

Characterization of Materials (MT 606)

MME 6th SEMESTER 2021
National Institute of Foundry and Forge



DR TAPABRATA MAITY (ASSISTANT PROFESSOR)

CHAPTER ONE

SOME CHARACTERIZATION TECHNIQUES



Scanning Electron Microscopy (SEM)

1.2.2

The Scanning Electron Microscope (SEM) is often the first analytical instrument used when a “quick look” at a material is required and the light microscope no longer provides adequate resolution. In the SEM an electron beam is focused into a fine probe and subsequently raster scanned over a small rectangular area. As the beam interacts with the sample it creates various signals (secondary electrons, internal currents, photon emission, etc.), all of which can be appropriately detected. These signals are highly localized to the area directly under the beam. By using these signals to modulate the brightness of a cathode ray tube, which is raster scanned in synchronism with the electron beam, an image is formed on the screen. This image is highly magnified and usually has the “look” of a traditional microscopic image but with a much greater depth of field. With ancillary detectors, the instrument is capable of elemental analysis.

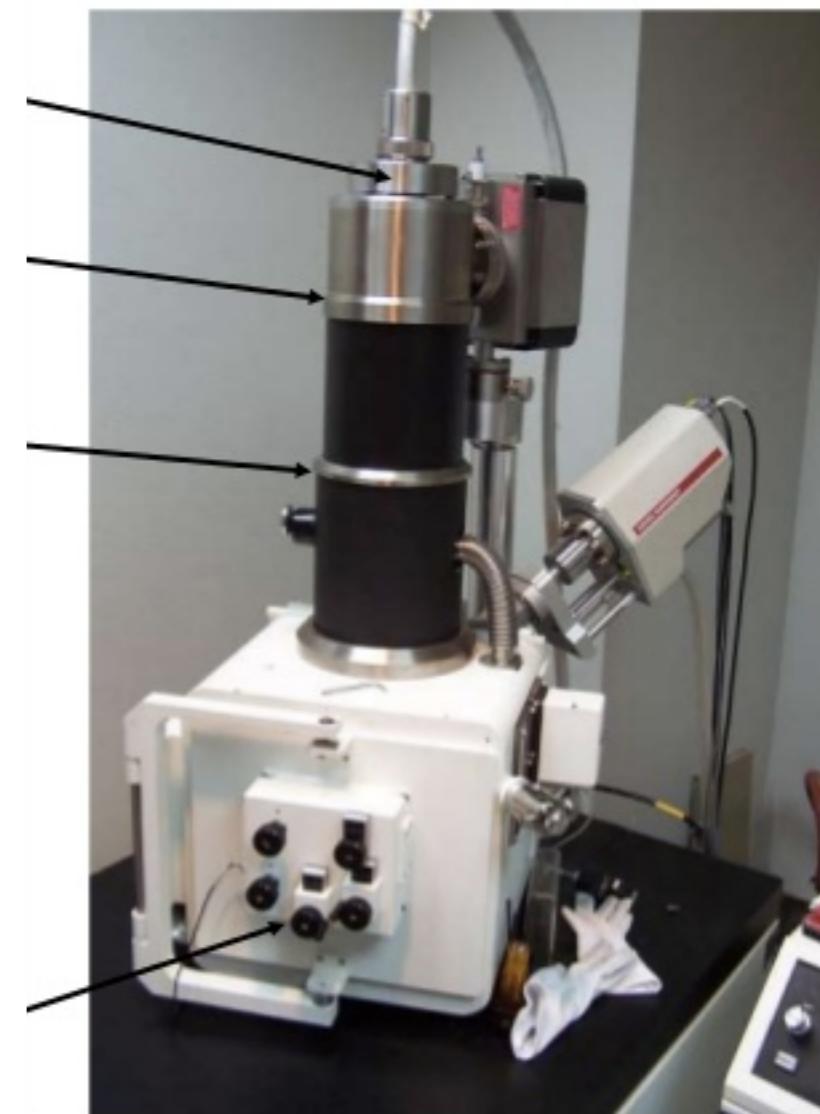
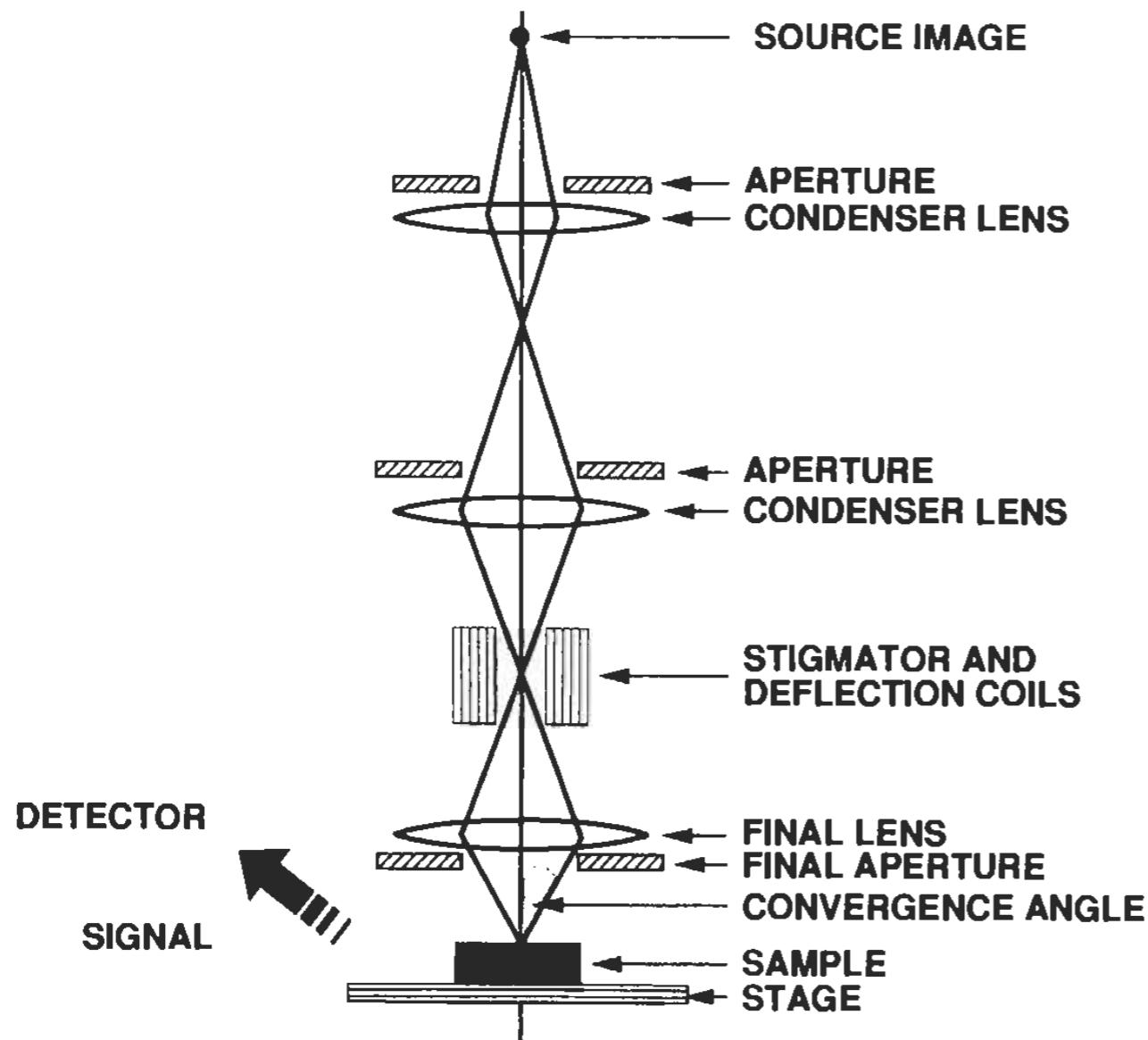
Main use	High magnification imaging and composition (elemental) mapping
Destructive	No, some electron beam damage
Magnification range	10×–300,000×; 5000×–100,000× is the typical operating range
Beam energy range	500 eV–50 keV; typically, 20–30 keV
Sample requirements	Minimal, occasionally must be coated with a conducting film; must be vacuum compatible
Sample size	Less than 0.1mm, up to 10 cm or more
Lateral resolution	1–50 nm in secondary electron mode
Depth sampled	Varies from a few nm to a few μm , depending upon the accelerating voltage and the mode of analysis
Bonding information	No
Depth profiling capabilities	Only indirect
Instrument cost	\$100,000–\$300,000 is typical

Electronics console 3 ft. \times 5 ft.; electron beam column
3 ft. \times 3 ft.



CHARACTERIZATION OF MATERIALS

Scanning electron microscopy



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Figure 4 Schematic of the electron optics constituting the SEM.

In Transmission Electron Microscopy (TEM) a thin solid specimen (≤ 200 nm thick) is bombarded in vacuum with a highly-focused, monoenergetic beam of electrons. The beam is of sufficient energy to propagate through the specimen. A series of electromagnetic lenses then magnifies this transmitted electron signal. Diffracted electrons are observed in the form of a diffraction pattern beneath the specimen. This information is used to determine the atomic structure of the material in the sample. Transmitted electrons form images from small regions of sample that contain contrast, due to several scattering mechanisms associated with interactions between electrons and the atomic constituents of the sample. Analysis of transmitted electron images yields information both about atomic structure and about defects present in the material.

