Chapter 4
Scanning Electron Microscopy: Principle and Applications in Nanomaterials Characterization

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4.1 Introduction

The human eyes have some limit and are able to resolve two points that are 0.2 mm apart from each other, called as the resolution power of the human eye. However, by the addition of lens or group of lenses (aided eye), the human eye is enabled for high resolution and can resolve the two dots that are closer than 0.1−0.2 mm from each other. Anything below 0.1–0.2 mm requires some sort of magnification; therefore, to overcome these limitations of human eyesight, the microscope was developed and used as an efficient magnifying tool. Microscope has a much higher resolution and has been used as a powerful tool for studying and characterizing a wide range of materials.

The microscope resolving power not only depends on the quality and number of the lenses used, but also the light wavelength or source to produce image is highly considered. Therefore, microscope can be divided into two categories on the basis

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of source to produce image, i.e. optical or light microscope (OM) and electron microscope (EM). Both OM and EM have the same working principle, but the major difference is the source, i.e. OM uses visible light as a source while EM uses focused accelerated electrons beam. Surface investigation of the materials can be achieved through both microscopes. However, the resolution of optical microscope is very limited by diffraction properties. Instead, a much higher resolution data can be attained by using one of the electron microscopic methods. Because electrons have shorter wavelength than visible light and thus are more energetic then visible light photon, a beam of highly accelerated electrons are focused on the surface of materials, thus creating the image. EM is an imaging tool with much better imaging resolution as compared to OM.

The use of the accelerated electrons beam in EM featured by short wavelength causes the diffraction effects to occur at much smaller physical dimension, which in turn helps resolve atomic features ranging from nanometre to micrometre particle size. In the case of EM, focused accelerated electrons are used to see through the sample and scan materials on a fine and very small scale. As a result, it gives images of higher magnification with better resolution. The main reason for the development of electron microscopes was the precincts and limitation of OM. Two main types of EM are available, scanning electron microscope (SEM) and transmission electron microscope (TEM) [1, 2]. The first EM, i.e. TEM, was invented in 1931 by Knoll and Ruska in Germany, and ever since it was considered as a valuable instrument that has been used to understand scientific phenomena in diverse fields, such as nanotechnology, science, medicine and many others [1, 2]. The SEM was first introduced in 1938 (Von Ardenne), and in 1965 the first SEM instrument came into market.

4.2 Comparison Between Optical Microscope and Electron Microscope

Optical microscope (OM) and electron microscope (EM) are analogous in many ways; however, they also show differences. Both types of microscopes exhibit certain similarities as follows:

(i) EM and OM are identical both fundamentally and functionally.
(ii) Magnify those objects which normally cannot be seen to the naked eyes.
(iii) Present similar component terminology and overall design.
(iv) Contain a source of illumination and condenser lens system which direct parallel radiation onto the specimen.
(v) Contain a series of imaging lenses which form the image of the specimen.

In addition, the EM and OM also show dissimilarities:

(i) Illumination beams are different; the EM uses very energetic electrons as a source instead of visible light used in the OM, i.e. a lamp produces the light

beam (including UV rays) in the OM while an electron gun produces electron beam in EM.

(ii) Optical lens in OM while electron lens (magnetic or electrostatic) in EM.

(iii) Accelerated electrons used in EM have very short wavelength (0.859−0.037 Å, 20−100 kV) and thus give a high resolution which is the limitation of OM ($\lambda = 7500-2000$ Å) and thus make it possible to see very small features.

(iv) EM needs high vacuum while OM can operate in any atmosphere.

(v) EM has a capability of higher magnification (90−800,000×) which can be varied continuously as compared to OM (10−2000×) which can be varied by exchange of lenses.

(vi) EM has higher resolving power (point to point: 3 Å, lattice: 1.4 Å), while OM has lower resolution (visible: 3000 Å, UV: 1000 Å).

(vii) EM has a larger depth of field and has better depth of focus than OM, making EM suitable for studying rough surfaces.

(viii) Focusing can be done electrically in EM while it is mechanically by OM. Thus, EM has higher magnification and lower depth of focus.

(ix) In an EM, the contrast is either by scattering absorption (SEM) or diffraction (TEM); while in an OM, it is by either absorption or reflection.

(x) EM gives information about composition and crystallography which are not possible by OM. Similarly, SEM and TEM are both electron microscopes but still have certain differences.

4.3 Difference Between SEM and TEM

There are certain differences between a scanning electron microscope (SEM) and transmission electron microscope (TEM), which are given as below:

(i) SEM detects scattered electrons emitted from the surface of the sample, while TEM detects transmitted electrons.

(ii) SEM provides information about surface morphology and composition of materials while TEM gives details about internal composition of materials. Thus, TEM can illustrate several characters of a material (morphology, crystallization, stress or even magnetic domains).

(iii) Both need electrically conductive materials to be tested. Non-conductive materials should be coated with a conductive layer of metal or carbon.

(iv) The accelerated voltage ranges from 10 to 40 kV for the SEM, while for TEM, it is >100 kV.

