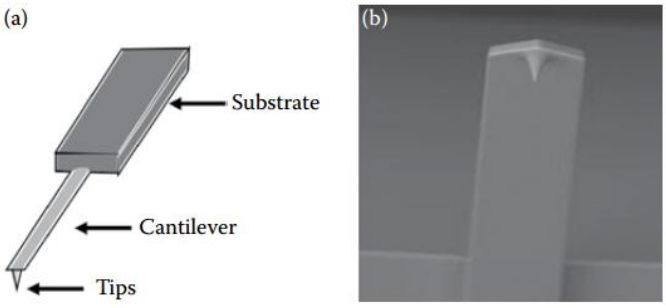


FIGURE 7.5
Diagram of AFM probe (a). SEM image of AFM probe (b).

2.3.2 AFM Operation

As the tip approaches the surface, attractive intermolecular forces exist between surface and tip atoms. When the cantilever is pushed into the surface, repulsive forces are observed because the tip is attempting to displace the atoms on the surface. Attractive and repulsive forces displace the cantilever (deflection); and cantilever displacement is used to measure surface topography and properties. The AFM enables the measurement of forces as small as 10^{-12} N. The sample can be imaged in air, liquid, or vacuum. As an AFM tip tracks the sample surface, the force between the tip and the surface causes the cantilever to bend. An optical sensor measures the deflection of the cantilever. The most common optical sensor consists of a laser beam reflected from the metal-coated back of the cantilever onto a positional sensitive photodiode. The positional sensitive photodiode can measure changes in position of the incident laser beam as small as 1 nm, thus enabling subnanometer resolution. The piezoelectric scanner moves the tip over the sample surface. The force sensor monitors the force between the tip and the surface, and the feedback control feeds the
signal from the force sensor back into the piezoelectric to maintain a fixed force between the tip and sample. The feedback loop (Figure 7.6) is used to maintain a set force between the probe and the sample. If there is an increase in force (when the tip encounters a raised region on the sample), the feedback control causes the piezoelectric scanner to move the probe away from the surface. Conversely, if the optical sensor detects a decrease in force, the probe is moved towards the surface. The amount the z piezoelectric moves up and down to maintain the tip sample distance is assumed to be equal to the sample topography. In this way, by monitoring the voltage applied to the z piezo, a map of the surface shape (height image) is measured. The amount the z piezo moves to maintain the deflection set point is taken to be the sample topography. This signal, plotted versus distance, forms the height or topography image in contact-mode AFM (Figure 7.7). This signal is used to create a 3D image of the surface structure displayed on a screen (Figure 7.7a,b).

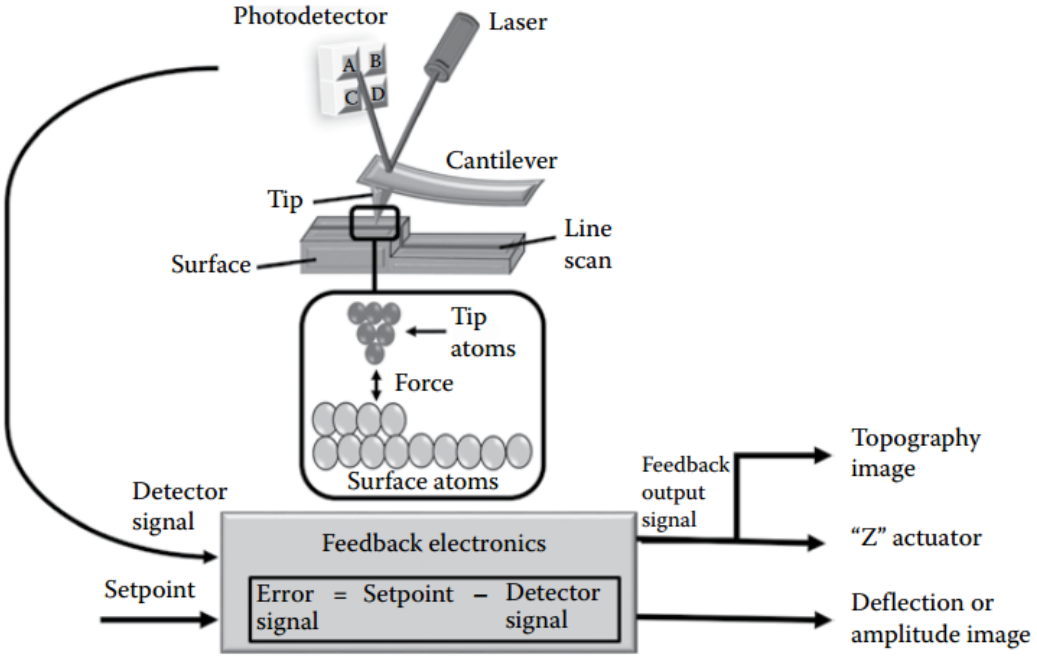


FIGURE 7.6
Schematic of the operation of an AFM feedback loop.