Range of elements	TEM does not specifically identify elements measured
Destructive	Yes, during specimen preparation
Chemical bonding information	Sometimes, indirectly from diffraction and image simulation
Quantification	Yes, atomic structures by diffraction; defect characterization by systematic image analysis
Accuracy	Lattice parameters to four significant figures using convergent beam diffraction
Detection limits	One monolayer for relatively high-Z materials
Depth resolution	None, except there are techniques that measure sample thickness
Lateral resolution	Better than 0.2 nm on some instruments
Imaging/mapping	Yes
Sample requirements	Solid conductors and coated insulators. Typically 3-mm diameter, < 200 -nm thick in the center
Main uses	Atomic structure and Microstructural analysis of solid materials, providing high lateral resolution
Instrument cost	\$300,000–\$1,500,000
Size	100 ft. ² to a major lab

Scanning electron microscopy

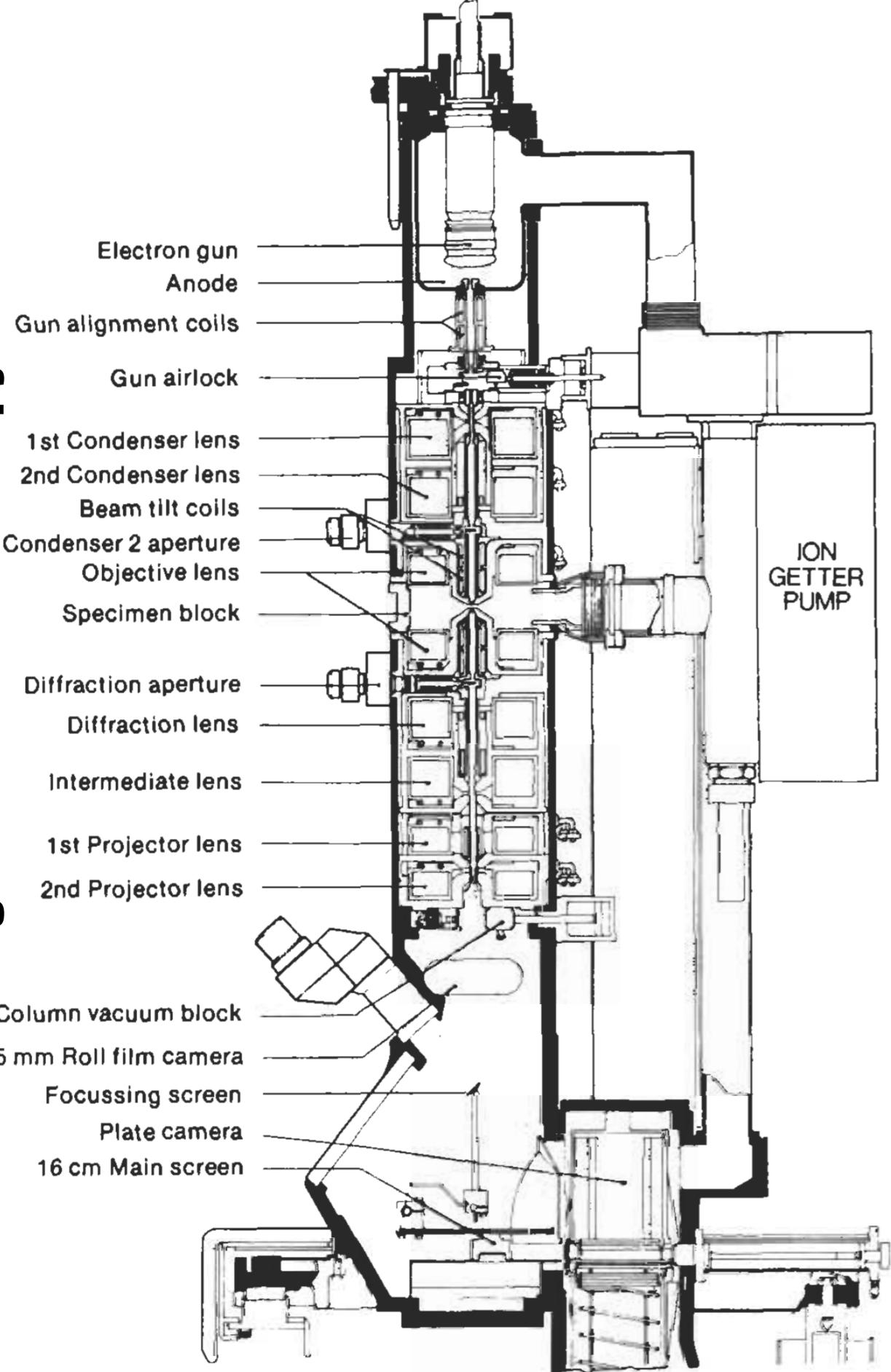
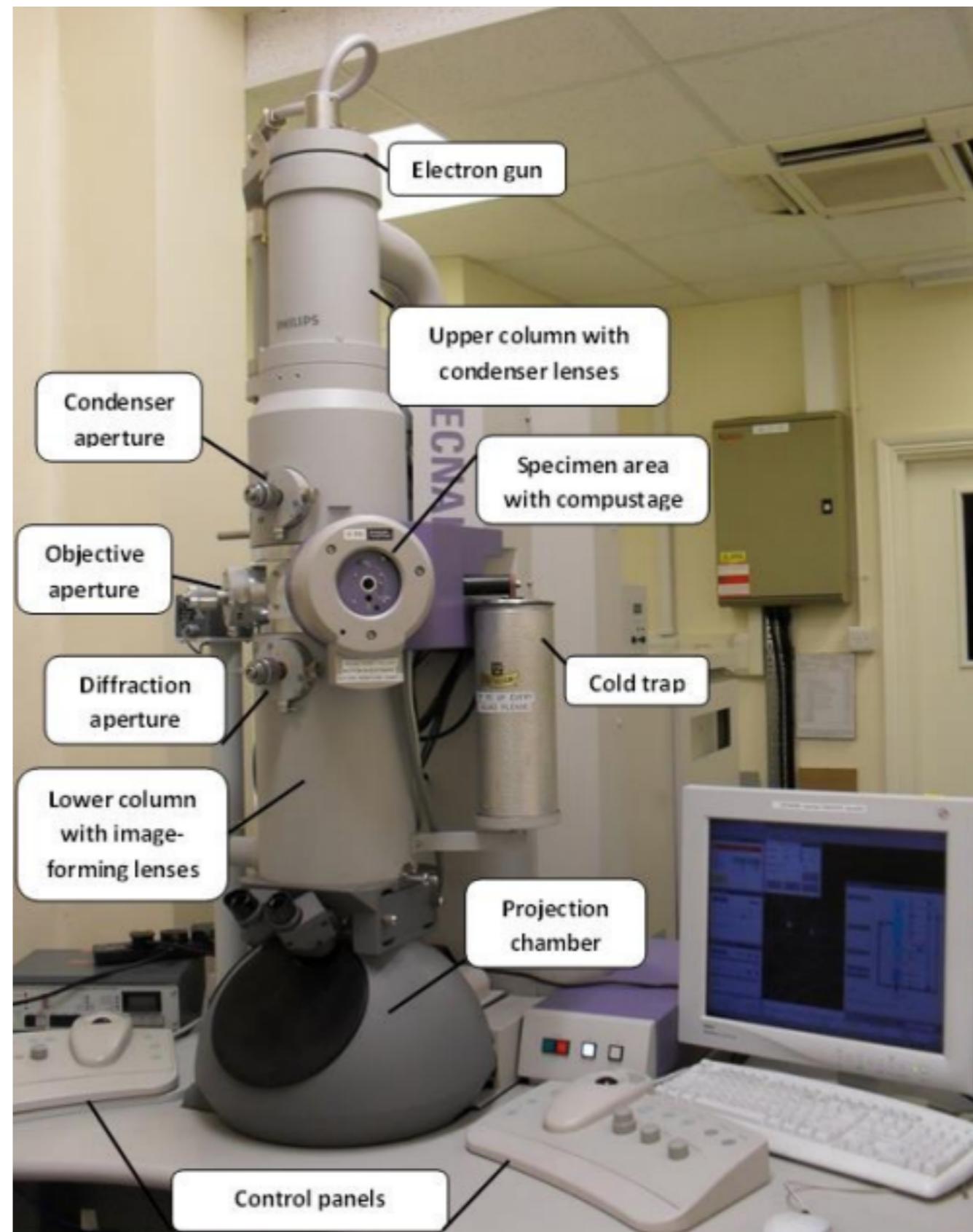


Figure 1a

Schematic diagram of a TEM instrument, showing the location of a thin sample and the principal lenses within a TEM column.



When the atoms in a material are ionized by a high-energy radiation they emit characteristic X rays. EDS is an acronym describing a technique of X-ray spectroscopy that is based on the collection and energy dispersion of characteristic X rays. An EDS system consists of a source of high-energy radiation, usually electrons; a sample; a solid state detector, usually made from lithium-drifted silicon, Si (Li); and signal processing electronics. EDS spectrometers are most frequently attached to electron column instruments. X rays that enter the Si (Li) detector are converted into signals which can be processed by the electronics into an X-ray energy histogram. This X-ray spectrum consists of a series of peaks representative of the type and relative amount of each element in the sample. The number of counts in each peak may be further converted into elemental weight concentration either by comparison with standards or by standardless calculations.

Range of elements	Boron to uranium
Destructive	No
Chemical bonding information	Not readily available
Quantification	Best with standards, although standardless methods are widely used
Accuracy	Nominally 4–5%, relative, for concentrations > 5% wt.
Detection limits	100–200 ppm for isolated peaks in elements with $Z > 11$, 1–2% wt. for low-Z and overlapped peaks
Lateral resolution	.5–1 μm for bulk samples; as small as 1 nm for thin samples in STEM
Depth sampled	0.02 to μm , depending on Z and keV
Imaging/mapping	In SEM, EPMA, and STEM
Sample requirements	Solids, powders, and composites; size limited only by the stage in SEM, EPMA and XRF; liquids in XRF; 3 mm diameter thin foils in TEM
Main use	To add analytical capability to SEM, EPMA and TEM

Scanning Transmission Electron Microscopy (STEM)

1.3.4

In Scanning Transmission Electron Microscopy (STEM) a solid specimen, 5–500 nm thick, is bombarded in vacuum by a beam (0.3–50 nm in diameter) of monoenergetic electrons. STEM images are formed by scanning this beam in a raster across the specimen and collecting the transmitted or scattered electrons. Compared to the TEM an advantage of the STEM is that many signals may be collected simultaneously: bright- and dark-field images; Convergent Beam Electron Diffraction (CBED) patterns for structure analysis; and energy-dispersive X-Ray Spectrometry (EDS) and Electron Energy-Loss Spectrometry (EELS) signals for compositional analysis. Taken together, these analysis techniques are termed Analytical Electron Microscopy (AEM). STEM provides about 100 times better spatial resolution of analysis than conventional TEM. When electrons scattered into high angles are collected, extremely high-resolution images of atomic planes and even individual heavy atoms may be obtained.