(v) SEM requires a very easy preparation technique, while TEM needs skill to prepare a very thin sample. The thickness of the specimen is not important in SEM, while specimen thickness is very important in TEM. The thickness of the specimens to be examined under TEM should be less than 100 nm. SEM is a better tool for surface characterization as compared to TEM which is better for internal structure analysis.

(vi) The resolution is much higher in TEM as compared to SEM.
(vii) TEM is used for high magnification compared to SEM.
(viii) In the case of SEM, the electron beam scans over the surface of the sample, while in the case of TEM, the electron beam passes through the sample.
(ix) SEM has a comparatively low resolution than TEM, while TEM has high resolution.
(x) SEM has a high depth of field, while TEM has moderate.
(xi) SEM has lower magnifying power, while TEM has high magnifying power.
(xii) In SEM, the specimen contrast is by electron absorption, while it is by electron scattering in TEM.
(xiii) SEM produces three-dimensional black and white images, while TEM produces two-dimensional black and white images.

4.4 Scanning Electron Microscope (SEM)

SEM is a versatile advanced instrument which is largely employed to observe the surface phenomena of the materials. The sample is shot in a SEM using high-energy electron, and the outcoming electrons/X-rays are analysed. These outcoming electrons/X-rays give information about topography, morphology, composition, orientation of grains, crystallographic information, etc. of a material. Morphology indicates the shape and size, while topography indicates the surface features of an object or "how it looks", its texture, smoothness or roughness. Likewise, composition means elements and compounds that constitute the material, while crystallography means the arrangement of atoms in the materials. SEM is the leading apparatus that is capable of achieving a detailed visual image of a particle with high-quality and spatial resolution of 1 nm [3–5]. Magnifications of this kind of apparatus can extend up to 300,000 times. Although SEM is used just to visualize surface images of a material and does not give any internal information [2], it is still considered as a powerful instrument that can be used in characterizing crystallographic, magnetic and electrical features of the sample and in determining if any morphological changes of the particle has occurred after modifying the sample surface with other molecules [3].

SEM is able to provide several qualitative information of the specimen including its topography, morphology, composition and crystallographic information. In other words, it provides information about the surface features and texture, shape, size and arrangement of the particles lying on the sample's surface. The type of elements and compounds the sample consists of and their relative ratios as well as the arrangement of atoms in the single crystal particles and their degree of order can also be provided [2, 6]. Thus, SEM is a multipurpose instrument which is able to examine and analyse the materials with high resolution.

4.5 Importance of Electron Beam in SEM

Let's suppose two objects are there that can be easily recognized as separate objects if they are separate and far away from each other. Let's take two Airy discs having a small spot surrounded by halos, and the radius of the halo is 1.22 Fλ/d (see Fig. 4.1). If they are close in such a way where the maximum of the first Airy disc coincides with the first minimum of the second Airy disc, the separation between the two peaks is 1.22 Fλ/d. The images are too close and overlap but still can be distinguished where the human eye can still see the two separate points. Then a limit point is reached where lesser separation would result in formation of a continuous blur and this limit is referred to as the Rayleigh criterion. The Rayleigh criterion for the resolution of an optical system states that two points can be resolved if the maximum of the intensity of the Airy disc from one of them coincides with the first minimum intensity of the Airy disc of the other [7]. According to Abbe the minimum resolvable separation d_0 or resolution ρ (the resolving power) is given~by:

$$d_0 = \rho = 1.22\lambda/2\,(n \sin\alpha) = 0.61\lambda/\,(n \sin\alpha) = 0.61\lambda/\mathrm{NA} \tag{4.1}$$

where λ is the wavelength, n is the refractive index and α is the semiangle of the specimen; NA = n sin α is the numerical aperture. According to Eq. (4.1), the resolving power will be limited by several factors, and λ is the most important factor if we want to raise resolving power.

According to de Broglie, λ of electrons is determined by the accelerating voltage on the filament from which they are emitted. A moving electron has a dual character as a moving charged particle or as a radiation with associated wavelength, and λ of an electron is inversely proportional to the momentum $p = mv$ of the electron by:

$$\lambda \propto 1/p$$

$$\lambda = h/p$$

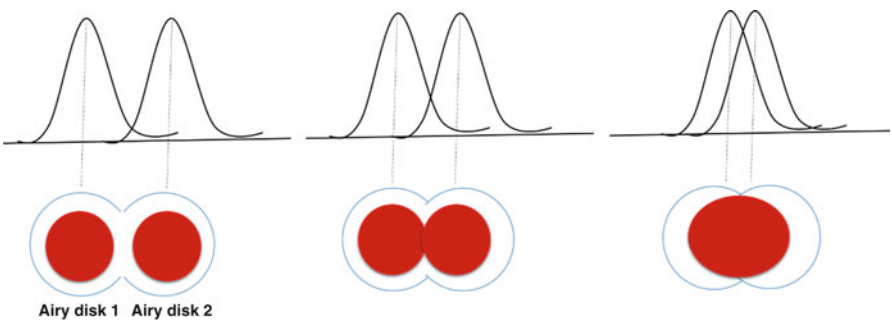

Fig. 4.1 Airy patterns and Rayleigh criterion

$$\lambda = h/mv$$

where λ is the de Broglie wavelength of the electrons, h Planck constant, m mass of electron and v velocity of the electron. So, if electron beam is used as a source, the wavelength will be very short and can be calculated by the following relation:

$$\lambda = 1.22/(\upsilon)\,\frac{1}{2}$$

Therefore, electron beam as an illuminate is important for high resolution. Basically, SEM is utilized to image the sample surface through detecting different signals generated from the impact of focused highly energetic electrons (primary electrons) at the sample surface [5]. These electrons have very short wavelength (λ) which can vary as per the applied high voltage.