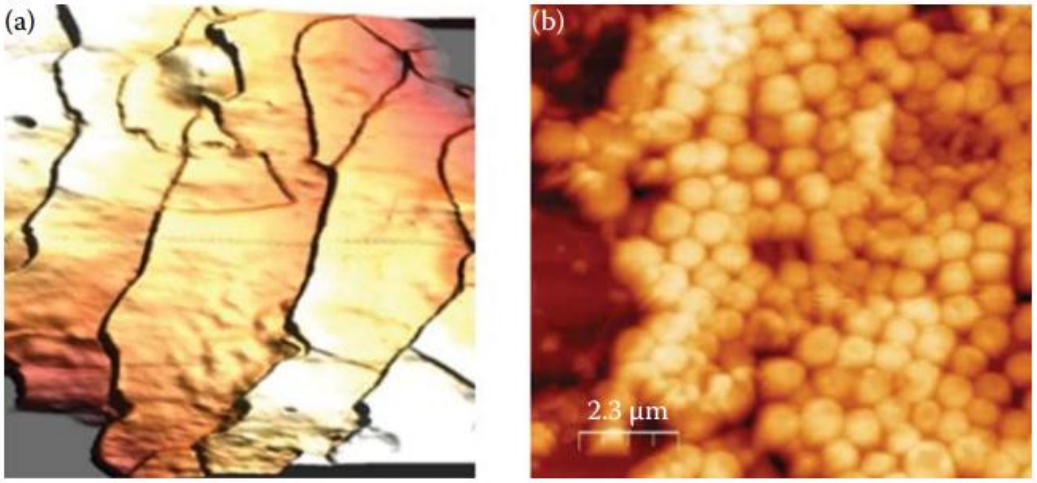


FIGURE 7.7
3D AFM image of human hair (a) and 2D AFM image of bacteria (b).

2.3.3 Operating Modes of AFM

Contact mode involves direct contact between the tip and the sample surface. When the AFM tip encounters surface features, the AFM system adjusts the vertical position of the tip so that the force between the tip and sample

remains constant. Consequently, during contact mode, the tip makes direct contact with the surface during scanning and can cause physical damage to soft materials. In tapping mode, the cantilever is vibrated at or near its resonance frequency allowing the tip to contact the surface intermittently (Figure7.8a). Intermittent contact reduces possible surface damage or tip contamination while maintaining resolution. In noncontact mode, the attractive intermolecular forces are measured by oscillating the cantilever approximately 5 to 10 nm above the sample surface (Figure 7.8b). When the oscillating probe approaches the sample surface, the oscillation changes due to the interaction between the probe and the forces from the sample. This leads to a reduction in the frequency and amplitude of the oscillation. The oscillation is monitored by the optical sensor, and the scanner adjusts the z height via the feedback loop to maintain a constant vibrational amplitude.

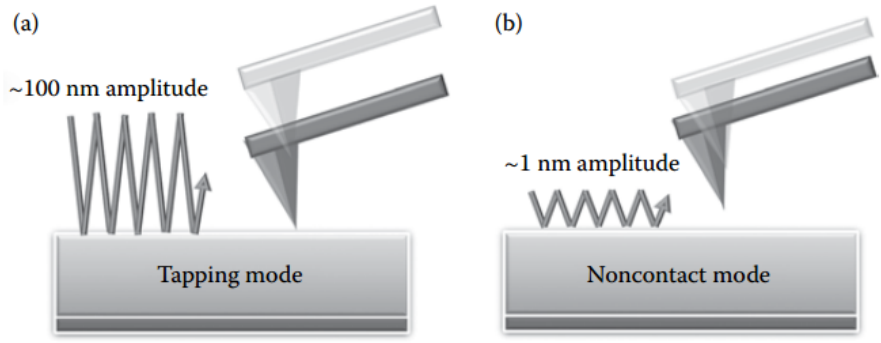


FIGURE 7.8
Tapping mode AFM (a) and noncontact mode AFM (b).

2.3.4 Force Curves

Tip-sample interactions can be used to generate a force curve (Figure 7.9). Force curve data can be used to examine forces between the tip and the sample. Regions in force curves includes the following action:

A—the cantilever is lowered to the surface.

B—tip snaps into contact when it is 1–10 nm away from the sample surface.

C—as the cantilever is lowered, the cantilever bends up because the tip is pushing against the sample surface.

D—the cantilever is pulled away from the sample surface and the tip holds onto the surface causing the cantilever to bend down due to intermolecular interactions between the surface atoms and tip atoms.

E—tip detaches from the sample surface.

Force curve data allows scientists to study nanomechanical phenomena, as shown in Figure 7.10. In these experiments, one end of the molecule is

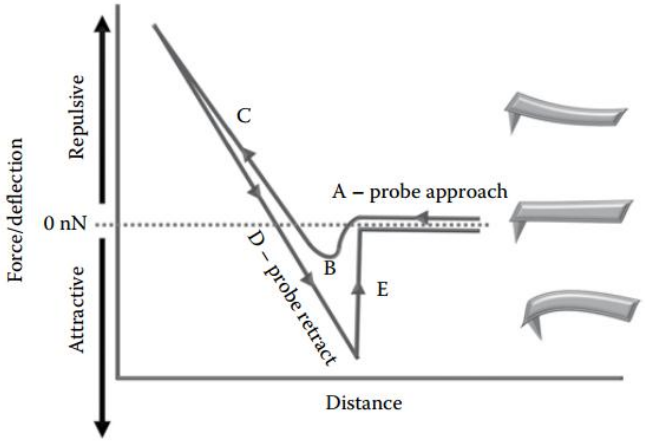


FIGURE 7.9
Example of a force curve.

