people by 2050. Note that it was just 1 billion in 1820, 2 billion in 1930, 3 billion in 1960, 4 billion in 1974, 5 billion in 1988, and 6 billion in 2000; in other words we have grown six times in just 180 years. The way in which we manage our lives has created widespread problems of over-population, industrial disasters, pollution (air, water, acid rain, toxic substances), loss of vegetation (over-grazing, deforestation, desertification), loss of wildlife, and degradation, depletion and erosion of the soil. Obviously with national boundaries and with each nation having its own problems and priorities, these issues will never be solved to the satisfaction of all. There is a larger problem of the distribution of wealth. The per capita gross domestic product (GDP) of the United States is $37,800, 13 times higher than that of India on a purchasing power parity basis (2004 estimate). What this obviously means is that a lot needs to be done to achieve a comparable quality of life for everyone. Achieving this goal would necessitate a completely new kind of technological initiative. Agriculture, which currently contributes 23.6 per cent to the GDP in India, will not be in a position to contribute further. Globally, it contributes only 4 per cent to the GDP. In the US, its contribution is only 1.4 per cent. Obviously, people don't live on food alone these days. Money is made largely by industries and services, but the new industry must not only be kind towards nature but also as efficient as the latter. Where can one look for solutions? Nanotechnology does offer solutions to some of these issues though it is not a savior for all.

1.3 Nano—The Beginning

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' (*http://personal.bgsu.edu/~nberg/faraday/diary2.htm*). The solutions he prepared are preserved in the Royal Institution, see Fig. 1.1 (Plate 1).

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. A review of the historical developments in the area of gold colloids can be found in Ref. 3.

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 helped if 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" (Ref. 4). However, the world had to wait a long time to put down atoms at the required place. In 1981, the

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).*

Plate 1

Fig. 1.1: *Faraday's gold preserved in Royal Institution. From the page, http://www. rigb.org/rimain/heritage/faradaypage.jsp.*

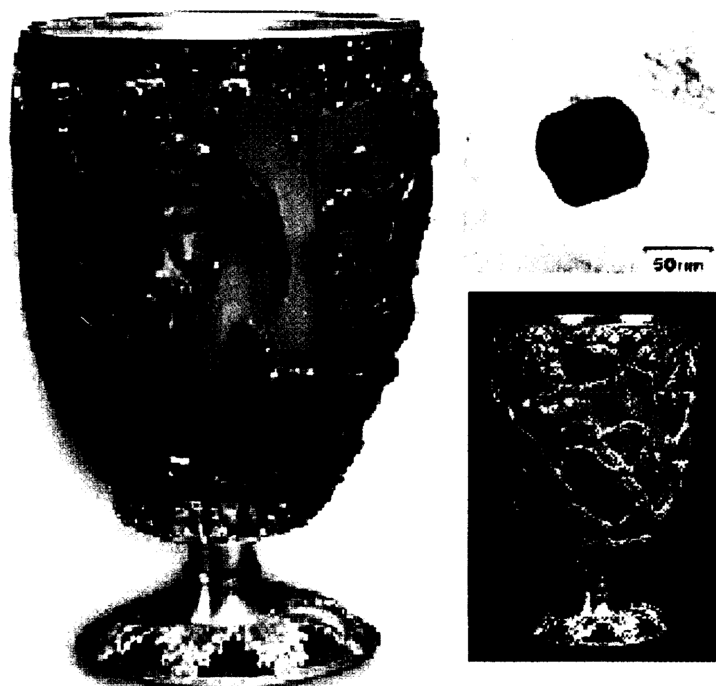


Fig. 1.2: *The Lycurgus Cup made from glass appears red in transmitted light and green in reflected light. The glass contains 70 nm particles as seen in the transmission electron micrograph. The cup itself is dated to 4th century AD, but the metallic holder is a later addition. From the site, http:// www.thebritishmuseum.ac.uk.*

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 co-founder 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

Obviously, with all these developments, new nanotech products will indeed reach the marketplace in the immediate future. However, the answer to when this need will be felt by the people varies. Many believe that there will be nanotech laws in the near future as there can be economic, social, health and security implications related to nanotechnology which would be of concern to many nations. The implications of nanotechnology for society may be significant enough for nations to discuss it as part of their election

campaigns. A detailed discussion of such aspects is given in the last chapter. In between the first and the last chapters, we have highlighted the various aspects of this rapidly emerging and fascinating science.

Review Questions

1. What is nanoscience?
2. What is nanotechnology?
3. What are nanomaterials?
4. Why nanotechnology now? Why we did not hear about it in the past?
5. Is there a systematic evolution of nanotechnology from microtechnology? Will there be picotechnology?
6. Are there nano objects around you? Are there such objects in your body? Name a few.
7. Have a look at natural objects such as sea shells, wood, bone, etc. Is there any nanotechnology in them?
8. If nature is full of nano, what limits us from making nanomaterials or nanodevices?
9. What are the likely impacts of nanotechnology?

References

1. Drexler, K.E., (1986), *Engines of Creation*, Garden City, Anchor Press/Doubleday, New York; Drexler, K.E., and C. Peterson, and G. Pergamit, (1991), *Unbounding the Future: The Nanotechnology Revolution*, William Morrow and Company, Inc. New York.
2. The term, 'wet nanotechnology' was first introduced by R.E. Smalley.
3. M–C. Daniel and D. Astruc, *Chem. Rev.*, **104** (2004), 293–346.
4. *http://www.zyvex.com/nanotech/feynman.html.*

PART

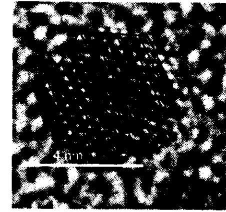
TWO

Experimental Methods

Contents:

- Investigating and Manipulating Materials in the Nanoscale

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?