4.6 Fundamental Principles of SEM

SEM has a specific sample holder where the stub should be fixed containing the sample on the surface. Generally, carbon tap is used for sticking the sample to the stub. First two-sided carbon tap should fix on the stub and then a thin layer or a small amount of material will be placed on the carbon tap because the thin layer properly sticks with the carbon tap which reduces the charging problem and help in getting a good image. Some requirements are needed when operating SEM analysis. Additionally, when using SEM, the samples have to be electrically conductive to avoid overcharging on the surface. This overcharging may introduce extreme brightness and poor images. Thus, non-conductive samples like polymers are usually sputter coated [4] with a thin layer of carbon [1] or metal that readily reflects electrons and provides a conductive surface for electrons, e.g. gold and platinum [2, 8]. The non-conductive materials must be sputtered in order to reduce the charging problem. After that the sample-covering stub will be fixed in the sample holder and should be put in the sample-holding chamber or specimen chamber. In contrast to TEM, relatively thick samples can be examined by scanning electron microscopy.

The SEM instrument is based on the principle that the primary electrons released from the source provide energy to the atomic electrons of the specimen which can then release as the secondary electrons (SEs) and an image can be formed by collecting these secondary electrons from each point of the specimen, the basic requirement for SEM to operate under a vacuum to avoid interactions of electrons with gas molecules in order to obtain high resolution. In addition, the primary electrons produced and emitted from the electron gun are accelerated by heating or applying high energy in the range of 1−40 keV [2, 4]. These emitted electrons are focused and confined to a monochromatic beam (to a diameter of 100 nm or less)

by magnetic field lenses and metal slits within a vacuumed column. The confined primary electrons are scanned across the sample surface by scanning coils in a raster pattern [1, 2]. Once the primary electron beam hits the sample surface, it will interact with the near-surface area of the sample to a certain depth in many different ways [4]. The impinging electrons accelerated towards the specimens have substantial quantities of kinetic energy, which lose their energy inside the sample by generating several signals from the interactions of electrons with specimen. It scattered both elastically and inelastically in the sample.

The scattering of electrons and interaction volume depends on the atomic number, concentration of atoms of the analysed sample and the incoming electron energy (accelerating voltage). Increasing the electron energy (accelerating voltage) will increase the interaction volume and scattering process, and if the concentration of atoms and atomic number of the element is high, then the interaction volume and scattering will be low. Similarly, angle of incidence of the electron beam also play an important role in the interaction volume and scattering process. Thus the angle of incidence of the electron beam, atomic number of the material under examination and accelerating voltage are the main factors for the volume inside the specimen in which interactions occur. The materials having higher atomic number absorb or stop more electrons and will thus generate smaller interaction volume. Similarly, if high voltages are applied, it will generate electrons with high energy and will thus penetrate farther into the sample and generate a larger interaction volume. Similarly, the greater the angle of incidence (further from normal), the smaller will be the interaction volume.

In consequence, it will emit a variety of signals due to Coulomb (electric charge) field interaction of incoming electrons with specimen nucleus and electrons, such as secondary electrons (SEs), backscattered electrons (BSEs), photons (X-rays used for elemental analysis) and visible light (cathodoluminescence – CL) [1, 8]. The signals are gathered by electron collectors (detectors), which are then manipulated by the computer to form the required image. According to the detected signal (secondary electrons, backscattered electrons or X-rays), different information about the sample could be observed [2]. The two routinely used electrons for sample image creation are the backscattered and secondary electrons. However, secondary electrons are considered the most important electrons, indicating sample morphology and topography, while backscattered electrons are used for demonstrating the contrasts in multiphase samples composition (i.e. for prompt phase judgement). Similarly, X-rays are generated by the inflexible impacts of the incident electrons with the electrons available in the orbitals of sample atoms. After this the electrons are excited to the higher energy levels; when it comes back to the lower energy levels, it emits X-rays, having a specified wavelength, depending on the difference in energy level of various elements. In this way each element generated a characteristic X-ray after the impinging of electrons beam. SEM is non-destructive, as the generation of X-rays does not lead to any loss in the volume of the specimen; therefore, one can repeatedly analyse the same material (Fig. 4.2).