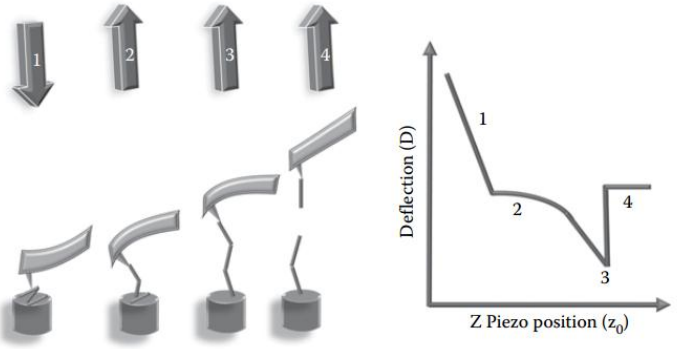


FIGURE 7.10
Force curve analysis used for the determination of the mechanical properties of molecules. Molecules are tethered between the tip and sample (1). The tip is withdrawn from the sample (2). The maximum force is applied to the molecule without breaking as the tip continues to move away from the sample surface (3). Rupture of the molecular tether (4).

attached to the AFM tip and the other end is attached to the surface of a substrate. Data collected from force curve measurements includes adhesive forces and rupture forces needed to break the bonds in a molecule.

2.3.5 Nanoshaving

The sharpness of tips used in atomic force microscopes has allowed researchers to move atoms on surfaces and to fabricate nanopatterns in thin films. In nanoshaving (Figure 7.11a), the AFM tip exerts high force on a sample surface. This pressure causes the displacement of absorbed molecules or thin films. Holes and trenches can thus be fabricated (Figure 7.11b). This procedure allows precise control over the size and geometry of the fabricated features. Additionally, this technique makes it possible to obtain an edge resolution better than 2 nm.

2.3.6 Dip-Pen Nanolithography

Dip-pen nanolithography (DPN) uses an "ink"-coated AFM tip to pattern surfaces (Figure 7.12a). DPN is a direct-write "additive" process, which allows soft and hard materials to be printed from AFM tips onto a surface substrate. It is important to point out, that no premodification of the substrate surface is required prior to DPN. DPN can deposit organic molecules via a meniscus onto a substrate surface under ambient conditions. With DPN, an organic molecule such as a thiol is used as "ink" and is transported from an AFM tip through a liquid meniscus onto a gold surface. Onemolecule thick nanostructures with micron to sub-100 nm dimensions can be fabricated with DPN (Figure 7.12b).

2.4 Scanning Electron Microscopy

Electron microscopy is a technique involving the use of an electron beam to form magnified images of specimens. The principle advantage of using electrons, rather than light, to form magnified images is electrons provide as much as a thousand-fold increase in resolving power. The resolving power of a modern light microscope is approximately 200 nm. A transmission electron microscope (TEM) can resolve detail to approximately 0.2 nm, and a scanning electron microscope (SEM) to approximately 3 nm. Development

of the SEM began in 1935 with Max Knoll at the Technical University in Berlin. Knoll used an electron beam to scan specimens in a modified cathode ray-tube. However, the instrument could not see samples at high magnification due to the use of an electron beam with a large diameter. Electrostatic lenses were used in later electron microscopes to produce a narrower electron beam with a diameter of 50 nm. Further improvements followed when electromagnetic, rather than electrostatic lenses were used; this produced electron beams with diameters less than 20 nm. In current electron microscopes (Figure 7.13), the lenses used are electromagnetic in natur.