Range of elements	Lithium to uranium
Destructive	Yes, during specimen preparation
Chemical bonding information	Sometimes, from EELS
Quantification	Quantitative compositional analysis from EDS or EELS, and crystal structure analysis from CBED
Accuracy	5–10% relative for EDS and EELS
Detection limits	0.1–3.0% wt. for EDS and EELS
Lateral resolution	Imaging, 0.2–10 nm; EELS, 0.5–10 nm; EDS, 3–30 nm
Imaging/mapping capabilities	Yes, lateral resolution down to < 5 nm
Sample requirements	Solid conductors and coated insulators typically 3 mm in diameter and < 200 nm thick at the analysis point for imaging and EDS, but < 50 nm thick for EELS
Main uses	Microstructural, crystallographic, and compositional analysis; high spatial resolution with good elemental detection and accuracy; unique structural analysis with CBED
Instrument cost	\$500,000–\$2,000,000

Scanning transmission electron microscopy

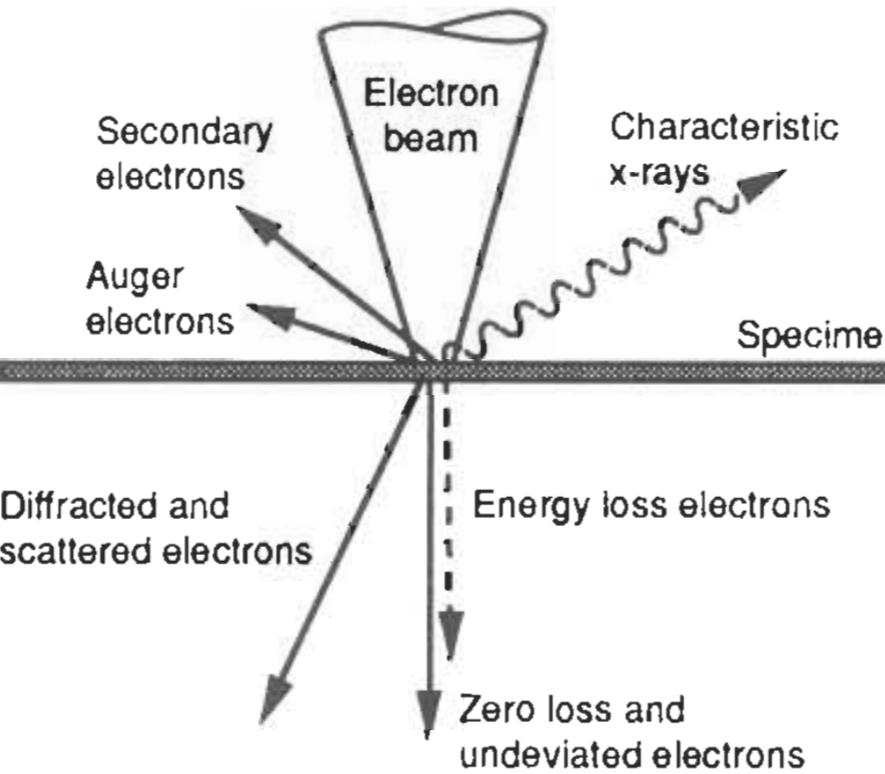


Figure 1 Signals generated when the focussed electron beam interacts with a thin specimen in a scanning transmission electron microscope (STEM).

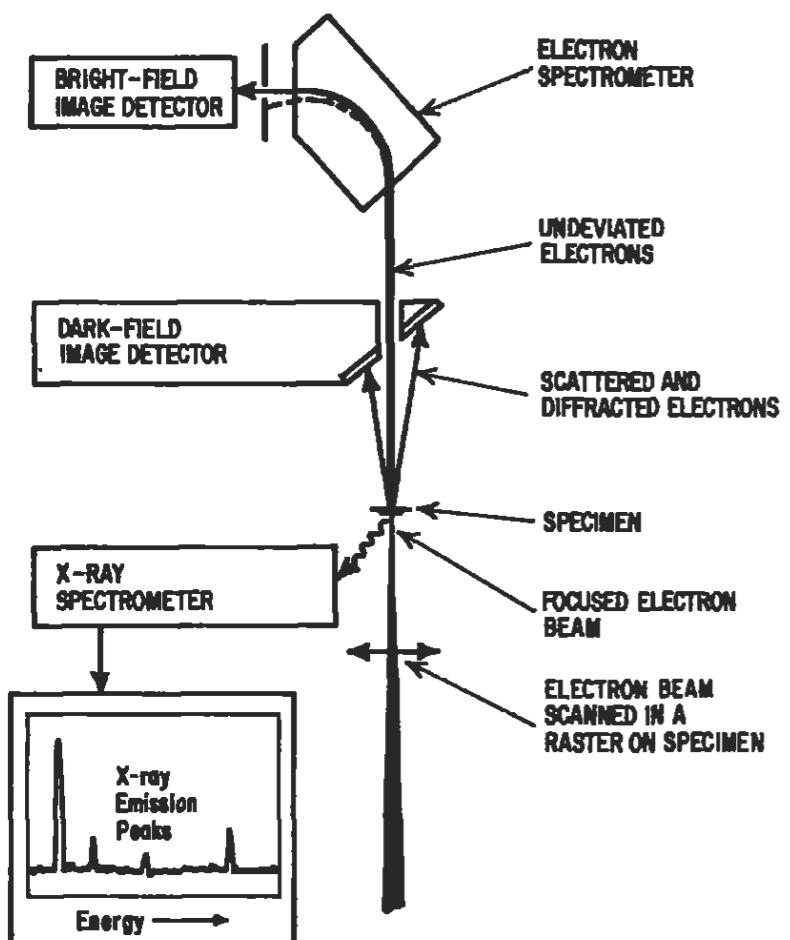


Figure 2 Schematic of a STEM instrument showing the principal signal detectors. The electron gun and lenses at the bottom of the figure are not shown.

In X-Ray Diffraction (XRD) a collimated beam of X rays, with wavelength $\lambda \sim 0.5\text{--}2 \text{ \AA}$, is incident on a specimen and is diffracted by the crystalline phases in the specimen according to Bragg's law ($\lambda = 2d \sin \theta$, where d is the spacing between atomic planes in the crystalline phase). The intensity of the diffracted X rays is measured as a function of the diffraction angle 2θ and the specimen's orientation. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties, including strain (which is measured with great accuracy), epitaxy, and the size and orientation of crystallites (small crystalline regions). XRD can also determine concentration profiles, film thicknesses, and atomic arrangements in amorphous materials and multilayers. It also can characterize defects. To obtain this structural and physical information from thin films, XRD instruments and techniques are designed to maximize the diffracted X-ray intensities, since the diffracting power of thin films is small.

Range of elements	All, but not element specific. Low-Z elements may be difficult to detect
Probing depth	Typically a few μm but material dependent; monolayer sensitivity with synchrotron radiation
Detection Limits	Material dependent, but $\sim 3\%$ in a two phase mixture; with synchrotron radiation can be $\sim 0.1\%$
Destructive	No, for most materials
Depth profiling	Normally no; but this can be achieved.
Sample requirements	Any material, greater than $\sim 0.5 \text{ cm}$, although smaller with microfocus
Lateral resolution	Normally none; although $\sim 10 \mu\text{m}$ with microfocus
Main use	Identification of crystalline phases; determination of strain, and crystallite orientation and size; accurate determination of atomic arrangements
Specialized uses	Defect imaging and characterization; atomic arrangements in amorphous materials and multilayers; concentration profiles with depth; film thickness measurements
Instrument cost	\$70,000–\$200,000
Size	Varies with instrument, greater than $\sim 70 \text{ ft}^2$