Generally, there are two types of interaction such as inelastic interaction and elastic interaction. Inelastic interactions are those in which interaction takes place

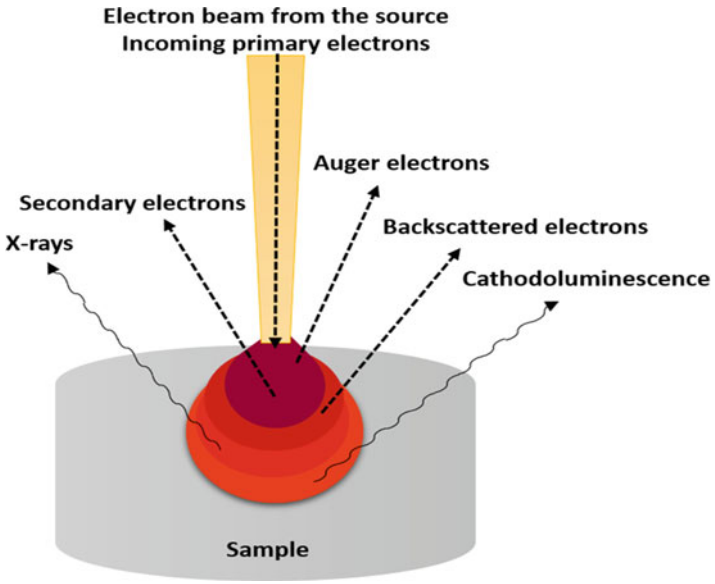

Fig. 4.2 The interaction of electron beam with specimen and the signal emitted from the sample

between the beam electron and electric field of a specimen atom electron, where transfer of energy from the beam electron to the specimen atom takes place which results in potential ejection of an electron from that atom as SEs have usually energy less than 50 eV. The vacancy created by the emission of a secondary electron is filled from a higher-level orbital, and an X-ray characteristic of that energy transition is produced [8].

Elastic interactions are those interactions that take place between the primary electrons and electric field of the nucleus of a specimen atom, and due to these interactions, the direction of the primary electrons changes without a significant change in the energy of the primary electron (<1 eV) [9]. If these elastically scattered electrons deflect back out of the specimen, these electrons are called BSEs, having energy from 50 eV $\sim$ to energy almost equal to the incident beam electrons. Usually, mainly BSEs maintain a minimum of 50% of the incident beam energy. Thus, the beam electron distributes due to these elastic and inelastic interactions over a three-dimensional "interaction volume". Secondary and backscattered electrons escape from different depths of the sample, and therefore their energy remains different. SEs generally escape from the depth of approximately 5−50 nm, while BSEs escape from a depth of several times greater than the depth of SEs, and X-rays greater yet [9]. Thus, greater escape depths generally translate to wider lateral dimension from which the signal can generate and thus lower potential resolutions, but the real size and shape of the interaction volume depend upon accelerating voltage, atomic number and tilt.

4.6.1 Accelerating Voltage

The accelerating voltages control the dimensions of the interaction volume. The increase in accelerating voltage helps in increasing the size of interaction volume. The increase in beam energy reduces the energy loss rate in the specimen, and as result the beam electrons enter deeply into the specimen. Moreover, if the elastic scattering is less, the beam paths close to the specimen surface become straight and the beam electrons enter more deeply [9]. Ultimately, several elastic scattering collectively push some electrons back towards the surface of the specimen and as a result increasing the interaction volume.

4.6.2 Atomic Number

Atomic number is another factor which affects the interaction volume. The higher the atomic number of the elements, the lower will be the interaction volume, because if the atomic number is higher, the rate of energy loss of the electron beam will be higher, and as a result electrons will not penetrate deeply into the specimen. Also, the probability for elastic scattering and the average scattering angle increase with atomic number – causing the interaction volume to widen [8].

4.6.3 Tilt

After tilting the sample, the incident beam electrons move along greater distances in the region near the surface. Due to this occurrence more SEs are produced in this area as compared to areas which are normal to the beam, and these SE signal-produced images reveal the so-called edge effect. Edges and ridges of the sample due to emission of more SEs look brighter in the image.

Secondary electrons are stated as the electrons that escaped from the sample surface (only electrons ~10 nm near to the surface) when some of the energy (~5 eV) is transferred from the primary electrons to the specimen electrons, mostly in the K-shell. These electrons can be used to image the topography and morphology of the sample [1, 2]. After striking the electrons on the surface of the material emerging from the primary electron probe, electrons emit from the materials surface; these electrons are called secondary electrons. These secondary electrons are set free to the detector, where it forms the surface image of the materials. The secondary electrons interact with the surface of the materials by creating a different signal, providing the information about the morphology and composition of the materials. Secondary electrons and backscattered electrons are usually utilized for material imaging: secondary electrons are mainly important

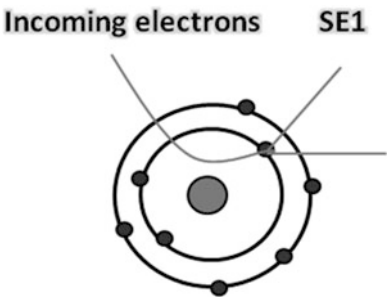

Fig. 4.3 The secondary electrons (SE1) emitted from the sample

for screening morphology and topography of materials [1–11]. Thus, secondary electrons are those which are generated by:

(i) Collision among the primary electrons and the weakly bonded outer electrons.
(ii) These are low energy electrons (less than 50 eV but mostly in the range of 2–5 eV).
(iii) SEs are produced near the surface and thus give information about topography.
(iv) The number of SEs remains higher as compared to the number of incoming electrons.
(v) SE coefficient (δ) which is the ratio of the number of SE to the number of primary electrons which strike the specimen is comparatively insensitive to atomic number.
(vi) SE coefficient (δ) increases with decrease in beam energy (accelerating voltage) which is due to the decrease in interaction volume.
(vii) SEs have very low escape depth because of their low energies.