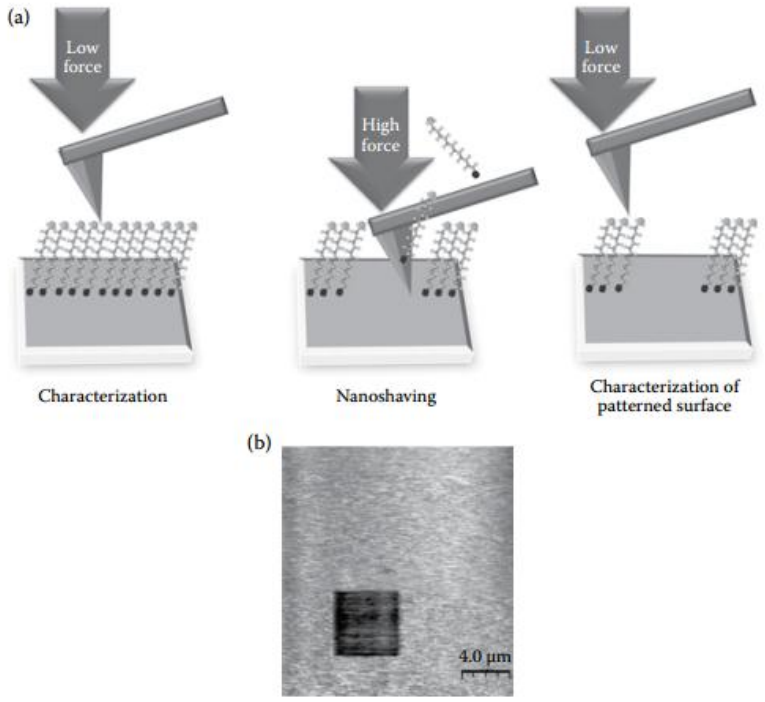


FIGURE 7.11
Nanoshaving a pattern on a SAM surface (a). A patterned etched in a mercaptohexadecanoic acid self-assembled monolayer (SAM) (b).

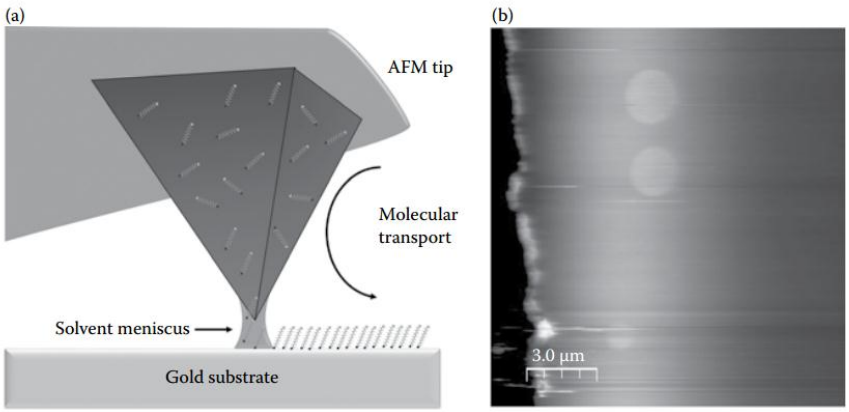


FIGURE 7.12
Process of dip-pen nanolithography (a). Alkanethiols deposited on a gold surface using dip-pen nanolithography (b).

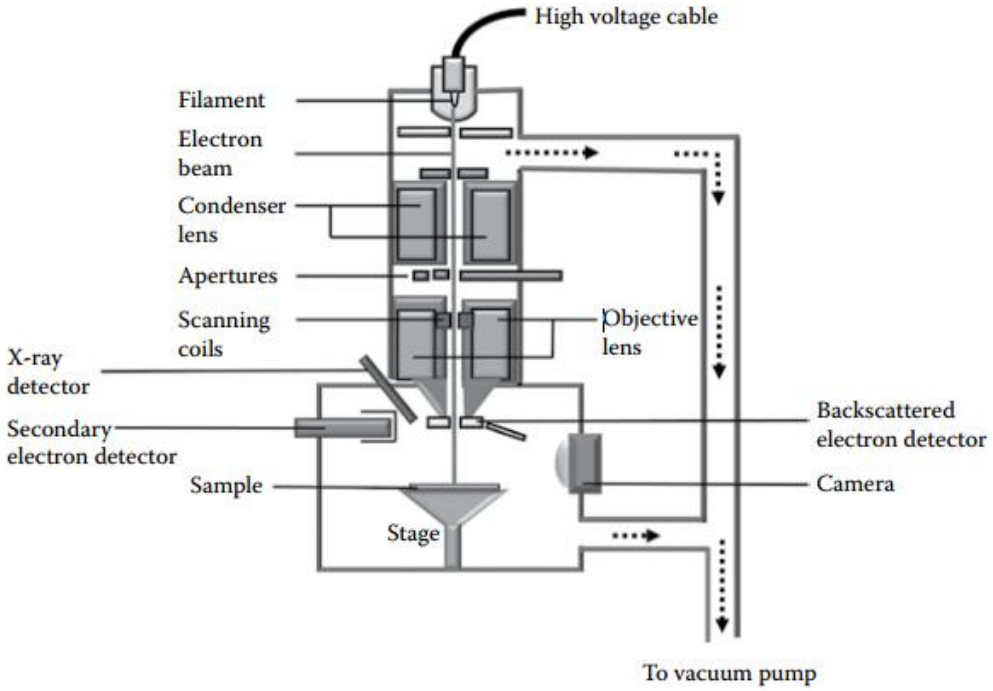


FIGURE 7.13
Schematic diagram of a SEM.