basic feature of typical XRD equipment

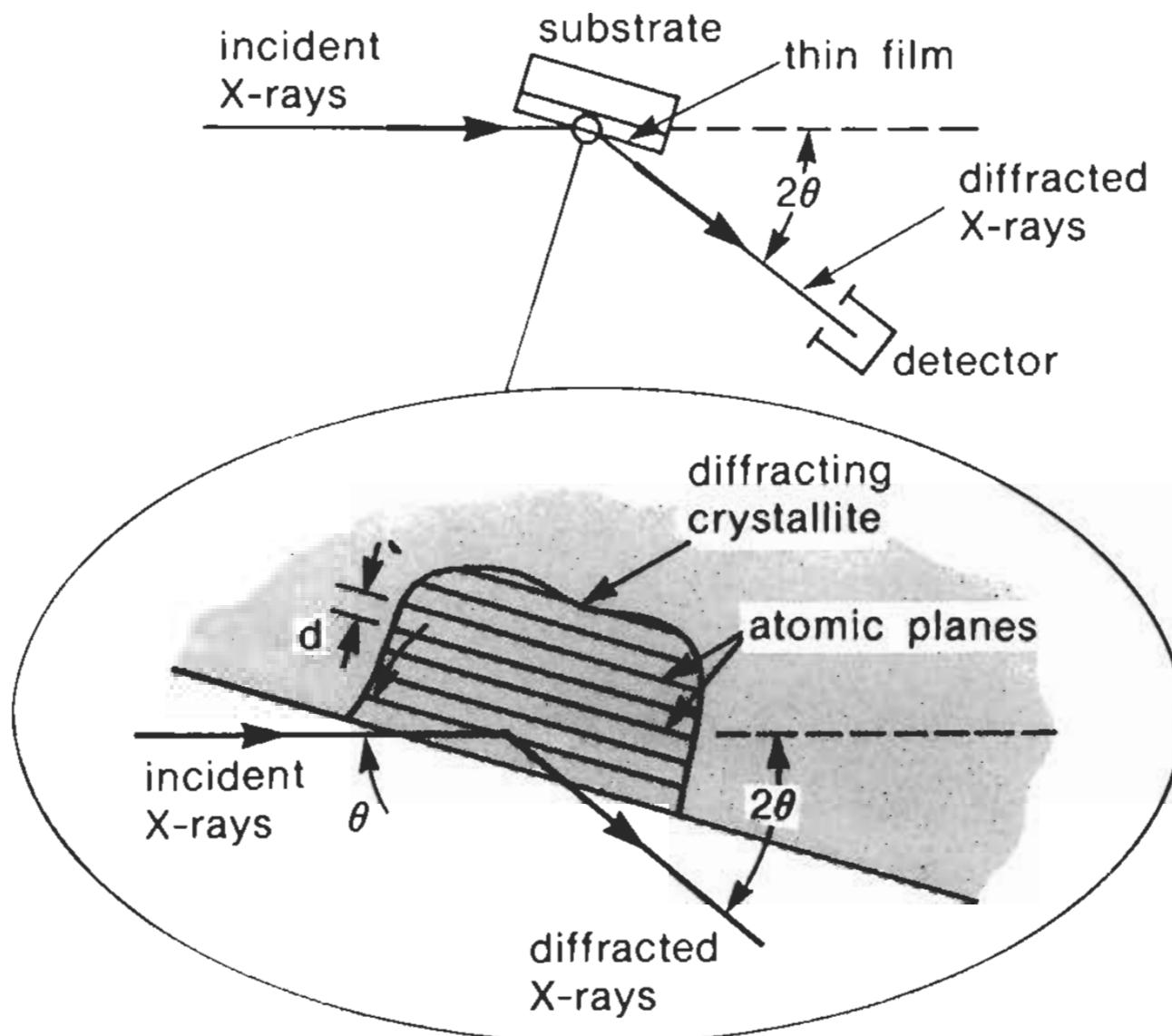


Figure 1 Basic features of a typical XRD experiment.

X-Ray Photoelectron and Auger Electron Diffraction (XPD and AED)

1.4.4

In X-Ray Photoelectron Diffraction (XPD) and Auger Electron Diffraction (AED), a single crystal or a textured polycrystalline sample is struck by photons or electrons to produce outgoing electrons that contain surface chemical and structural information. The focus of XPD and AED is structural information, which originates from interference effects as the outbound electrons from a particular atom are scattered by neighboring atoms in the solid. The electron–atom scattering process strongly increases the electron intensity in the forward direction, leading to the simple observation that intensity maxima occur in directions corresponding to rows of atoms. An energy dispersive angle-resolved analyzer is used to map the intensity distribution as a function of angle for elements of interest.

Range of elements	All except H and He
Destructive	XPD no; AED may cause e-beam damage
Element specific	Yes
Chemical state specific	Yes, XPD is better than AED
Accuracy	Bond angles to within 1°; atomic positions to within 0.05 Å
Site symmetry	Yes, and usually quickly
Depth Probed	5–50 Å
Depth profiling	Yes, to 30 Å beneath the surface
Detection limits	0.2 at.%
Lateral resolution	150 Å (AED), 150 µm (XPD)
Imaging/mapping	Yes
Sample requirements	Primarily single crystals, but also textured samples
Main use	To determine adsorption sites and thin-film growth modes in a chemically specific manner
Instrument cost	\$300,000–\$600,000
Size	4 m × 4 m × 3 m

Auger Electron Spectroscopy (AES) uses a focused electron beam to create secondary electrons near the surface of a solid sample. Some of these (the Auger electrons) have energies characteristic of the elements and, in many cases, of the chemical bonding of the atoms from which they are released. Because of their characteristic energies and the shallow depth from which they escape without energy loss, Auger electrons are able to characterize the elemental composition and, at times, the chemistry of the surfaces of samples. When used in combination with ion sputtering to gradually remove the surface, Auger spectroscopy can similarly characterize the sample in depth. The high spacial resolution of the electron beam and the process allows microanalysis of three-dimensional regions of solid samples. AES has the attributes of high lateral resolution, relatively high sensitivity, standardless semi-quantitative analysis, and chemical bonding information in some cases.

Range of elements	All except H and He
Destructive	No, except to electron beam-sensitive materials and during depth profiling
Elemental Analysis	Yes, semiquantitative without standards; quantitative with standards
Absolute sensitivity	100 ppm for most elements, depending on the matrix
Chemical state information?	Yes, in many materials
Depth probed	5–100 Å
Depth profiling	Yes, in combination with ion-beam sputtering
Lateral resolution	300 Å for Auger analysis, even less for imaging
Imaging/mapping	Yes, called Scanning Auger Microscopy, SAM
Sample requirements	Vacuum-compatible materials
Main use	Elemental composition of inorganic materials
Instrument cost	\$100,000–\$800,000
Size	10 ft. × 15 ft.

In X-Ray Fluorescence (XRF), an X-ray beam is used to irradiate a specimen, and the emitted fluorescent X rays are analyzed with a crystal spectrometer and scintillation or proportional counter. The fluorescent radiation normally is diffracted by a crystal at different angles to separate the X-ray wavelengths and therefore to identify the elements; concentrations are determined from the peak intensities. For thin films XRF intensity–composition–thickness equations derived from first principles are used for the precision determination of composition and thickness. This can be done also for each individual layer of multiple-layer films.

Range of elements	All but low- <i>Z</i> elements: H, He, and Li
Accuracy	±1% for composition, ±3% for thickness
Destructive	No
Depth sampled	Normally in the 10-μm range, but can be a few tens of Å in the total-reflection range
Depth profiling	Normally no, but possible using variable-incidence X rays
Detection limits	Normally 0.1% in concentration.
Sensitivity	10–10 ⁵ Å in thickness can be examined
Lateral resolution	Normally none, but down to 10 μm using a microbeam
Chemical bond information	Normally no, but can be obtained from soft X-ray spectra
Sample requirements	≤5.0 cm in diameter
Main use	Identification of elements; determination of composition and thickness
Instrument cost	\$50,000–\$300,000
Size	5 ft. × 8 ft.

Diffraction is a technique that uses interference of short wavelength particles (such as neutrons or electrons) or photons (X or γ rays) reflected from planes of atoms in crystalline materials to yield three-dimensional structural information at the atomic level. Neutron diffraction, like X-ray diffraction is a nondestructive technique that can be used for atomically resolved structure determination and refinement, phase identification and quantification, residual stress measurements, and average particle-size determination of crystalline materials. The major advantages of neutron diffraction compared to other diffraction techniques, namely the extraordinarily greater penetrating nature of the neutron and its direct interaction with nuclei, lead to its use in measurements under special environments, experiments on materials requiring a depth of penetration greater than about 50 μm , or structure refinements of phases containing atoms of widely varying atomic numbers.

Range of elements	All elements detected approximately equally, except vanadium
Destructive	No
Bonding information	No
Depth probed	Yields bulk information of macro-sized samples (thin films for determining magnetic ordering)
Lateral resolution	None
Quantitation	Can be used to quantify crystalline phases
Structural accuracy	Atomic positions to 10^{-13} m, accuracy of phase quantitation ~1% molar
Imaging capabilities	None to date
Sample requirements	Material must be crystalline at data collection temperatures
Main uses	Atomic structure refinements or determinations and residual stress measurements, all in bulk materials
Instrument cost	Instruments are at government-funded facilities; cost for proprietary experiments \$1000–\$9000 per day

In Scanning Tunneling Microscopy (STM) or Scanning Force Microscopy (SFM), a solid specimen in air, liquid or vacuum is scanned by a sharp tip located within a few Å of the surface. In STM, a quantum-mechanical tunneling current flows between atoms on the surface and those on the tip. In SFM, also known as Atomic Force Microscopy (AFM), interatomic forces between the atoms on the surface and those on the tip cause the deflection of a microfabricated cantilever. Because the magnitude of the tunneling current or cantilever deflection depends strongly upon the separation between the surface and tip atoms, they can be used to map out surface topography with atomic resolution in all three dimensions. The tunneling current in STM is also a function of local electronic structure so that atomic-scale spectroscopy is possible. Both STM and SFM are unsurpassed as high-resolution, three-dimensional profilometers.

Parameters measured Surface topography (SFM and STM); local electronic structure (STM)

Destructive No

Vertical resolution STM, 0.01 Å; SFM, 0.1 Å

Lateral resolution STM, atomic; SFM, atomic to 1 nm

Quantification Yes; three-dimensional

Accuracy Better than 10% in distance

Imaging/mapping Yes

Field of view From atoms to > 250 μm

Sample requirements STM—solid conductors and semiconductors, conductive coating required for insulators; SFM—solid conductors, semiconductors and insulators

Main uses Real-space three-dimensional imaging in air, vacuum, or solution with unsurpassed resolution; high-resolution profilometry; imaging of nonconductors (SFM).

Instrument cost \$65,000 (ambient) to \$200,000 (ultrahigh vacuum)

Size Table-top (ambient), 2.27–12 inch bolt-on flange
(ultrahigh vacuum)



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CHAPTER TWO

SCANNING ELECTRON MICROSCOPE



The Scanning Electron Microscope (SEM) is often the first analytical instrument used when a “quick look” at a material is required and the light microscope no longer provides adequate resolution. In the SEM an electron beam is focused into a fine probe and subsequently raster scanned over a small rectangular area. As the beam interacts with the sample it creates various signals (secondary electrons, internal currents, photon emission, etc.), all of which can be appropriately detected. These signals are highly localized to the area directly under the beam. By using these signals to modulate the brightness of a cathode ray tube, which is raster scanned in synchronism with the electron beam, an image is formed on the screen. This image is highly magnified and usually has the “look” of a traditional microscopic image but with a much greater depth of field. With ancillary detectors, the instrument is capable of elemental analysis.

Main use	High magnification imaging and composition (elemental) mapping
Destructive	No, some electron beam damage
Magnification range	10 \times –300,000 \times ; 5000 \times –100,000 \times is the typical operating range
Beam energy range	500 eV–50 keV; typically, 20–30 keV
Sample requirements	Minimal, occasionally must be coated with a conducting film; must be vacuum compatible
Sample size	Less than 0.1 mm, up to 10 cm or more
Lateral resolution	1–50 nm in secondary electron mode
Depth sampled	Varies from a few nm to a few μm , depending upon the accelerating voltage and the mode of analysis
Bonding information	No
Depth profiling capabilities	Only indirect
Instrument cost	\$100,000–\$300,000 is typical
Size	Electronics console 3 ft. \times 5 ft.; electron beam column 3 ft. \times 3 ft.