Secondary electrons (SEs) are produced by two mechanisms and can be further differentiated as SE1 and SE2:

SE1 are those secondary electrons which are produced by the primary electron beam. Once the primary electrons enter the surface of materials, some of the energy is transferred to the specimen electrons and gives high-resolution signal limited by the electron beam diameter (Fig. 4.3).

SE2 are those secondary electrons which are produced by those electrons that first undergo several inelastic scatterings and then come to the surface. SE2 generate from a surface area greater than the incoming electrons' spot. SE1 resolution remains stronger than for SE2. Electron beam energy, electron beam current, atomic number, local curvature of the surface and work function of the surface are the factors which disturb and affect SE emission. Higher atomic number creates more SE2. The effect of atomic number is much more prominent at lower beam energies [9] (Fig. 4.4).

Backscattered electrons (BSEs) are referred as primary electrons that are reflected back from the atoms surface. The energy of BSEs differs according to the atoms density from which these electrons are reflected. Therefore, they are used in visualizing the contrast variation in surface composition, showing brighter images for atoms with higher atomic number. If the scattered electrons maintained

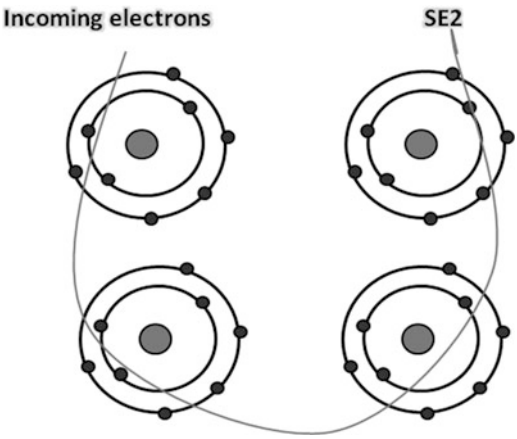

Fig. 4.4 The secondary electrons (SE2) emitted from the sample

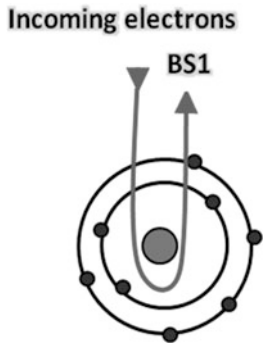

Fig. 4.5 The backscattered electrons (BS1) emitted from the sample

their energy, they are called elastic scattered electrons. These electrons are useful in getting information about orientation and arrangement of atoms. Transmitted electrons are stated when the primary electrons pass through the sample without interacting with their atoms. They are used to develop an image of thin samples. Backscattered electrons are mainly important for showing discrimination of phases and composition of any multiphase samples. BSEs are the incident electrons which repelled and escaped from the surface by the electromagnetic field of the nucleus. These are elastically scattered high-energy electrons which are less than SEs [9] (Fig. 4.5).

Backscatter coefficient (η) which is the ratio of the number of BSEs to the number of primary electrons that strike the specimen is sensitive to atomic number. It increases with increase in atomic number. Materials possessing higher atomic number elements discharge more backscatter signal and thus appear brighter in the image. Accelerating voltage has less effect on η and slightly changes it. η increases in case of tilted surface but in a direction away from the incident beam. With no tilt, η follows a distribution that approximates a cosine expression. What this means is that the maximum number of backscattered electrons travel back along the incident beam [9] (Fig. 4.6).

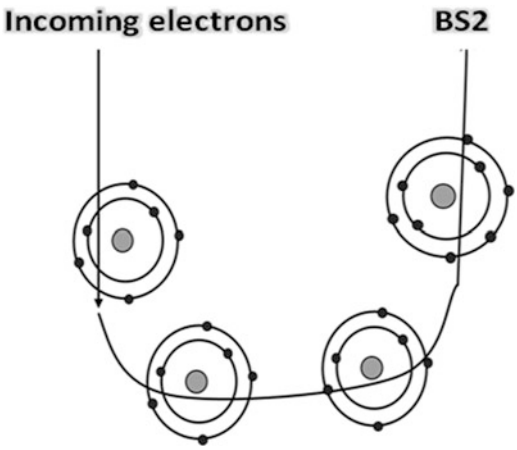

Fig. 4.6 The backscattered electrons (BS2) emitted from the sample

Other interactions such as Auger electrons and X-rays occur to release the excess energy gained after hitting and exciting the atoms with incident beam. Auger electrons can be used in chemical analysis, while X-rays are used in energy-dispersive X-ray (EDX) analysis to identify the elements and their concentrations in the sample [1]. X-rays are generated by inelastic interaction of the incident electrons with electrons in discrete orbitals (shells). These are photons, not electrons. Each element has its own special X-ray signal *fingerprint*.