In a SEM, an electron gun emits a beam of electrons, which passes through a condenser lens and is refined into a thin stream. A condenser lens condenses the beam of electrons using electromagnetic coils. SEM is primarily used to image surface morphology. Since electron microscopes use electrons instead of light to carry the information generated during image formation, all

images are black and white. Color itself is a function of visible light, and no visible light is used to generate images in an electron microscope. The SEM has a large depth of field (the amount of the sample that can be in sharp focus at one time). Depth of field can be up to four hundred times greater than a light microscope. Apertures are used in conjunction with the electromagnetic lenses. An aperture is a piece of metal with a small round hole to limit the diameter of the beam of electrons. They are also used to eliminate stray or widely scattered electrons. Vacuum systems are a necessity in the operation of all electron microscopes. An electron beam cannot be generated or maintained in a gas-filled environment because gas within the chamber (oxygen) and the heated electron emitter react, and the filament burns out. At room temperature and pressure, a cubic meter of air contains about 2.5×1025 molecules with a mean free path of about 65 nm between collisions. A typical vacuum reached in an electron microscope column contains gases with a mean free path of 6.5 m.

2.4.1 Lenses and Scan Coils

The electron beam in a SEM is controlled using a series of electromagnets. Electromagnetic lenses consist of coils of wire enclosed in an iron casing and are used to create a magnetic field upon application of current in the coils. Coils of wire, called the scan coils, are located within the objective lens. A varying voltage is applied to the scan coils, creating a magnetic field which deflects the beam of electrons back and

forth in a pattern called a raster. Scan coils allows images to be formed using a point-by-point method. A set of scan coils for the x-direction and the y-direction can be found in scanning electron microscopes. The scan coils move the electron beam across the specimen.

2.4.2 Electron Guns

Electrons are generated in the electron gun, located at the top of the column. The major types of electrons guns used in electron microscopes are tungsten filaments, lanthanum-hexaboride guns, and field emission guns. Tungsten filaments are the most common. A tungsten filament is referred to as a thermionic emitter because electrons are emitted by exceeding the work

function of the metal by using a high surface temperature between 2000 and 2700 K. There are some disadvantages associated with tungsten-filament electron guns. Filaments evaporate as a result of high operating temperatures, and as a result, the wire gets thin enough to break. Lanthanum-hexaboride (LaB6) guns contain a crystal of LaB6 that is heated and emits electrons. These electron guns are brighter than tungsten guns and produce a smaller electron beam diameter. Field emission guns use a very high voltage to pull electrons off the wire. These electron guns are referred to as cold cathode guns because heating is not used to generate electrons. Field emission guns are a thousand times brighter than tungsten filaments, have a smaller beam diameter, and possess higher lifetimes.

2.4.3 Beam-Specimen Interactions

When incident-beam electrons strike the surface of a sample, they undergo a series of complex interactions with the nuclei of the atoms in the sample. The interaction is usually described as teardrop or pear shaped (Figure 7.14). In samples, the volume (depth and width) of the interaction varies directly with the acceleration voltage and inversely with the average atomic number of the sample.

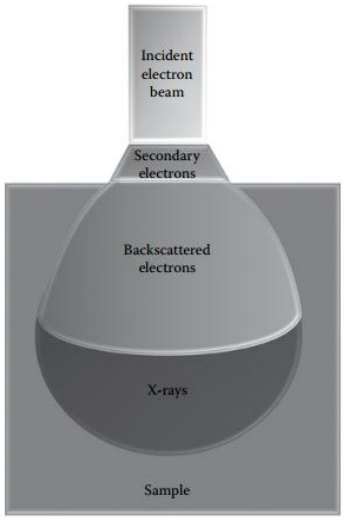


FIGURE 7.14
Interaction volume and signals generated during beam/specimen interactions.

2.4.3.1 Secondary Electrons

When the primary beam strikes sample surfaces, it results in ionization of specimen atoms. This encourages loosely bound electrons to be emitted (Figure 7.15). These electrons are referred to as secondary electrons. They have low energy, so they can only escape from a region within a few nanometers of the material's surface. The maximum escape depth had been calculated as 5 nm in metals and 50 nm in insulators. Secondary electrons are used to produce topographic images with good resolution (Figure 7.16a–c).

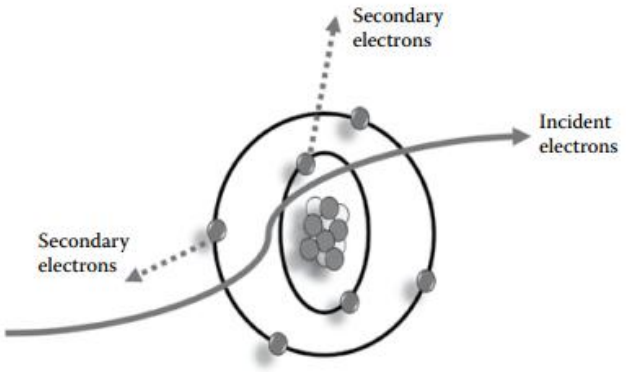


FIGURE 7.15
Production of secondary electrons.