Schematic diagram of a SEM



Figure 5.1 Scanning electron micrograph of the surface of a nickel alloy containing dendritic (tree shaped) particles of silica.

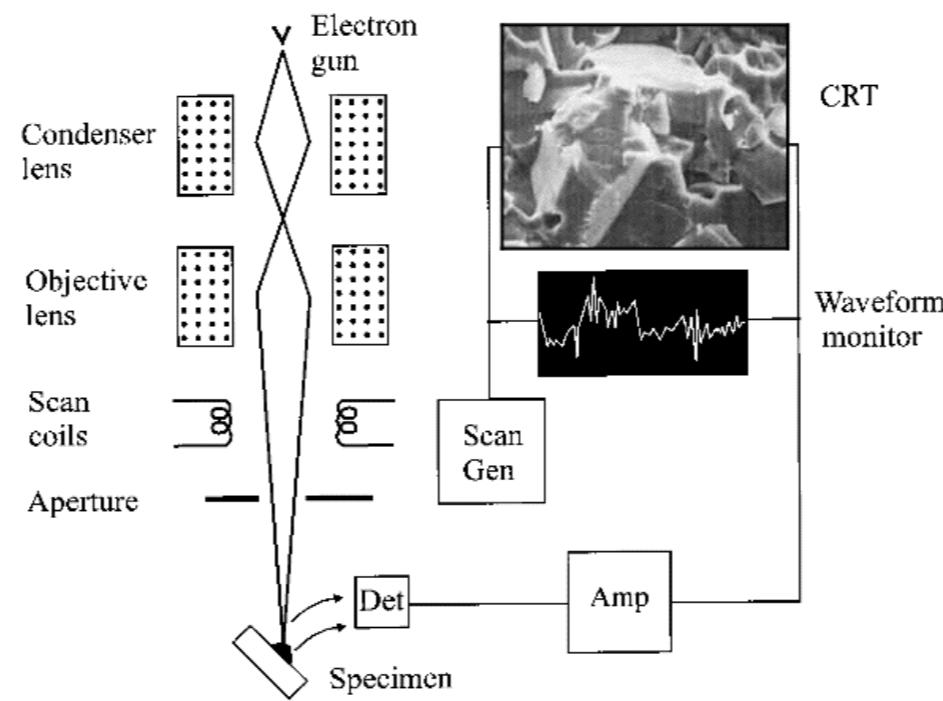


Figure 5.2 Schematic diagram showing the main components of a scanning electron microscope.

Signal which may be used in the SEM

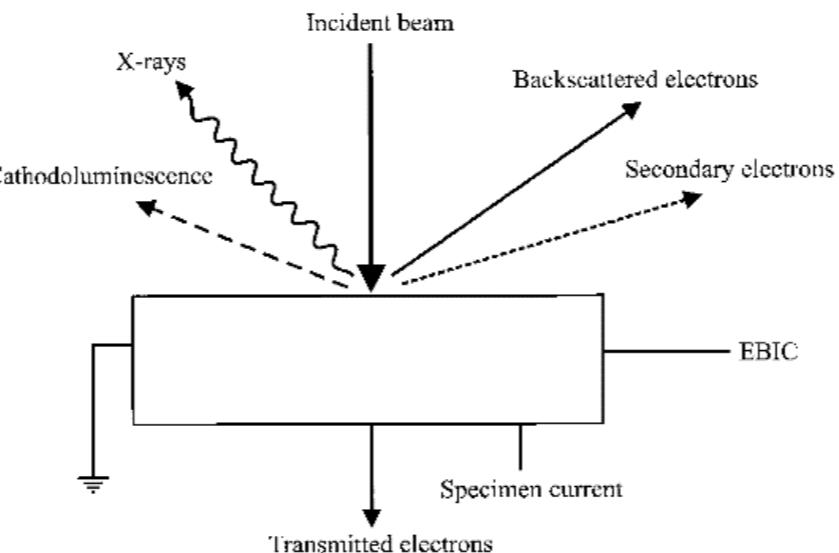


Figure 5.5 Some of the signals which may be used in the SEM.

Figure 5.5 shows schematically some of the signals which may be used in the SEM.

All scanning electron microscopes normally have facilities for detecting *secondary electrons* and *backscattered electrons*, and we will discuss their detection below. Of the other radiations, X-rays are used primarily for chemical analysis rather than imaging, and will be discussed in detail in Chapter 6. Auger electrons are of such low energy, and are so easily absorbed that they require an ultra high vacuum system and specialized equipment for their efficient use. Auger spectroscopy and the scanning Auger microscope are important surface analytical techniques which will be discussed in Chapter 7. The other signals have important but more specialized applications, and we will discuss them later in this chapter.

We discussed the trajectory of an electron through a solid in Chapter 2. Monte Carlo simulations such as that shown in Figure 2.5, and also direct experiments, have shown that the electrons are scattered in the specimen within a region such as that shown in Figure 5.6.

Interaction volume X

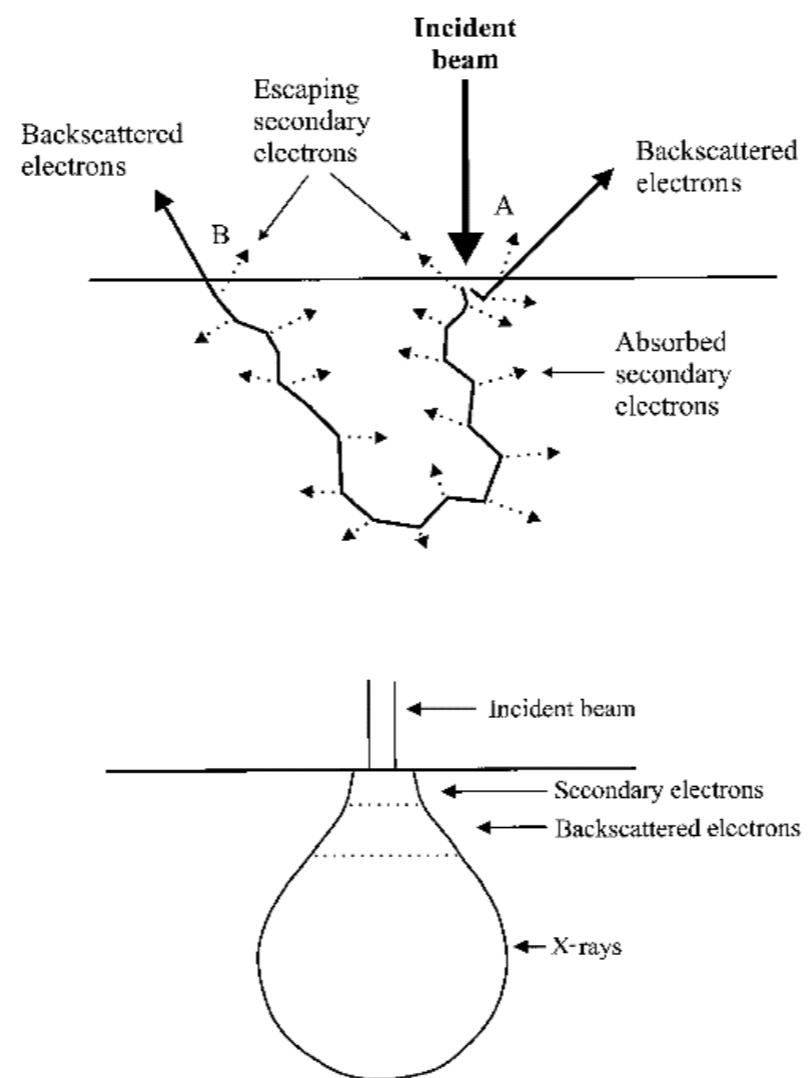


Figure 5.6 The interaction volume and the regions from which secondary electrons, backscattered electrons, and X-rays may be detected.

The region into which the electrons penetrate the specimen is known as the interaction volume, and throughout it, the various radiations are generated as a result of inelastic scattering, although as the primary electrons lose energy the amount and type of the secondary radiations will alter.

Even though radiation is generated within this volume, it will not be detected unless it escapes from the specimen, and this will depend on the radiation and the specimen. Thus, X-rays are not easily absorbed, and most will escape from the specimen. Therefore, as will be discussed in more detail in Chapter 6, the volume of material contributing to the X-ray signal, or *sampling volume*, is of the same order as the interaction volume, which may be several micrometres in diameter. Electrons will not be backscattered out of the specimen if they have penetrated more than a fraction of a micrometre, and the backscattered signal

If the electron yield is not equal to unity, then unless the sample is a conductor, it will tend to become charged during examination as discussed in section 5.11. Figure 5.8(b) indicates that careful control of the accelerating voltage can produce an electron yield of unity which will overcome this effect (see section 5.11).

5.2.1 Detecting secondary electrons

By far the most widely used signal in the scanning electron microscope is that from secondary electrons. Secondary electrons are detected by a scintillator–photomultiplier system known as the Everhart–Thornley detector. The detector is shown schematically in Figure 5.9.

The secondary electrons strike a scintillator, e.g. a phosphor, which then emits light. The light is transmitted through a light pipe, and into a photomultiplier which converts the photons into pulses of electrons, which may then be amplified and used to modulate the intensity of the CRT.