4.7 Instrumentation

SEM is an electronic and optical system which consists of the following components:

(i) Electron gun
(ii) Vacuum
(iii) Column: condenser lens, scanning coil, objective lens, stigmator, sample holder and detector

In principle, first the gun emits the electron beam which is held within a vacuum which follows a vertical travel path through electromagnetic fields and lenses. The electron beam is focussed by objective lens on the specimen. Then the focussed beam scans over a specific area of the specimen surface where the focussed beam is rastered across the surface of the materials with help of deflector coils, which is controlled by the scan generator. Magnification controls the size of the rastering pattern. The changes in magnification change the size of the rastered area on the sample. When the electron beam hits the material, this strike produces a huge number of signals, i.e. electrons and X-rays are emitted from the specimen. These signals are detected by the detector (depending on the

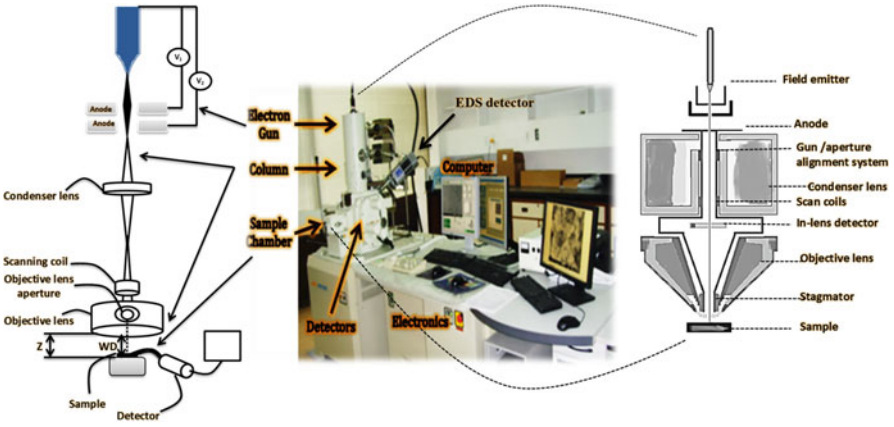

Fig. 4.7 The external and internal configuration of FESEM

type of detector) and converted to signals where images are produced from the signals. The signal that originates from electron-sample interaction gives detailed information about the material such as external morphology (texture), chemical composition and crystalline structure and orientation of materials making up the sample. The scanning electron microscope has several advantages because it has a big profundity of field which permits to focus more specimens at one time. The SEM also has much superior resolution, so narrowly spaced specimens can be magnified at many advanced levels. The bigger advantage of SEM is that it provides the researcher much more control in the degree of magnification as lenses are replaced by electromagnets. The permutation of enhanced magnification, bigger depth of focus, superior resolution and ease of sample surveillance make the SEM one of the most profoundly used instruments in research areas nowadays [1–11] (Fig. 4.7).

4.7.1 Electron Gun

Electron gun provides the electron beam whose energy can vary as per need of material to get an image with the best resolution with minimum sample charging and damage. The function of the electron gun is to provide a large and stable current in a small beam. The electron gun or emission source is of two types, i.e. thermionic emitter and field emitter [11]. The main difference between SEM and FESEM is the type of emitter, i.e. thermionic emitter is used in SEM while field emitter is the electron gun utilized in FESEM.

4.7.1.1 Thermionic Emitters

In this case, a filament made up of tungsten (W) and lanthanum hexaboride (LaB_6) is heated up using electrical current. When the heat is enough to overcome the work function of the filament material, the electrons escape from the material itself. Thermionic sources have relatively low brightness, evaporation of cathode material and thermal drift during operation [11]. The source of electron is a tungsten filament with diameter of about 0.1 mm and electrically heated to about 2700 K. The Wehnelt cylinder is potentially more negative than the filament and helps to emit the electron from one point. This point is also called crossover, and the Wehnelt cylinder helps to control the diameter of crossover and also control the number of emitting electrons. Lanthanum or cerium hexaboride are high brightness electron sources, but higher vacuum is required. To produce vacuum in the chamber, a vane-type rotary pump and a turbo molecular pump are used to produce a vacuum of 10^{-5} mbar.

4.7.1.2 Field Emitters

Field emission gun (FEG) generates electrons without heating and thus avoids the heating problem. Therefore, FEG is also called a cold cathode field emitter. In FEG, a wire of tungsten with a sharp point (tip, radius = less than 100 nm) is used as filament where the emission of electron takes place by employing the filament in a huge electrical potential gradient. The significance of the small tip radius ($\sim$100 nm) is that an electric field can be concentrated to an extreme level, becoming so big that the work function of the material is lowered and electrons can leave the cathode [11]. Field emission electron microscope (FESEM) thus introduced a different electron gun design. In this technology, field emission cathode releases the electrons by applying a high electric field near the filament tip. The speed with which the electrons are ejected from the electron reservoir in the filament is organized by the degree and proximity of the electric field to the reservoir. This technology can tolerate high current and offer higher stability by producing finer beams with emission 1000$\times$ the emission of a traditional tungsten wire. This design required considerably higher vacuum conditions. As a result, an improved spatial resolution and minimal sample charging is provided. Therefore, FESEM offers high performance, i.e. high resolution which means large probe current and small diameter electron probes over a wide energy range (1$-$30 keV).