2.4.3.2 Backscattered Electrons

When an electron from the beam encounters a nucleus in the specimen, the resultant attraction produces a deflection in the electron's path. Backscattered electrons are beam electrons which have been scattered backward. They are scattered out of the sample from the same side they entered (Figure 7.17). A few of these electrons will be completely backscattered, reemerging from the surface of the sample. Backscattered electrons are not strongly absorbed by the sample because of their high energy, and a high percentage do escape the sample. The maximum escape depth (and width) can range from a fraction of a micrometer to several micrometers. Due to the large escape depth, the backscattered electron images are less sensitive to differences in surface topography. Since the extent of scattering is strongly dependent on the atomic number of the

nucleus involved, the backscattered electrons produce images containing information about a sample's atomic composition. Backscattered electrons are very useful in detecting the presence of differences in average atomic number of a sample. Elements with higher atomic numbers produce more backscattered electrons and appear brighter than the components with lower atomic numbers (Figure 7.18).

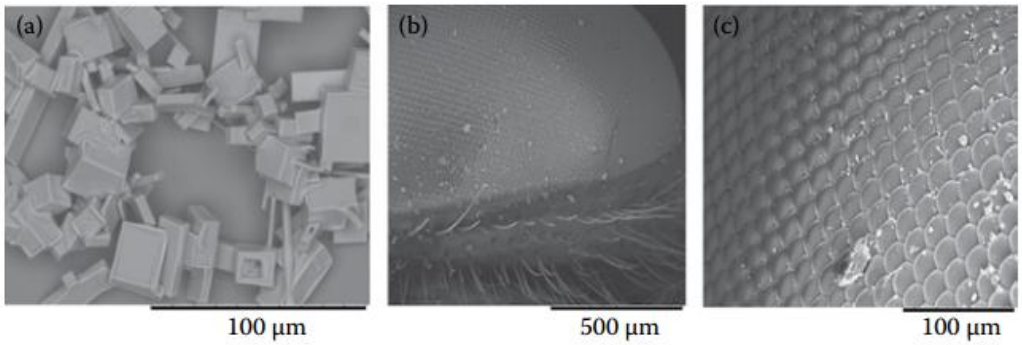


FIGURE 7.16
Secondary electron images of table salt (a), a fly eye at 150× magnification (b), and 600× magnification (c).

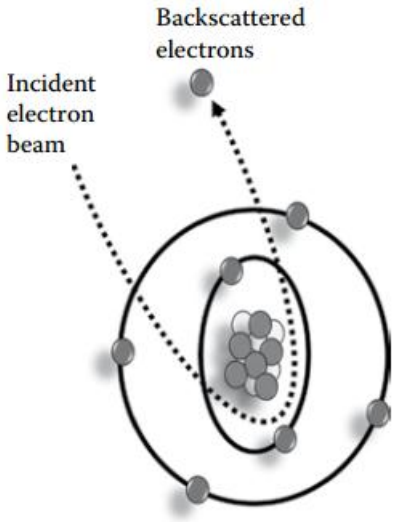


FIGURE 7.17
Production of backscattered electrons.

2.4.3.3 X-Rays

The analysis of characteristic X-rays to provide chemical information is the most widely used microanalytical technique in the SEM. When an inner shell electron is displaced by collision with an incident electron, an outer shell electron may fall into the inner shell. When this happens, the resulting imbalance may

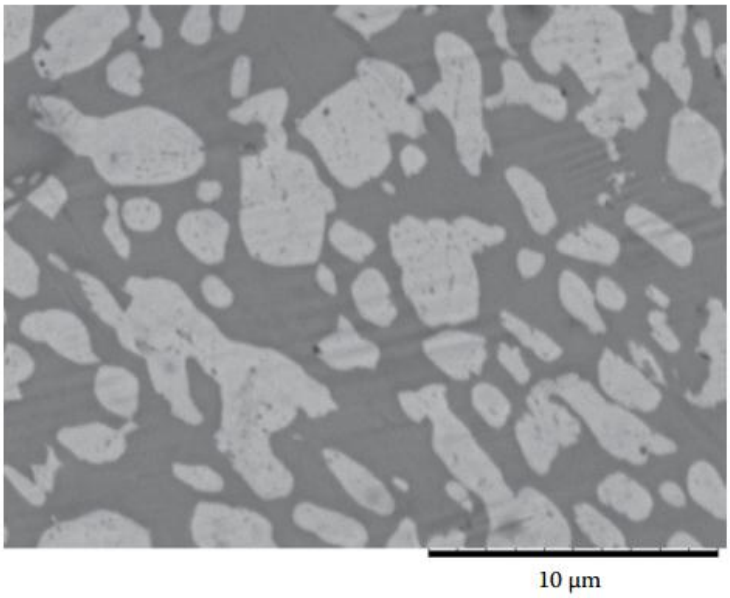


FIGURE 7.18
Backscattered electron image of lead-tin solder. The brighter areas correspond with lead and darker areas with tin.

be corrected by the production of an X-ray (Figure 7.19). This technique is referred to as energy-dispersive X-ray spectroscopy (EDS), and is commonly used for the elemental analysis or chemical characterization of a sample. Measurement of the energy or the wavelength of the resulting X-ray can be used to determine the elemental composition of the sample (Figure 7.20).