The energy of the secondary electrons (10–50 eV) is too low to excite the scintillator, and so they are first accelerated by applying a bias voltage of $\sim +10\text{ keV}$ to a thin aluminium film covering the scintillator. A metal grid or collector, at a potential of several hundred volts, surrounds the scintillator and this has two purposes. First it prevents the high voltage of the scintillator affecting the incident electron beam, and secondly, it improves the collection efficiency by attracting secondary electrons, and thus collecting even those which were initially not moving towards the detector, as shown in

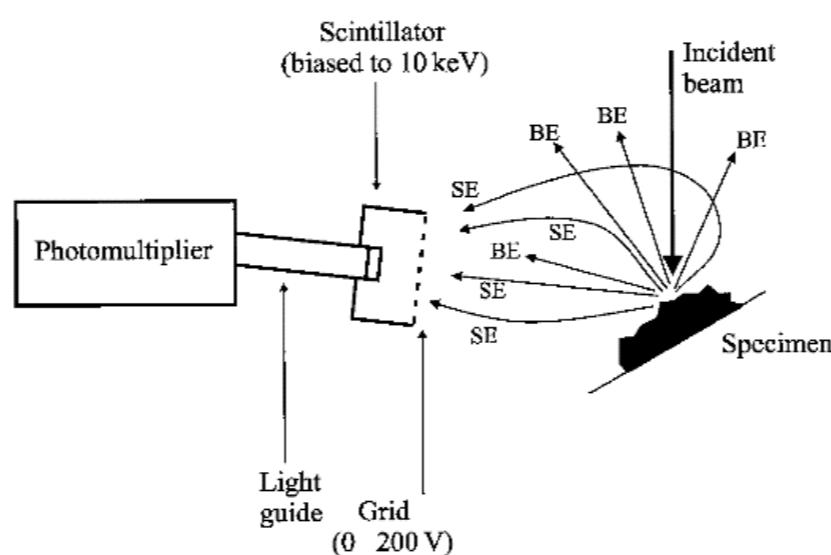


Figure 5.9 Schematic representation of the Everhart–Thornley secondary electron detector, showing the paths of secondary (SE) and backscattered (BE) electrons.

Figure 5.9. The Everhart–Thornley detector system is very efficient, and for flat specimens, almost all the secondary electrons are collected.

5.2.2 Detecting backscattered electrons

Backscattered electrons which are travelling in the appropriate direction will of course hit the scintillator of the Everhart–Thornley detector and be detected. Therefore we should note that the signal discussed in the previous section is not purely due to secondary electrons as it does contain a small backscattered component. If the scintillator bias is switched off, or the collector given a small negative voltage, then secondaries are excluded from the detector, and the backscattered signal is obtained. However, only those electrons travelling along the direct line of sight towards the detector will be collected, and thus the geometric efficiency is very low. This method of detection is now rarely used, and most microscopes are fitted with purpose built backscattered electron detectors, which can be of three types.

Scintillator detectors

These detectors are of the scintillator/light pipe/photomultiplier type, and are designed to maximize the solid angle of collection. A good example of this is the Robinson detector shown schematically in Figure 5.10(a). The advantage of these detectors is their rapid response time, which means that, like the Everhart–Thornley detector, they may be used in conjunction with rapid scan rates. However, they are bulky, and may restrict the working distance of the microscope, and may need to be retracted if, for example, it is necessary to detect X-rays.

Solid-state detectors

When a high-energy electron impinges on a semiconductor, it produces many electron-hole pairs. Normally these will rapidly recombine, but if a voltage is applied to the semiconductor, for example, by the self-bias generated by a P–N junction, then they may be separated, thus producing a current, which can subsequently be amplified. Figure 5.10(b) is a schematic diagram of such a detector. The detector is usually in the form of a thin flat plate, which is mounted on the objective polepiece, and thus does not interfere with normal operation of the instrument. The detector consists of up to four such elements whose outputs may be measured independently. The main disadvantage of a solid-state detector is its relatively slow response time, and hence its unsuitability for rapid scan rates.

Detecting backscattered electrons

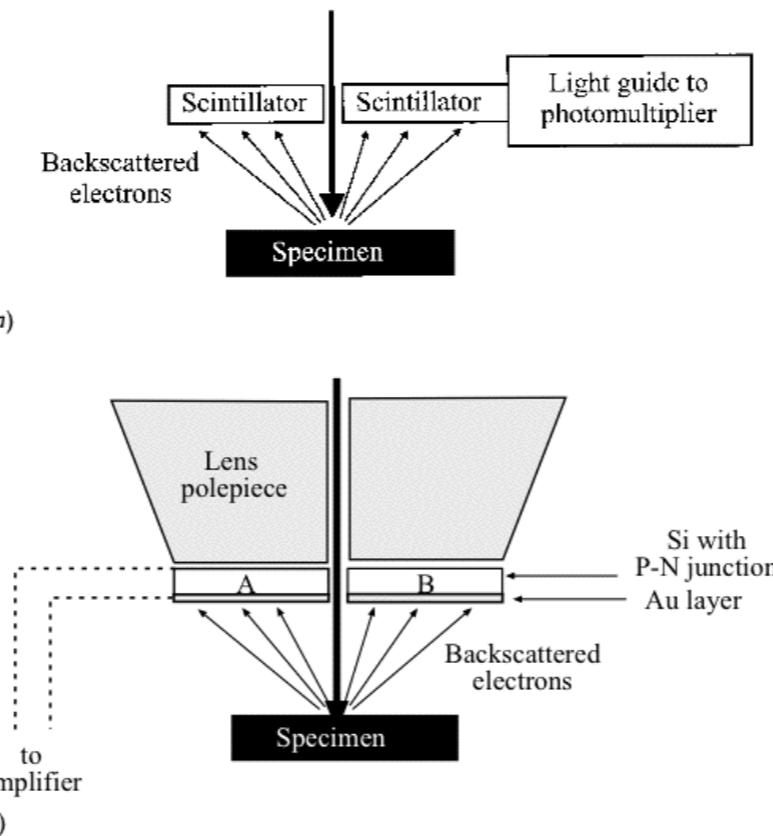


Figure 5.10 (a) A large area, Robinson type scintillator detector. (b) A solid state silicon detector with two elements A and B.

Through-the-lens detectors

In high resolution SEMs a different type of electron detection system is sometimes used. Such instruments have specially designed objective lenses with very large magnetic fields and low spherical aberration and the sample may be placed within the strong magnetic field of the lens. A scintillator detector is placed within the lens and backscattered and secondary electrons pass upwards through the lens to this detector. Such a system has a very good collection efficiency and allows the microscope to operate at very short working distances. However in some instruments such an arrangement places severe restrictions on the size and movement of the sample.

5.3 The optics of the SEM

The purpose of the lenses in the SEM is to produce a fine beam of electrons incident on the specimen. Figure 5.11 is a simplified ray diagram of a microscope which has two lenses, a condenser lens and an objective lens. We can understand the main features of the microscope by treating the electromagnetic

Electromagnetic fields are also used to deflect the entire beam of electrons, for example to scan the beam back and forth in a scanning electron microscope. For these applications the field needs to be perpendicular to the electron beam, but much smaller fields suffice for these smaller deflections so the coils are quite small. Most microscopes will contain a dozen or more such coils, designed to enable the microscopist to optimize the position of the beam in the column of the microscope.

The working of a typical lens, together with the operation of lenses and deflection coils, is demonstrated in the MATTER module ‘Introduction to Electron Microscopes’.

2.5 The scattering of electrons by atoms

In almost all types of electron microscope *primary* electrons enter the specimen and the same or different electrons leave it again to form the image. Consequently it is vitally important to understand the interactions which are possible between high energy electrons and the atoms of the specimen. Without this understanding it is not possible to interpret the image, diffraction pattern or analytical spectrum which each type of microscope produces.

There is a set of terminology common to all electron scattering and we will consider this first. The probability that a particular electron will be scattered in a particular way is usually described in terms either of a *cross-section*, σ , or of a *mean free path*, λ . A cross-section is expressed as the area which the scattering particle *appears* to present to the electron. If there are N particles per unit volume of the specimen and the cross-section for a particular scattering event is σ then the probability of a single electron being scattered in this way in its passage through a thickness dx of the specimen is $N\sigma dx$. An alternative way of expressing the same idea is to define the mean free path for the scattering as

$$\lambda = 1/N\sigma \quad (2.6)$$

λ has the dimension length and is effectively the *average* distance which an electron will travel before being scattered in the specified way.

Mean free paths for many scattering processes are similar to the thickness of a TEM specimen. This means that electrons will tend to be scattered either once or not at all while passing through a thin specimen. On the other hand if an electron is incident on a thick specimen (e.g. in an SEM) it will be scattered many times until it effectively comes to rest. The terms *single scattering*, *plural scattering* and *multiple scattering* are often used to describe the situations in which electrons are scattered no more than once, several times and many times respectively.

In single or plural scattering situations the probability of an incident electron suffering n scattering events while travelling a distance x is given by the Poisson equation

$$p(n) = (1/n!)(x/\lambda)^n \exp(-x/\lambda) \quad (2.7)$$

Thus the probability of an electron undergoing exactly two scattering events with a mean free path λ in a distance t is $p(2)$ and is given by

$$p(2) = (1/2)(t/\lambda)^2 \exp(-t/\lambda)$$

Notice that $p(0)$ is the probability of the electron not being scattered by this process and that $1 - p(0)$ is therefore the probability of it being scattered once or more.

The Poisson equation approach is not much use for multiple scattering, where all primary electrons can be assumed to be scattered very many times, possibly by several different mechanisms. In these cases other averaging approaches are more fruitful; one example, the Monte Carlo method, is illustrated in section 2.7.

2.6 Elastic scattering

Elastic scattering is defined as a process which, although it might change the direction of the primary electron, does not change its energy detectably. This type of scattering results from Coulombic interactions (i.e. involving electrostatic charges) between the primary electron and both the nucleus and all the electrons around it. This is known as Rutherford scattering and it gives rise to a strongly ‘forward peaked’ distribution of scattered electrons. If the energy of the primary electron is E_0 , the probability $p(\theta)$ of it being scattered through an angle θ is given by

$$p(\theta) \propto \frac{1}{E_0^2 \sin^4 \theta} \quad (2.8)$$

The probability of a small angle of scatter is very much greater than that of a large angle. Notice too that the probability of scattering through any angle decreases as the energy of the electron increases.

The mean free path for elastic scattering depends quite strongly on the atomic number of the scattering atom. To give an example for 100 kV electrons, λ is about 5 nm for gold (atomic number $Z = 79$) but about 150 nm for carbon ($Z = 6$).

Elastic scattering is important in electron microscopy because it is a major mechanism by which electrons are deflected and also because elastically scattered electrons are the main contributors to diffraction patterns. Most of Chapter 3 thus refers implicitly to elastic scattering. The strength of scattering by an atom depends on its atomic number and is usually described in terms of its atomic scattering factor, f . This is defined as the amplitude of scattering from the atom divided by the amplitude of scattering from a single electron.