2.1 Introduction

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 (marked with an asterisk) 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 the 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**

**Tools which are either microscopy or with which microscopy is possible.*

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. Any microscope is designed to magnify the image falling on the retina. The advantage of a microscope is that it effectively brings the object closer to the eye. This allows us to see a magnified image with greater details.

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

While the first three categories are more common, others are also used for nano measurements. A few of the techniques which are also useful as spectroscopies, are also discussed. In this chapter, we review all these forms of microscopic tools in detail. The discussion, however, does not include the theoretical aspects in such detail. The texts listed in the bibliography contain in-depth discussions of each technique. Every topic, however, may not be discussed to the same extent.

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.

2.2 Electron Microscopies

Microscopes consist of an illumination source, a condenser lens to converge the beam on to the sample, an objective lens to magnify the image, and a projector lens to project the image onto an image plane which can be photographed or stored. In electron microscopes, the wave nature of the electron is used to obtain an image. There are two important forms of electron microscopy, namely scanning electron microscopy

and transmission electron microscopy. Both these utilize electrons as the source for illuminating the sample. The use of optical analogy makes it easier to understand the functioning of a microscope. Both the tools use similar illumination sources, but they differ in a number of other aspects. The lenses used in electron microscopes are electromagnetic lenses, which are widely different from glass lenses, though similar principles apply in both cases.

Due to its simplicity, scanning electron microscopy (SEM) will be discussed before transmission electron microscopy (TEM). The discussion of TEM will be brief because even though TEM is more complex in usage, an understanding of SEM makes it easier to use TEM. Several other modifications to each of these techniques are possible and we will highlight these advanced tools at the appropriate places.

2.2.1 Scanning Electron Microscopy

Basics

The de Broglie wave equation relates the velocity of the electron with its wavelength, $\lambda = h/mv$ (h is Planck's constant, m is the rest mass of electron and v is its velocity). An electron of charge e (1.6×10^{-19} coulomb), and mass m (9.11×10^{-28} gm), when passing through a potential difference of V volts (expressed in joules/coulomb), acquires a kinetic energy of $1/2mv^2$ = eV. This will give: $v = \sqrt{(2\,\text{eV/m})}$ and $\lambda = \sqrt{(h^2/2\,\text{meV})}$. Substituting (with conversion factors, 1 joule = 10^7 dyne.cm = 10^7 cm^2.gm/sec^2), λ (in nm) = $1.23/\sqrt{V}$. When V = 60,000 volts, λ = 0.005 nm. This shows that the velocity of electrons will reach the speed of light in vacuum ($c = 3.10^{10}$ cm/sec) at high extraction potentials. The electron velocities at various acceleration voltages are given in Table 2.2.

Table 2.2: *Electron velocities at different acceleration voltages*

V	λ(nm)	v($\times 10^{10}$ cm/sec)	v/c
50,000	0.0055	1.326	0.442
100,000	0.0039	1.875	0.625
1,000,000	0.0012	5.930	1.977

However, the equation breaks down when the electron velocity approaches the speed of light as mass increases. At such velocities, one needs to do relativistic correction to the mass so that it becomes $m = m_0/\sqrt{[1 - (v^2/c^2)]}$. This makes $\lambda = 1.23/(V + 10^{-6}V^2)$ nm.

After including the relativity effects, the velocities and the wavelengths achieved are as shown in Table. 2.3.

Table 2.3: *Voltage and velocity after inclusion of relativity effects*

V	$v(\times 10^{10}$ cm/sec)	v/c
50,000	1.283	0.414
100,000	1.699	0.548
1,000,000	2.917	0.941

Resolving Power

1. Abbe criterion: In 1893, Abbe showed that, the smallest resolvable distance between objects is about half the wavelength of the light used. What does this mean for magnification? The maximum magnification that can be used is equal to the resolving power of the eye divided by the resolving power of the microscope. In the case of light microscopes, the resolving power is about 250 nm. What we can see with our naked eye without difficulty is about 250 μm. So the useful magnification is 250/0.25 = 1000X (X means diameter). A magnification higher than this has no value as it represents empty magnification, the effect of which is only a magnified blur. The resolving power of an electron microscope would be 0.0027 nm for an electron energy of 50,000 V. This means that one can obtain a magnification of the order of 100,000,000. However, this is not achieved due to aberrations of the electron lenses and the complex nature of electron–sample interactions. It is important to know that we have achieved the theoretical limit of resolution as far as optical microscopes are concerned as the various aberrations have been resolved.

2. Rayleigh criterion: An ideal lens projects a point on the object as a point on the image. But a real object presents a point as a disk in the image plane. This disk is called the Airy disk named after George Airy (Fig. 2.1). The diameter of the disk depends on the angular aperture of the lens. If two points are placed close to each other, the closest distance at which they appear to be separated in the image is about half the width of the disks. This separation (shown in the arrow) can be given as: $d = 0.61\ \lambda/n \cdot \sin\theta$, where n is the refractive index of the medium and θ is the semi-angular aperture of the lens. The quantity $n \cdot \sin\theta$ is the numerical aperture (NA) of the lens.