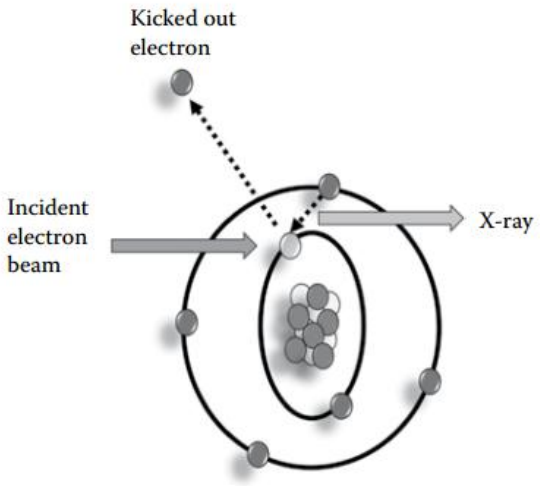


FIGURE 7.19
Production of an X-ray.

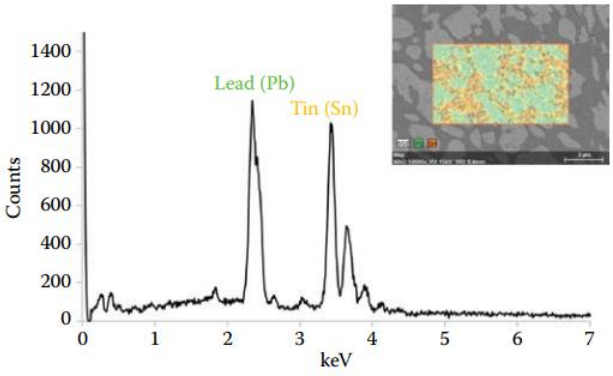


FIGURE 7.20
X-ray analysis of tin-lead solder.

2.5 TEM

In TEM, transmitted electrons are used to create magnified images of samples. A TEM is primarily used for imaging thin sections or small particles. The TEM has a resolving power of approximately 0.2 nm. To produce a standard TEM image, the electron beam must be able to penetrate the sample. A TEM works much like a slide projector, where a beam of light passes through the slide. The light passing through the slide is subjected to changes by structures and objects on the slide and as a result, only certain parts of the light beam is transmitted through certain parts of the slide.

Material thicknesses for TEM samples are prepared in advance to allow electrons to be transmitted through the sample. A scattering mechanism is used to generate an image in TEM. Scattering occurs when the electron beam interacts with matter. The recombination of transmitted and scattered beams produces a phase contrast image.

2.5.1 TEM Components

At the top of the TEM column (Figure 7.21) is a filament producing a stream of electrons. The stream is focused to a small, thin, coherent beam using a condenser lens. Additionally, apertures protect the specimen from too many stray electrons. The condenserlens system also controls electron illumination on the specimen. The beam strikes the specimen and parts of it are transmitted. In TEM images, the darker areas represent areas of the sample through which fewer electrons were transmitted (those areas were thicker or denser in the sample); the lighter areas of the image represent those areas of the sample through which more electrons were transmitted (those areas where thinner or less dense), as shown in the TEM image of gold nanoparticles in Figure 7.22.

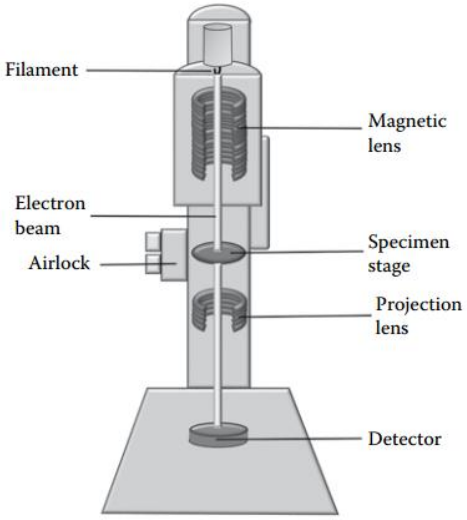


FIGURE 7.21
Components of a TEM.

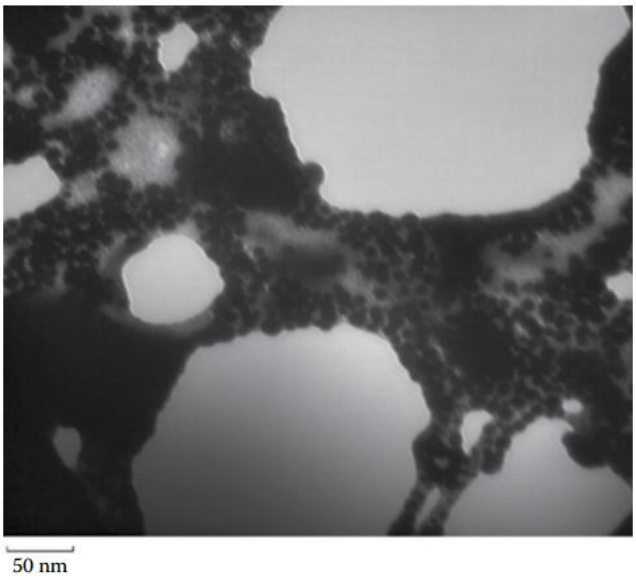


FIGURE 7.22
TEM image of gold nanoparticles.