FESEM uses a field emission gun to produce a cleaner image, less electrostatic distortions and spatial resolution <2 nm (that means three or six times better than SEM). The FESEM has two anodes for electrostatic focusing. A voltage (0$-$5 kV) between the field emission tip and the first anode (anode 1), called the extraction voltage, controls the current emission (1$-$20 μA). The potential difference V_1 which are applied between anode 1 and emission tip generated an electric field which results in the emission of electrons (emission current). The velocity at which the electrons move into the column is determined by the beam energy. A voltage (1–30 kV), called the accelerating voltage (V_0), when applied between the cathode and

the second anode (anode 2) increases the beam energy. The higher the V_0, the faster the electrons travel down the column and the higher the penetrating power. This voltage combined with the beam diameter determines the resolution (capacity to resolves two closely spaced point as two separates entities), which increases with increase in voltage [11].

In FESEM, electrons are emitted from the field emission cathode by applying a high electric field near the filament tip. The degree to which electrons are expelled out of the electron reservoir in the filament is controlled by the magnitude and proximity of the electric field to the reservoir. Even though this design required considerably higher vacuum conditions [1], it has greater stability, can tolerate higher current and hence produces finer beams [5] with 1000× the emission of a traditional tungsten wire [1]. As a result, an improved spatial resolution and minimal sample charging is provided [5]. There are different types of FEGs such as cold FEG (JEOL 6700) and thermally assisted FEG (JEOL 6500). In the cold FEG, the electric field produced by the extraction voltage lowers the work function barrier and allows electrons to directly tunnel through it – thus facilitating emission. The thermally assisted FEG (Schottky field emitter) uses heat in addition to voltage to overcome the potential barrier level [9].

Three parameters, i.e. brightness, source size and energy spread, are important in electron emitters and can be compared for various types of electron emitters. Although the FEG has a moderate emission current, its brightness is higher than the thermionic tungsten and LaB_6 sources (Table 4.1). Brightness is dependent on accelerating voltage, which increases linearly with accelerating voltage [9]. The high brightness value of FEGs is also due to the small source size. In FEGs, the source size is in nanometre while it is in micron in other emission sources, and thus the current emission in FEGs takes place in an extremely small source size as the beam leaves the gun. Thus, sufficient probe current in a small diameter probe lets the FEGSEM get a better resolution. The ability to achieve a small probe diameter is directly related to the source size or the diameter of the electron beam exiting the gun. An electron beam emanating from a small source size is said to have high spatial coherency. Electron beams can also be characterized in terms of temporal coherency. A beam with high temporal coherency will have electrons of the same wavelength. There is a certain "Energy Spread" associated with the beam. As we will see, lower energy spreads result in better resolution and are particularly important in low accelerating voltage imaging [9].

In addition, proper vacuum, lifetime, cost and expected mode of use are also important factors for SEM. Source size is the apparent size of the disc from which the electrons come. A small source size is good for high resolution and less demagnification. A large source size is sometimes good. For example, for large probe sizes and high beam current, electrons leave guns with an energy spread that depends on the cathode type. Lens focus varies with energy, so energy spread spoils high-resolution and low-energy images. The cold field emission gun offers the best performance parameters in all three categories for most purposes. Field emission guns are best for high-resolution and low-voltage operation. Thermionic emitters have advantages when very high-beam current and large spot sizes are required. At

Table 4.1 Different parameters in electron emitters and their comparison with others

	Tungsten	LaB_6	Thermal FEG	Cold FEG
Brightness (A/cm^{2}str)	10^5	10^6	10^8	10^8
Lifetime (hrs)	40–100	200–1000	>1000	>1000
Source size	30–100 um	5–50 um	<5 nm	<5 nm
Energy spread (eV)	1–3	1–2	1.0	0.3
Current stability (%hr)	1	1	5.0	5
Vacuum (Torr)	10^{-8}	10^{-7}	10^{-11}	10^{-11}

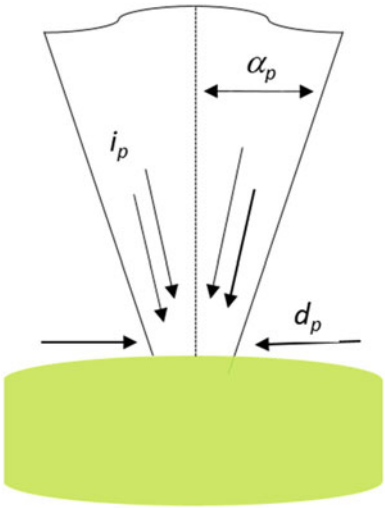

Fig. 4.8 The electron beam parameters which has impact on sharpness, resolution and visibility of SEM images

a typical imaging current, FEGSEM spot size is set only by lens quality. Lower brightness guns must use bigger spots to give the same beam. This is brightness-limited imaging. The best resolution is always obtained at the smallest working distance (WD), but the minimum WD value varies with beam energy. The sharpness, contrast and depth of field depends upon three major electron beam parameters, i.e. electron probe size (d_p), electron probe current (i_p) and electron probe convergence angle (α_p) (Fig. 4.8).