In order to maximize resolving power, λ must be decreased, and n or θ increased. Recall that, at the moment, we are concerned with an **aberration-free** optical system. In the case of light microscopes, with oil immersion optics ($n = 1.5$), $\sin\theta = 0.87$ and $\lambda = 400$ nm (for the blue end of the visible spectrum), the limit is $d = 0.2\ \mu$m. In the case of TEM, $n = 1$ (vacuum), $\sin\theta = 10^{-2}$ and λ is of the order of 0.005 nm and $d = 0.3$ nm.

Classical vs. Electron Optics

Light is refracted by lenses. This is the property used for magnifying or demagnifying an object. At the lens surface, the refractive index changes abruptly and remains constant between the surfaces. Imaging lenses are constructed by using the principles of refraction. Glass surfaces of the lenses are shaped in order to obtain the desired results. In electron optics, the trajectory of the electrons is changed by applying electric

or magnetic fields. This change is continuous depending on the electric and magnetic fields. Electromagnetic lenses, which have fewer aberrations than electrostatic lenses, are used in electron microscopy.

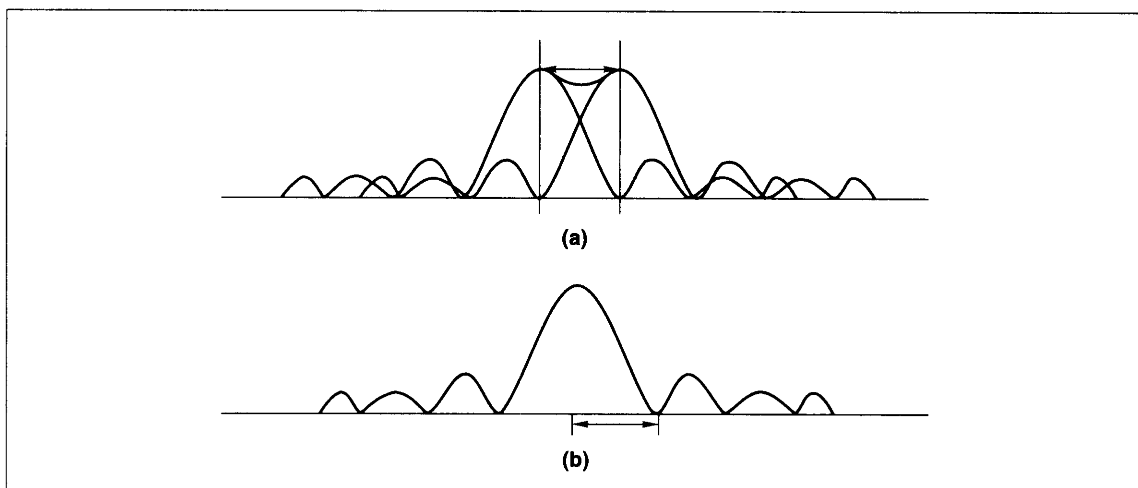


Fig. 2.1: *(a) Intensity distribution at the image plane forming an Airy disk. The points are considered resolved if the intensity maxima are separated at half the height. (b) Rayleigh criterion of resolution.*

What does an SEM contain?

The principal elements of an SEM are discussed below.

1. Electron gun: The electron gun provides a stable beam of electrons. The most common form of an electron gun is a thermionic emitter, wherein the work function of the metal is overcome by the surface temperature of the filament. Typically a hairpin filament made of a tungsten wire of 100 μm, with a tip radius of 100 μm, is used to generate electrons. The filament is held at a negative potential and heated to about 2000–2700 K by resistive heating. The electrons are confined and focused by a grid cap (Wehnelt cap) held at a slightly higher negative potential than the filament. The confined beam is accelerated to the anode held at the ground potential and a portion of the beam is passed through a hole. The beam current measured at the anode is used to regulate the power supply which drives the electron gun for the desired current. The tungsten wire gradually evaporates due to the high operating temperature, its resistance decreases and finally it becomes so thin that it breaks. Higher temperature (higher operating current) increases the evaporation rate and reduces the filament life.

The filament characteristic is given in terms of brightness which is given as current/area.solid angle. The brightness is of the order of 10^5 (A/cm^2 sr) for the tungsten filament. An order of magnitude increased brightness is possible in the case of lanthanum hexaboride (LaB_6)-based guns and a still larger brightness is possible in the case of field emission guns. This is achieved by reducing the emission area, which results in significant reduction in the demagnification required in the operation.

LaB_6 has greater brightness and a longer lifetime as compared to tungsten. The emitter is a single crystal of LaB_6 of 10 μm diameter with 500 μm length. The tip is ground to a sharp point of 10 μm and the crystal is mounted on a rhenium or graphitic carbon base. The base is resistively heated so that the tip emits electrons. The gun requires a better vacuum than that needed for a tungsten filament as the tip can be contaminated easily. The filament lifetime is of the order of 1000 h and the increased brightness justifies an order of magnitude increase in cost.