Elastic scattering

2.7 Inelastic scattering

Inelastic scattering is a very general term which refers to any process which causes the primary electron to lose a detectable amount of energy, ΔE . In terms of the facilities usually available to electron microscopists, ΔE would need to be substantially more than 0.1 eV before it could be detected. There are many interaction processes which could cause energy to be lost by the primary electron and transferred to the electrons or atoms of the specimen. We will only consider four of the most probable types of scattering event. It is important to realize that the inelastic scattering processes (probably in combination) are eventually responsible for the stopping of an electron by a solid. Almost all of the kinetic energy which was carried by the primary electron will end up as heat in the specimen. A small proportion of the energy may escape as X-rays, light or secondary electrons and these may prove extremely useful for both imaging and analysis, as we show in Chapters 5 and 6. Secondary effects are dealt with in the next section; first let us consider the main types of inelastic scattering process.

2.7.1 Phonon scattering

Phonons are the quanta of elastic waves, that is of atomic vibrations in a solid. A primary electron can lose energy by exciting a phonon and effectively heating the solid slightly. The amount of energy lost in doing this is rather small, generally less than 1 eV, and the mean free path for high energy electrons is quite large, of the order of μm . These facts do not mean that phonon scattering is unimportant, for two main reasons. All electrons which remain in the solid are likely to excite phonons eventually, perhaps after they have lost larger amounts of energy by other means (see below) and this is how the solid is heated by the electron beam. Also, when phonon scattering occurs the scattered electron is generally deflected through quite a large angle, typically 10 degrees. This will be significant in the discussion of image contrast in Chapter 4.

2.7.2 Plasmon scattering

A plasmon is a wave in the ‘sea’ of electrons in the conduction band of a metal. There are similar effects among the bonding electrons of non-metals. In exciting a plasmon the primary beam loses 5–30 eV and the mean free path for this event is short – a few hundred nm in most materials. Consequently plasmon scattering is a frequent occurrence in all electron–solid interactions. We shall see in Chapter 6 that these energy losses dominate the ‘energy loss spectrum’ but are not very useful for analysis because the energy loss is not particularly characteristic of the scattering element. The Poisson equation (2.7) can be used to calculate how many plasmons an electron is likely to excite in traversing a thin specimen.

2.7.3 Single valence electron excitation

It is possible, but less likely, that a primary electron will transfer some energy to a single valence electron rather than to the ‘sea’ collectively. The mean free path for this process is quite large (μm), the energy loss is small (about 1 eV) and the typical scattering angle is also small so the process is not exploited in electron microscopy.

2.7.4 Inner shell excitation

A rare but valuable form of inelastic scattering is the knocking out of an inner shell electron. Because the binding energy of such K and L shell electrons may be high the energy lost by the primary electron can be quite large. For example it takes 283 eV to remove a carbon K electron, 69 508 eV to knock out a tungsten K and 1100 eV to excite a copper L. The mean free path for this type of scattering is quite large (μm), so the process occurs much less frequently than, say, plasmon scattering. However the secondary effects produced when the excited atom relaxes are almost ideal for analysis, as the next section shows. The cross-section for inner shell excitation, in common with that for most scattering processes, drops as the primary electron energy E_0 increases. It is also lower for elements of higher atomic number Z , since E_c (the critical energy to excite an X-ray) increases with Z and

$$\sigma \propto 1/E_c E_0 \quad (2.9)$$

2.7.5 Inelastic scattering and absorption

In all but the thinnest specimen it is clear that more than one of the inelastic scattering processes can take place. In a ‘solid’ specimen many such events will occur until the electron is stopped or leaves by the surface it entered. The trajectories of a few typical electrons, calculated by a Monte Carlo method which introduces the angles of scattering with their appropriate probabilities, are shown in Figure 2.6. It can be seen that the majority of electrons are brought to a halt within the solid but a few are *backscattered* and leave the specimen. The volume within which 95% or so of the primary electrons are brought to rest is generally referred to as the *interaction volume* and will be discussed in greater detail in Chapters 5 and 6. An interactive Monte Carlo simulation is available in the MATTER software module ‘Electron Beam – Specimen Interactions’.

In the case of a solid specimen it is clear what is meant by *absorption*. For a thin specimen, through which many or most of the electrons are eventually transmitted, the term has to be defined very carefully. The geometry of an electron detection system is typically like that shown in Figure 2.7. By ‘absorbed’ we mean ‘not detected in our experiment’ and for this geometry that means ‘scattered through an angle greater than θ ’. If the atomic

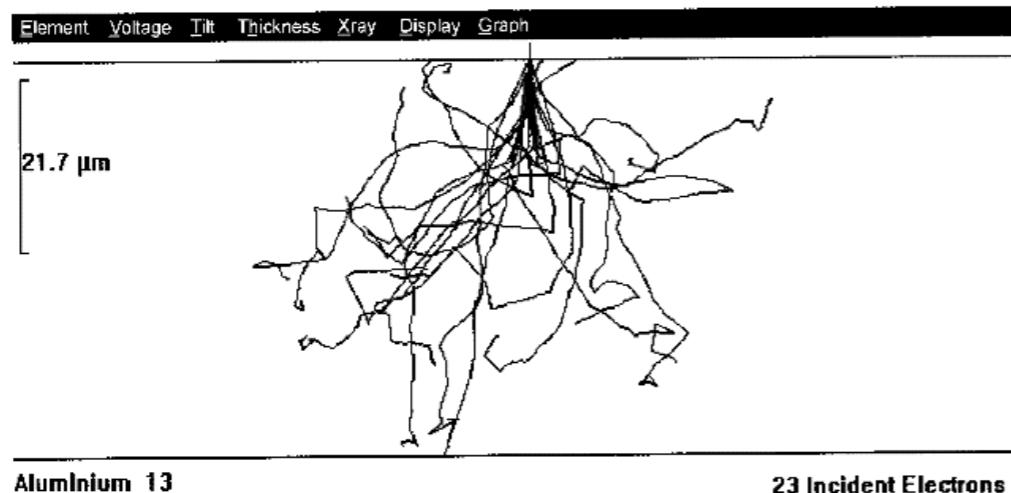


Figure 2.6 Electron trajectories in aluminium calculated by a Monte Carlo procedure. Twenty three electrons are shown in this figure, of which three escape and are thus back-scattered.

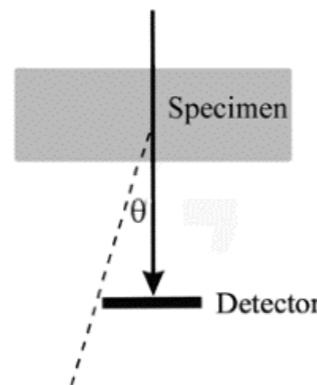


Figure 2.7 The geometry of an electron detection system. Electrons which are deflected through an angle greater than θ after passing through the specimen are not registered by the detector and have thus effectively been 'absorbed' in this experiment.

cross-section for scattering through θ or more is σ_a then it is possible to describe absorption using the conventional Lambert–Beer law. The equation is:

$$I/I_0 = \exp(-N\sigma_a x) \quad (2.10)$$

This describes the fractional intensity, I/I_0 which remains after absorption in a thickness x . N is the number of scattering atoms per unit volume which is often convenient to write in terms of Avogadro's number, N_A , as $N = N_A \rho/A$ where ρ is the density and A the atomic mass.

Remember that all scattering mechanisms, elastic and inelastic, are strongly forward peaked so that the cross-section which is appropriate in equation 2.10 will depend quite sensitively on the angle θ subtended by the detector.

Secondary and backscattered electrons

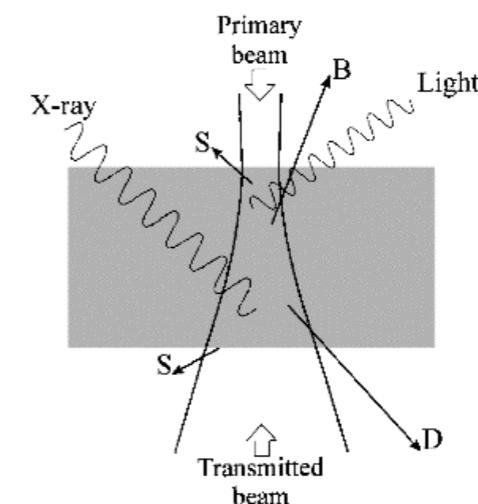


Figure 2.8 A summary of the effects which may be detected when a primary beam of high energy electrons hits a specimen. S = secondary electrons; B = backscattered electrons; D = diffracted electrons.

2.8 Secondary effects

A secondary effect can be loosely defined as an effect caused by the primary beam which can be detected outside the specimen. The secondary effects with which we will be mainly concerned are either electrons or electromagnetic radiation. They are summarized in Figure 2.8. For the present purpose it is convenient to categorize them into five types which relate to the way in which each effect is exploited.

2.8.1 Secondary electrons

This is not a very accurate term, but is used to describe those electrons which escape from the specimen with energies below about 50 eV. They could conceivably be primary electrons which at the very end of their trajectory (Figure 2.6) reach the surface with a few eV remaining. However they are more likely to be electrons to which a small amount of energy has been transferred (by one of the processes outlined in section 2.7) within a short distance of the surface. The *yield* of secondary electrons, that is the number emitted per primary electron, can be as high as, or higher than, 1. Secondary electrons are therefore abundant and are the most commonly used imaging signal in scanning electron microscopy (Chapter 5).

2.8.2 Backscattered electrons

It has already been shown in Figure 2.6 that some primary electrons may leave the surface before giving up all their energy. It turns out that they are most likely to do this while they still have a large fraction of their incident energy. Backscattered electrons are not usually as numerous as secondary electrons but

Relaxation of excited atoms

most of them carry high energies. They are used for imaging, diffraction and analysis in the SEM (Chapter 5).