7.6 End-of-Chapter Questions

1. The smallest distinguishable distance between two objects is referred to as:

___ resolving power
___ resolution

2. Which of the following is an inherent property of the microscope used?

___ resolving power
___ resolution

3. Scanning probe microscopy is a term that describes:

___ scanning tunneling microscopy and scanning electron microscopy
___ scanning electron microscopy and transmission electron microscopy
___ scanning electron microscopy and atomic force microscopy
___ scanning tunneling microscopy and atomic force microscopy

4. Which of the following generated the first real-space images of surfaces with atomic resolution?

___ the AFM

___ the STM
___ the SEM
___ the TEM

5. The STM functions by scanning a tip along a conducting surface and measuring _____ between the tip and sample.
___ atomic forces
___ intermolecular forces
___ hydrogen bonding
___ tunneling current

6. Tunneling current _____ exponentially with decreasing tip-sample distance.
___ increases
___ decreases

7. Separation distance between the tip and sample in scanning tunneling microscopy needs to be approximately _____ nm in order to detect tunneling current.
___ 20
___ 10
___ 5
___ 1

8. Conductive and nonconductive samples can be imaged with scanning tunneling microscopy.
___ true
___ false

9. A small _____ applied between the tip and sample is necessary for electron tunneling to occur.
___ force
___ voltage

10. The horizontal resolution of the STM is _____ pm and the vertical resolution _____ pm.
___ 1, 200
___ 200, 1
___ 100, 20
___ 20, 100

11. What is used to keep the tunneling current constant during STM imaging?

___ tip
___ tip voltage
___ feedback loop
___ sample conductivity

12. The feedback loop in STM keeps tunneling current constant by adjusting:
___ tip height
___ sample conductivity
___ tip voltage
___ tunneling current cannot be kept constant

13. AFM tip diameters can be as small as:
___ 10 nm
___ 5 nm
___ 15 nm
___ 20 nm

14. The AFM scanner uses _____ materials to move a tip across a sample surface.
___ electromechanical
___ piezoelectric
___ glass
___ graphite

15. AFMs measure _____ on a surface by scanning a sharp tip attached to a flexible cantilever across the sample.
___ magnetism
___ electricity
___ atomic forces
___ light emission

16. The AFM can measure forces as small as:
___ 10^{-2} N
___ 10^{-5} N
___ 10^{-12} N
___ 10^{-7} N

17. The feedback loop in atomic force microscopy (AFM) is used to maintain constant _____ between the tip and sample.
___ magnetism

___ force
___ electrostatic attraction
___ none of the above
18. Which of the following is NOT an operating mode of AFM?
___ tapping mode
___ contact mode
___ scanning electron mode
___ noncontact mode
19. In _____, the cantilever pushes lightly against the surface and follows the surface structure.
___ contact mode
___ tapping mode
20. Which AFM mode is less disruptive to soft samples such as delicate biological molecules or certain surface features?
___ contact mode
___ tapping mode
21. Nanomechanical information can be obtained using:
___ topography data
___ force curve data
___ the feedback loop
___ none of the above
22. The form of AFM lithography involving the removal of material on a substrate surface is:
___ vnanoshaving
___ dip pen nanolithography
23. The form of AFM lithography involving the addition of material on a substrate surface is:
___ nanoshaving
___ dip pen nanolithography
24. What generates the electron beam in the scanning electron microscope?
___ the anode
___ the electron gun
___ the scanning coil
___ the electron detector

25. _____ act as lenses in a scanning electron microscope (SEM).
___ glass
___ clear plastic
___ electromagnetic coils
___ thin films
26. What is used to move or raster the electron beam across the surface of a sample in SEM?
___ condenser coils
___ scan coils
___ electron gun
___ aperture
27. Which of the following is necessary for the successful operation of a SEM?
___ a tip
___ a cantilever
___ a vacuum
___ a scanner
28. In a SEM, loosely bound electrons that are emitted from the sample are referred to as:
___ backscatter electrons
___ X-rays
___ secondary electrons
___ none of the above
29. In a SEM, electrons that are scattered out of the sample are referred to as:
___ X-rays
___ backscatter electrons
___ secondary electrons
___ none of the above
30. Which of the following signals is used to produce topographical images?
___ X-rays
___ backscattered electrons
___ secondary electrons
___ none of the above
31. Which of the following signals can be used to obtain compositional

information?
___ X-rays
___ backscattered electrons
___ secondary electrons
___ none of the above
32. Which of the following signals is used for elemental analysis?
___ X-rays
___ backscattered electrons
___ secondary electrons
___ none of the above.
33. Electrons _____ are used to produce 2D images in a TEM.
___ reflected off the sample
___ transmitted through the sample
___ emitted by the sample
___ none of the above
34. TEMs are used to primarily image what type of samples?
___ thin
___ conductive
___ nonconductive
___ radioactive
35. Darker areas in TEM images represent _____ areas in a sample.
___ thicker
___ thinner
36. Brighter areas in TEM images represent _____ areas in a sample.
___ thicker
___ thinner