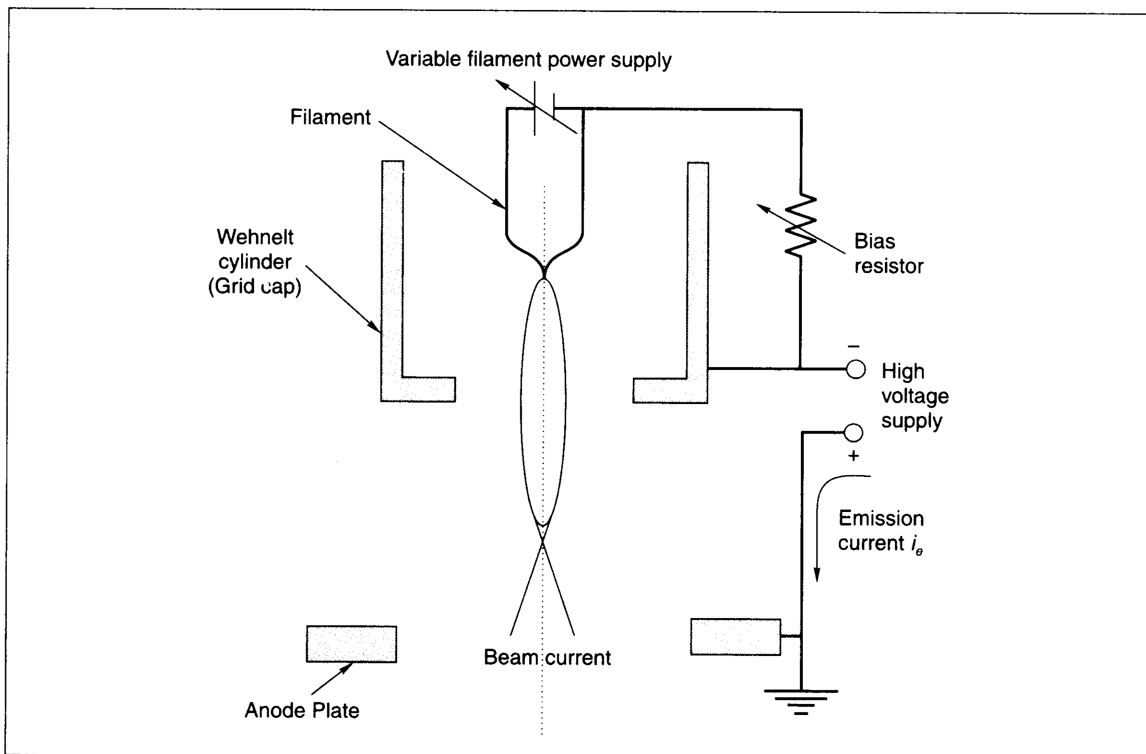


Fig. 2.2: *Schematic of an electron gun. The gun is normally operated at a constant emission current, which implies regulation of the current supplied to the filament. Adapted from J.I. Goldstein, et al. (2003) (Ref. 1).*

Field emission is another way of making electrons. This kind of source has a high brightness. In field emission, the field at the tip of the emitter reaches a magnitude of 10 V/nm, and the potential barrier for electron emission gets reduced and becomes narrower so that electron can tunnel and escape the cathode. Two kinds of field emission sources are commonly used, i.e. the cold field emitter (CFE) and the Schottky field emitter (SFE). In CFE, a sharp single crystal of <310> tungsten tip is spot-welded on a tungsten wire. The tip is made of tungsten as it has the strength required to withstand the mechanical stress produced at the tip. The tip itself is mounted in a triode configuration so that the potential difference between the tip

and the first electrode is of the order of 3–5 kV to produce 10 μA emission. The potential difference between the second electrode and the tip determines the beam energy. Field emission is sensitive to adsorbed gases and the surface can be cleaned by flashing the tip to a temperature of 2500 K. After flashing, the emission is high but soon it reduces and stabilizes as the surface is covered. The tip has to be re-flashed to get a clean surface again after several hours of operation. In each flashing, the tip gets more blunt and after several thousands of flashes, the tip is rendered unfit for use and it has to be changed. This occurs only after several years as one flashing is enough for a day.

SFEs are operated at high temperatures. They are self-cleaning and their tips sharpen in the extraction field. In SFEs, the field at the tip is used to reduce the work function barrier. The tip is held at a high temperature. In order to achieve better reduction of the work function, the surface is coated with ZrO_2 from a dispenser. The SFE gun is run continuously even when no current is drawn. This keeps the system clean. However, as the ZrO_2 reservoir is finite, the lifetime is finite and a replacement is needed every year.

2. Electron lenses: An electromagnetic lens used in electron microscopy is shown in Fig. 2.3(a). This consists of a coil of wire generating a magnetic field enclosed in an iron casing. A magnetic field is generated between the polepieces by applying a current through the coils. The electron in a magnetic field undergoes rotation. As the radial component of the magnetic field reverses after the center of the lens, the rotation in the first half of the lens is reversed. The electron leaves the lens without any net change in the angular momentum, but it undergoes deflection towards the axis. Since the radial force is directed toward the axis, the magnetic lens is always convergent. An electron travelling off-axis to the beam path will spiral through the lens towards the optic axis. The point from which the beam starts bending to the point where it crosses the lens axis is called the focal length. The focal length can be varied by changing the current in the coils and this is a difference from the optical lenses where the focal length is fixed. Referring to Fig. 2.3(b), the focal length can be given as $f = 1/p + 1/q$. From this, one can calculate the magnification, $M = q/p$ and demagnification, $m = p/q$, where p is the distance from the object to the centre of the lens and q is the distance from the image to the centre of the lens.