2.8.3 Relaxation of excited atoms

If a localized electron has been knocked out of an atom the atom is in an excited, high energy, state. At some later time the empty electron state will be filled and the atom will relax, giving off the excess energy as a secondary effect. There are essentially three ways in which this relaxation can happen. If the vacant electron state is an outer state then the energy to be given off will be small and is commonly emitted in the form of a photon which may be in the visible range. This effect is known as *cathodoluminescence*.

If on the other hand the vacant state is an inner state the amount of energy to be released is larger and there are two main possibilities: a characteristic X-ray or a characteristic (Auger) electron may be emitted. These two processes are shown schematically in Figure 2.9. If an X-ray is to be emitted a single outer electron jumps into the inner shell vacancy (Figure 2.9(a)). The energy of the X-ray is then the difference between the energies of the two excited states and this is characteristic of the particular atomic species. For example if a K shell electron has been knocked out of a molybdenum atom (Figure 2.1), and replaced by the ‘jumping in’ of an L electron the energy difference, ΔE , is 17 400 eV, which is emitted as the K_{α} X-ray of Mo. The wavelength of this X-ray can be calculated from

$$\lambda = \frac{hc}{\Delta E} \quad (2.11)$$

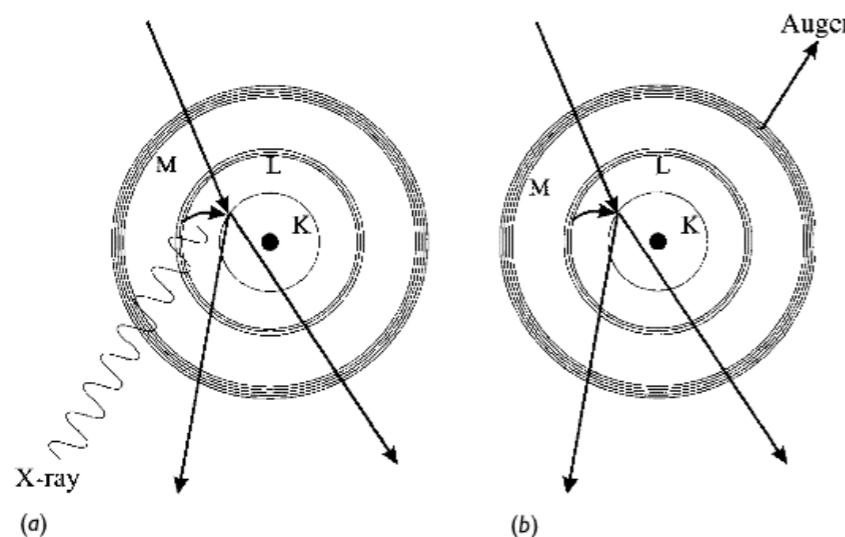


Figure 2.9 The two ways in which an inner-shell-excited atom can relax. In both cases a K shell electron has been knocked out – in (a) a characteristic (K_{α}) X-ray is emitted while in (b) an Auger electron (KLM) is ejected.

and in this case is 0.071 nm. If the vacancy had been filled by an M shell electron the energy difference would have been greater, 19 600 eV, and the X-ray emitted would have been the $Mo K_{\beta}$, with a wavelength of 0.063 nm. These energies and wavelengths are different for each atomic species and by measuring them we can determine which elements must have been present in the specimen. This is the basis of analytical electron microscopy and electron probe microanalysis (Chapter 6).

Inspection of Table 2.1 would lead to the conclusion that there should be very many characteristic X-rays for each atom, since transitions between all the possible states for each atom would appear to be possible. However a set of selection rules prohibit many of the transitions, so that for instance a 2s electron cannot jump to fill a 1s vacancy. The most useful X-rays are listed in Chapter 6.

It is possible for a primary electron to excite an X-ray without knocking out an inner shell electron. In this case the electron can lose any amount of energy (up to its total kinetic energy) and the X-ray is no longer characteristic of a particular atom. This process is called Bremsstrahlung (German for ‘braking radiation’) and leads to a background of X-rays in any electron-generated X-ray spectrum. Figure 2.10 shows a typical spectrum with both characteristic and Bremsstrahlung radiation.

An alternative to X-ray emission is the ejection of an outer electron carrying the excess energy as kinetic energy. This process, known as Auger emission, is shown in Figure 2.9(b). Three electrons are now involved; the original vacancy, the outer electron which jumps into it and the other outer electron which leaves carrying the surplus energy. Measurement of the energy of the characteristic Auger electrons forms the basis of *Auger electron spectroscopy*, which is discussed in Chapter 7.

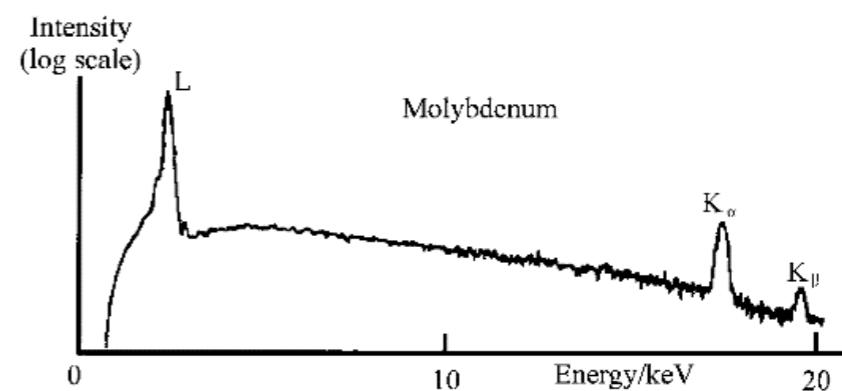


Figure 2.10 An X-ray spectrum excited from a solid specimen of molybdenum by a beam of 30 keV electrons. The K and L characteristic peaks are evident, superimposed on the Bremsstrahlung background. Notice that the intensity scale is logarithmic so that the background intensity appears to be rather higher in comparison with the characteristic peaks than it is in reality.

5.4.2 Depth of field

Apart from its good spatial resolution, one of the most important aspects of the scanning electron microscope is its large depth of field. If we compare images taken by an optical microscope and an SEM of the same object, at similar magnifications, as in Figure 5.14, then the difference is striking.

The important consequences of the large depth of field of the SEM cannot be overemphasized. As an example, over the past thirty years the SEM has contributed greatly to our understanding of fracture processes by providing a means of examining fracture surfaces at high resolution.

Figure 1.11 shows the electron beam emerging from the objective aperture (diameter A) and incident on a specimen. Although the beam is focused on the specimen, the convergence angle α is small, and, assuming a point focus, the beam diameter defocuses by less than s over a vertical distance of h , where

$$s = h\alpha \quad (5.5)$$

If the defocus is no greater than a specimen pixel, then the image will remain in focus, and thus from equations 5.4 and 5.5, the distance h over which the specimen will remain in focus, the depth of field, is given by

$$h = \frac{0.1}{M\alpha} \text{ mm} \quad (5.6)$$

From Figure 5.11, we see that the convergence angle α of the beam is given by

$$\alpha = \frac{A}{2WD} \quad (5.7)$$

Thus from equations 5.6 and 5.7, we find that the depth of field is

$$h = \frac{0.2WD}{AM} \text{ mm} \quad (5.8)$$

For typical values of aperture diameter of 100 µm, and a working distance of 20 mm, equation 5.8 shows that at a magnification of 1000 \times , the depth of field is 40 µm. By comparison, an optical microscope working at a magnification of 1000 \times with an objective lens of numerical aperture of 0.7 would have a depth of field of only \sim 1 µm. You can experiment with these variables in the MATTER module, ‘Using the Scanning Electron Microscope’.

5.5 The ultimate resolution of the SEM

We saw in the last section that the best working resolution of the SEM was the specimen pixel size p , given by equation 5.4, and that this depended on the magnification of the instrument. However, this resolution is only achieved if the diameter of the beam sampling volume is no larger than p . As discussed in section 5.2, and shown in Figure 5.6, the sampling volume depends on the signal being used. For example X-rays have large sampling volumes which

tivity of the specimen at that point, the lifetime of electrons and holes, and their mobility (the drift speed under unit potential gradient).

These three parameters are of extreme importance to the semiconductor industry, and if their variation across a specimen can be measured or made visible in the SEM, then faults such as impurities, poor contacts etc. within a single integrated circuit can be investigated without damaging it (Richards and Footner, 1992). It is even possible to study an integrated circuit chip while it is being used, with currents flowing through its various components.

5.9.2 Cathodoluminescence

Many materials emit light under electron bombardment, and if this is detected, we can display an image in the *cathodoluminescent mode*. We have already encountered this effect in the phosphor used on the viewing screens of the transmission electron microscope and CRT tube of the SEM, and in the scintillator electron detectors used in the SEM. Cathodoluminescence (CL) varies in colour and intensity as a function of the composition of many minerals, and in semiconductors such as gallium arsenide (GaAs). Consequently this mode of imaging is of particular importance in these fields of application. Cathodoluminescence is also observed in polymeric or biological material, and in the latter materials, cathodoluminescent species may be used to 'label' the material.

Because cathodoluminescence may originate within most of the interaction volume of the sample, the spatial resolution is much worse than for electrons and is comparable with X-ray signals (Figure 5.6). However, the spatial resolution may be much improved by the use of low accelerating voltages and field emission electron sources.

As light detectors are usually also sensitive to electrons, CL detectors have to be designed to remove the electrons. Perhaps the simplest CL detection is achieved by removing the scintillating material from an electron detector so that the light is collected directly by the light guide. A specialized CL detector system is shown schematically in Figure 5.27. This employs a semi-ellipsoidal mirror which collects the light from the specimen and focuses it into a light guide and out of the microscope for spectral analysis.

CL appears as a band of wavelengths with a peak at a photon energy which is related to the energy gap between the filled valence band and empty conduction band of semiconducting and insulating materials. Any alteration in the energy gap due to local changes of temperature, crystal structure or impurity level will lead to a change in emission. At temperatures at or near liquid helium temperature, the CL emission bands generally become more intense and much sharper, and the band may be resolved into a line spectrum. Analysis of such a spectrum enables very low levels of impurity (< 0.01 ppm.) to be identified. Note that this is several orders of magnitude more sensitive than X-ray analysis (Chapter 6).