An electron microscope contains two kinds of lenses. The condenser lens has a large bore giving a long focal length, while the objective lens has a strong field of short axial extent giving a short focal length, resulting in high magnification. In an electromagnetic lens, an electric current passing through a conductor gives rise to a magnetic field. If the conducting wire forms a solenoid (several turns around a cylinder), each turn contributes to the induced magnetic field at the centre. The flux density at the center is: $B = \mu(NI/l)$, where μ is the permeability of the surrounding material, N is the number of turns, I is the current flowing through the coil and l is the length of the solenoid. $H = NI/l$ and so by substituting, $B = \mu H$. So, μ is the flux density per unit field. For air and non-magnetic materials, $\mu = 1.0$ and $B = H$. The permeability of iron is field-dependent and it is unity at high field and so, $B = H$. At high magnetic fields, iron reaches magnetic saturation and that is the reason why $\mu = 1$. Due to the hysteresis of iron, the extent of current used to energize a magnetic lens cannot be used to get the lens characteristics such as focal length. Hysteresis has to be kept small and soft iron is used for this reason. The current results in the heating and cooling by water is needed to keep the system cool. The system is shielded from external magnetic fields. For this, a high permeability material is used (μ metal is one such material).

When the solenoid is encased in a case of soft iron, the magnetic field along the axis is increased. If the entire coil except at a narrow annular gap is made of soft iron, a greater concentration of the magnetic field along a short axial distance occurs. The polepieces are these annular rings which focus the magnetic field at a given location. The field strength used is below 20,000 gauss in typical instruments.

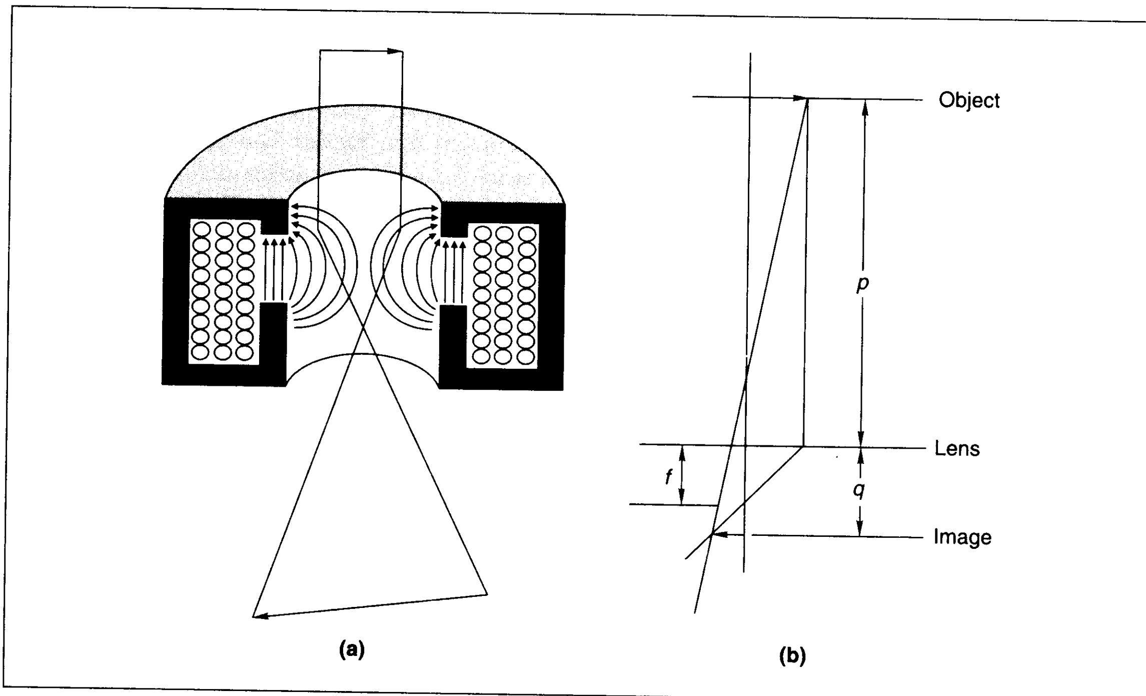


Fig. 2.3: *(a) Schematic of an electromagnetic electron lens. The magnetic field lines are shown. (b) Illustration of the concept of magnification.*

The focal length is given by $f = Kv/(NI)^2$ where K is a constant; v, the relativistically corrected accelerating voltage; and NI, the number of turns of the coils. Focusing is achieved by varying the current through the coils. It is important to note that the focal length is not linearly related to current. The focal length of the lens is directly proportional to the accelerating voltage. So the image quality is affected by varying the electron velocity.

Lens aberrations: Electron optics suffers from aberrations. But unlike in light optics, there is no way to solve these aberrations. All that can be done is to reduce them through proper design considerations.

Spherical aberration: Electrons in far away trajectories from the optic axis are bent more strongly. As a result, the electron beam entering the lens near the edge of the lens, is brought to focus at a different spot than the spots closer to the centre. This is schematically illustrated in Fig. 2.4(a). The error in the image due to this becomes more pronounced as the beam is moved further away from the optical axis of the lens.

Differential focusing causes the image at the perimeter to get smeared instead of at the centre. As a result of this, the image appears as a disk and not as a point. The smallest disk is called the spherical aberration disk of least confusion, $d_s = 1/2\ C_s\alpha^3$ where C_s is the spherical aberration coefficient and α is the angle of the outer ray through the lens. C_s is typically a few mm for lenses with short focal lengths. The spherical aberration can be minimized by removing the outer edge of the beam. This is achieved by placing a small-holed aperture at the centre of the magnetic field or immediately below it. However, a smaller diameter reduces the beam current and also leads to aperture diffraction.

Chromatic aberration: This aberration is due to the energy spread of the electrons. When light of different energies enters a converging lens at the same point, the extent of deflection will depend on the energy. In light optics, radiation of a shorter wavelength is deflected more strongly than that of a longer wavelength. In electron optics, the reverse happens, i.e. a shorter wavelength is deflected less strongly. This is due to the fact that electrons are subjected to lesser deflection when the beam energy is high. As a result, the beams of two different energies form images at different points as illustrated in Fig. 2.4(b). Due to this aberration, instead of a point, a disk results and the diameter of the disk of least confusion can be given as, $d_c = C_c\ \alpha\ (\Delta E/E_o)$, where C_c is the chromic aberration coefficient, E_o is the beam energy and ΔE is the energy spread. The fractional variation in beam energy is the significant factor.

Chromatic aberration can be reduced by stabilizing the energy of the electron beam. Stabilized acceleration voltage and improved gun design ensure the stability of the beam. The effect of chromatic aberration is pronounced near the perimeter of a converging lens and an aperture can be used to eliminate these electrons.

Aperture diffraction: The wave nature of electrons causes the beam to diffract upon passing through a narrow slit. Each beam passing through the slit sets up its own waves. These will interact to give a bright spot in the middle and a set of concentric rings in the image plane called the 'Airy disk'. If the intensity distribution is plotted in one dimension, it looks like that one shown in Fig. 2.4(c). The contribution to the spot size due to diffraction is given as the half diameter of the Airy disk, $d_d = 0.61\ \lambda/\alpha$, where λ is the wavelength of the beam and α is the aperture half angle. In order to reduce the effects of diffraction, it is necessary to have as great an angle as possible between the optical axis and the lens perimeter. That would amount to having no aperture at all. But a smaller aperture is needed to reduce the effects of spherical aberration and chromatic aberration, which would cause diffraction problems. Thus an optimum aperture size must be chosen.

Astigmatism: Astigmatism refers to the improper shape of the beam. A point object is focused to two-line foci at the image plane and instead of a point, an ellipse appears. The two-line foci may be forced to coincide for correcting this defect. Astigmatism occurs due to defects in the focusing fields, which could be due to several aspects related to electromagnetic lenses, apertures and other column components. Imperfection in machining can cause astigmatism. Astigmatism is corrected by a set of magnets called 'stigmators', which are placed around the circumference of the column. These are adjusted according to strength and position in an effort to induce an equal and opposite effect on the beam.

The effect of lens aberrations is important for the objective lens as the effects caused to the beam would be small in comparison to the diameter at other lenses. Typical spherical aberration can be corrected

Fig. 2.4: *Various aberrations of electromagnetic lenses. (a) Spherical aberration, (b) chromic aberration, (c) aperture diffraction, and (d) astigmatism. Adapted from Goldstein, et al. 2003 (Ref. 1).*

completely. But the correction leads to aperture diffraction and therefore these two should be controlled properly. Chromatic aberration is significant below an accelerating voltage of 10 kV.

3. Scan coils: The next part of the SEM consists of the scan coils. In SEM, the scanned image is formed point by point and the scan is achieved by the scan coils. There are two pairs of coils, one each for the *X*

and Y axes (Fig. 2.5). The scan coils lie within the column and move the electron beam as per the requirement across the specimen. They are electromagnetic coils and are energized by the scan generator. The scan generator is connected to other components such as the cathode ray tube (CRT) and the magnification module.

The scan is made as follows. The electron beam is swept across the sample. The pattern over the sample is synchronous with that observed in the CRT. The secondary electrons produced by the sample are detected. The intensity of the signal at the CRT is proportional to the secondary electrons. An intense signal can illuminate several dots on the screen, while a weak signal would mean that no dots will be illuminated by the electron gun. The detector therefore gives the intensity of the signal, while the raster pattern gives the location of the signal. In this way, the image on the CRT is built up point by point to match what is happening on the surface of the sample.

This manner in which an image is formed is the essential difference between the transmission and scanning types of microscopes. A couple of important observations need to be made in this type of image formation. Firstly, the focus is dependent upon the size of the electron beam spot. The smaller the spot on the sample, the better is the focus. Secondly, magnification is not produced by a magnification or enlarging lens but rather by taking advantage of the differential between the size of the scan pattern on the sample and the size of the CRT.

The size of the CRT is fixed. The size of the scan pattern on the sample is variable and is determined by the magnification module. By narrowing the size of the area which is scanned and conveying that to the CRT, we can increase the magnification of the image. The smaller the area scanned, the lesser is the distance between the raster points, and the smaller is the amount of current needed to shift the beam from point to point. The greater the area scanned, the lower is the magnification, while the greater the distance between the raster points, the greater is the amount of current needed to shift the beam from point to point. In this way, when we operate the SEM at relatively low magnifications, we actually push the scan coils to their extremes.

The scan generator changes the step current to the scan coils. This current is then multiplied by a constant by the magnification module and sent to the scan coils. The higher the total magnification, the lower is the multiplier constant.

4. Electron detector: There are two kinds of electrons coming out from the sample in an SEM; the backscattered electrons, with high energies being larger or lower than the primary beam energy, and the secondary electrons which have energies of a few eV, or less than a few tens of eV. The most common kind of detector used in SEM is the Everhart-Thornley (*E-T*) detector (Fig. 2.5). In this, a scintillator material is exposed to the electrons. Energetic electrons, upon impact with the material result in photon emission. The photons are transmitted through a light pipe. This is a glass rod or a piece of plastic. At the other end of the light pipe, a photomultiplier is placed, which converts the photons to electrons through photoemission. The electrons can be made to undergo a series of collisions on surfaces producing a cascade of electrons and a gain of 10^6 can be achieved this way. The detector has a high bandwidth, which means it responds to a rapidly varying signal. This would be the case when the primary beam is scanned over the sample at high speeds.

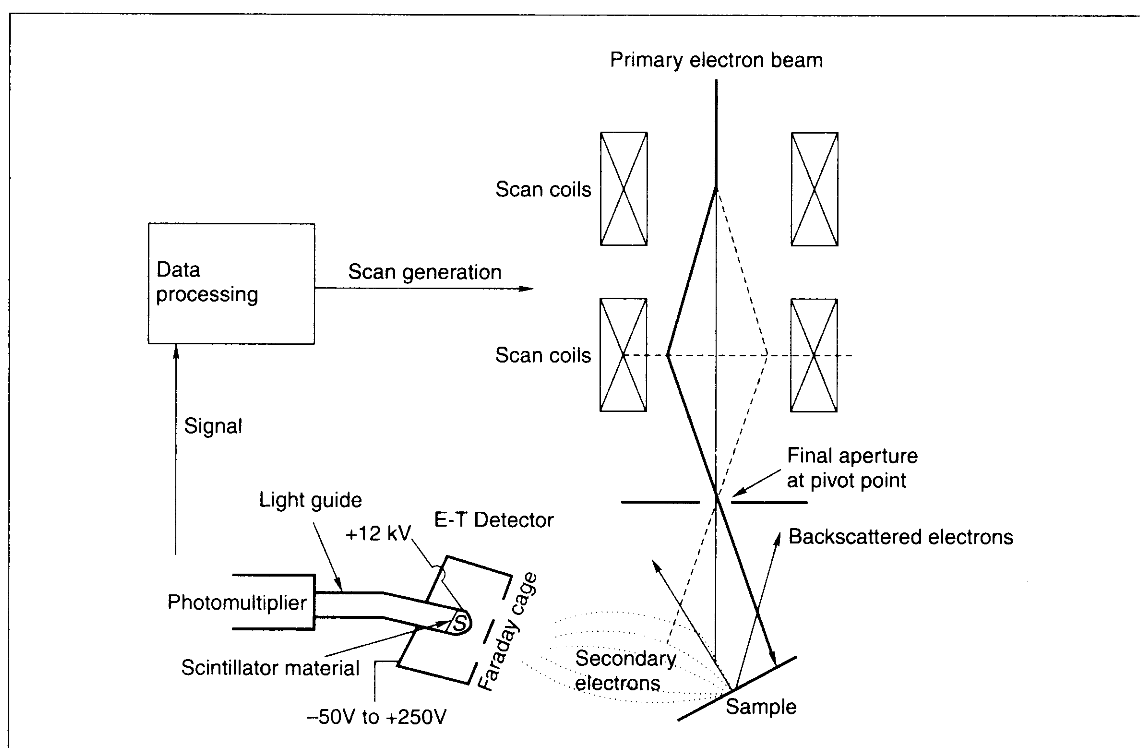


Fig. 2.5: *Schematic of an SEM. The electron beam is scanned by a set of scan coils and the secondary electrons are detected by the detector. By applying a negative potential to the Faraday cage, the secondary electrons are rejected completely. Adapted from Goldstein, et al. 2003 (Ref. 1).*

In the practical operation of the detector, a thin metal coating is applied on the surface of the scintillator. A high positive potential is applied to the metal surface so that all electrons, including the low energy secondary electrons, are accelerated to it so as to generate photons. The high voltage should not affect the primary beam and for this reason, a Faraday cage is kept over the scintillator, which is electrically insulated. By applying a desired potential in the range of –50 to +250 V to the Faraday cage, a complete rejection or collection of secondary electrons becomes possible.

For collecting backscattered electrons, a separate detector can be employed. Several kinds of detectors are used and one of the more popular ones is the solid state diode detector. This works on the principle that in a semiconductor, the electron impact can produce electron-hole pairs if the electron energy is above a threshold value, which is of the order of a few eV. Thus, when a high energy electron falls on it, several thousands of electron-hole pairs are formed. The charges can be swept in opposite directions if a bias is applied. The charge collected can be amplified and detected.

In low voltage SEM, the common electron detector is the channel plate. Here primary electrons make secondaries in a channel, and a cascade of secondary electrons is produced. Several such channels are

made on a disk which is a few cm in diameter, and the electrons coming out at the other side are collected and amplified. As the secondary electron yield increases in the low keV range, channel plate works well for low energy operation. Low energy secondary electrons require acceleration for detection by a channel plate.

SEM: Modern Advances

SEM is the most widely used electron microscopic technique. This is largely because of its versatility, its various modes of imaging, ease of sample preparation, possibility of spectroscopy and diffraction, as well as easy interpretation of the images. The method has high throughput making it an accessible facility. A very wide range of magnification is available which facilitates the visualization of virtually every detail. Best SEMs can obtain image resolutions in the range of 0.5 nm and for this, the sample need not be specially prepared. Sample size is not a limitation in SEM and samples as large 6" silicon wafers can be put directly in a modern machine.

Modern advanced SEMs utilize field emission sources. There have been numerous advances in various aspects of the hardware such as lenses, detectors and digital image acquisition. These advances in hardware, coupled with advances in other areas of instrumentation such as power supplies, high vacuum instrumentation have now made it possible to acquire SEM images from almost anything, including wet biological samples.

Low voltage SEM is another new development. The extreme surface sensitivity of this technique is a result of the reduced interaction volume. This allows the measurement of images with nanometer scale resolution with under 1 kV acceleration. At these low energies, charging is not an issue and it is possible to measure images without conductive coatings. The electron energy can be reduced further by applying a negative potential on the sample and in this way, the beam energy can be reduced to below 100 eV. It also makes ultra low voltage SEM (ULV-SEM) possible, which is extremely surface-sensitive and avoids beam-induced damage at surfaces.

When an electron beam interacts with matter, several processes occur. These result in particle or photon emission processes which are summarized in Fig. 2.6. The electron emission processes include elastic and inelastic scattering, and the emission of secondary electrons and Aüger electrons. Inelastic scattering occurs as the beam interacts with the sample and electronic excitations of the constituent atoms can occur. These excitations can lead to valence and core electron excitations and emission. The core hole thus created may get filled by electron de-excitation, resulting in X-rays. The de-excitation can also result in electron ejection, called Aüger emission. In addition, collision of the primary beam can also lead to excitations of lattice vibrations. All these electrons can be used to gather microscopic information of the sample. In addition, they can also be used to obtain chemical or compositional information as in the case of Aüger electrons or structural information as in the case of backscattered electrons. In a normal SEM image, only secondary electrons are detected. Emissions of characteristic X-rays as well as continuous X-rays occur. The characteristic X-rays are used for qualitative and quantitative information. In addition to these, electron-induced desorption, ion ejection, etc., also occur.

High resolution SEM is now a routine analytical tool. In nanoscience and technology, this becomes an important high throughput characterization tool. It is important to know the dimensions of the structures

fabricated and the materials prepared when characterizing device structures. Thus SEM becomes an indispensable tool in nanometrology (a branch involving nanoscale calibration).

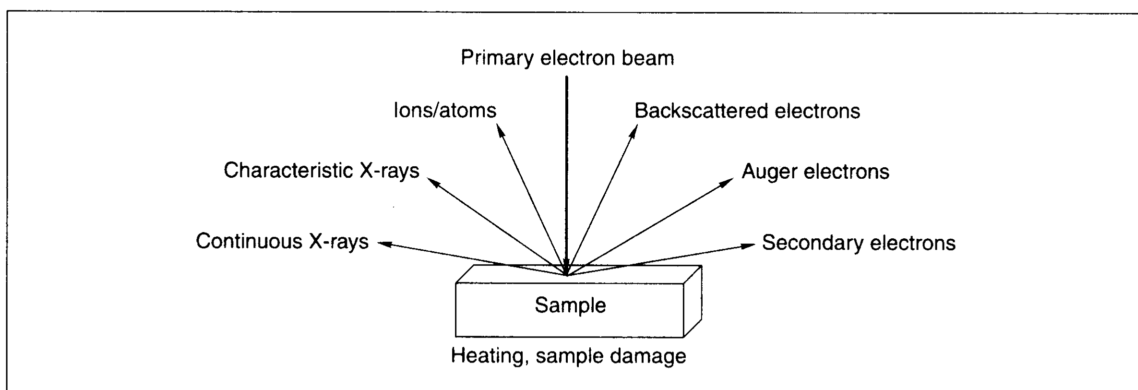


Fig. 2.6: *Electron beam-induced processes in the sample.*

Microanalysis

In both SEM and TEM, high spatial resolution microanalysis of materials is possible. The spatial resolution of the analysis is made possible by the small dimension of the excitation beam, which is of the order of a few nanometers in state-of-the-art instruments. The electron beam causes various excitations in the sample, which are characteristic of the elements present in the material. Characteristic X-rays emitted by the sample as a result of core hole decay can be used for elemental identification. The intensity of the signal can be used for quantitative analysis.

Microanalysis is done in two ways. One corresponds to the energy analysis called 'energy dispersive spectrometry' (EDS), while the other corresponds to wavelength analysis called 'wavelength dispersive spectrometry' (WDS). While improved energy resolution is possible in WDS, it is more cumbersome and time-consuming than EDS. In EDS, a signal from the detector is proportional to both the energy and intensity of the X-rays. In WDS, the wavelength and intensity of the X-ray are determined separately.

When an electron approaches the atom, it gets decelerated due to the coulombic field. This results in a loss of energy for the electron and that energy appears as photon, referred to as bremsstrahlung or 'breaking radiation'. This radiation contains photons of all energies till the energy of the original electron, as an electron can lose any energy, from zero to the energy of the primary electrons. The characteristic X-rays emitted by the atoms will appear as spikes on this large, smoothly varying photon intensity. There are several characteristic X-ray lines with which an atom can be identified. The intensities of these lines can be related to the concentrations of the emitting species in the sample, though various parameters determine the intensities. The important aspects related to X-ray emission intensity are, inner shell ionization cross section, X-ray absorption cross section of materials and X-ray production range.