The beam diameter (d_p) should be as small as possible for highest resolution. The emission current (i_p) must be as large as possible for the best image quality and X-ray analysis. For the best depth of field, the convergence angle (α_p) must be as small as possible.

FESEM is a high vacuum instrument and the vacuum allocates movement of electrons along the column devoid of scattering and spreading and avoids discharge in the interior gun zone. SEM requires operating under a vacuum to avoid interactions of electrons with gas molecules in order to obtain high resolution. The microscope must have vacuum system in order to achieve the required vacuum. The vacuum keeps the column free of molecules, and thus the beam will not interact with any molecules on the path down the column. The gun level of the column needs

vacuum in the range of 10^{-10}–10^{-11} Torr, while the specimen chamber requires vacuum in the range of 10^{-5}–10^{-6} Torr.

4.7.2 Column with Lenses and Apertures

Condenser lens, scanning coils, stigmator coils and objective lens and the apertures in the column focus the electron beam onto the surface of specimen. Each lens consists of copper wire carrying direct current surrounded by an iron shroud. Thus, electromagnetic lens contains copper wire coil within an iron pole piece. These coils create magnetic field when applying current through the coils, and this magnetic field converge the electron beam. Once an electron passes through an electromagnetic lens, it faces two vector forces at any particular moment [9]:

(i) A force parallel to the *Z*-axis of the lens and therefore is represented by Hz that causes spiralling of the electrons while passing through the lens
(ii) A force parallel to the radius of the lens and therefore is represented as HR, which causes focusing of the electrons while passing through the lens

When an electron is passing through the lens, it will experience a force parallel to the *Z*-axis, and this force will urge the electron to spiral through the lens. This spiralling causes the electron to experience another force parallel to the radius of the lens, and this force compress the beam towards the *Z*-axis. The magnetic field does not remain homogeneous. It remains strong close to the bore while weak in the centre of the gap. Thus, those electrons which pass close to the centre experience less force and are less strongly deflected, while those electrons which are passing the lens far from the axis experience more force and are more strongly deflected. Thus, electromagnetic lens produces electromagnetic fields which have axial and radial parts. The radial component keeps the electrons in helix path. If the beam diameter is smaller than the feature, in such a case, feature on the specimen surface can be resolved, and for this purpose, it is a must to condense the electron beam. Therefore, electromagnetic lenses are utilized to support in the demagnification of the beam. Field emission source has small crossover diameter, and therefore the beam condensation to a lower level is necessary because in such a case the probe will be valuable for image processing, and that is why the FESEM is the highest resolution instrument [9].

4.7.3 Condenser Lens

The condenser lens converges the cone of the electron beam to a spot below it, before the cone flares out again and is converged back again by the objective lens and down onto the sample. This initial convergence can be at different heights, i.e.

close to the lens or further away. The closer it is to the lens, the smaller the spot diameter at the point of convergence. The further away, the larger the diameter of this point. Therefore, the condenser lens currently controls this initial spot size and is referred to as the spot-size control. The diameter of this initial convergence (also called a crossover point) affects the final diameter of the spot the beam makes on the sample. The condenser lens reduces the diameter of the probe. Changing the current in the condenser lens will result in changing the diameter of the beam and can get a beam with a small diameter. A smaller probe diameter and narrow beam will enable better resolution. However, the drawback of a narrow beam is worse signal-to-noise ratio, while in the case of beam with large diameter, the signal-to-noise ratio will be better. The source size of the FEG is comparatively small so that the amount of demagnification necessary to produce small probe sizes is less than that of other electron sources [9–12].

4.7.4 Scanning Coils

Scanning coils which are also called beam deflection coils are used to scan the sample surface, and the current in these coils is increased in order to get a higher magnification. The role of the scanning coils is to deflect the electron beam above the object in a zigzag pattern, and with help of this scan movement, the creation of the image occurs on the monitor in synchrony. The refreshing rate on the screen and amount of noise in the image depends on the scan velocity. In case of slow scan, the refreshing will be slow; the signal will be high while the noise will be low. On the other hand, if the scan is fast, the refreshing will be fast, the signal will be low while the noise will be high. Scanning coils mostly contain upper and lower coils, which avoid the creation of a circular shadow at low magnification [9–12].

4.7.5 Objective Lens

The objective lens is the lowest lens in the column which focuses the probe on the sample. The objective lens is used to focus the beam on the specimen. Coarse focusing of the specimen can be done by choosing the working distance (WD = distance between the bottom of the objective lens and the specimen), focusing the objective lens to coincide with this value and then changing the physical height of the specimen to bring it into focus. Fine focusing can be subsequently done solely with the objective lens. WD needs to be decreased for a specimen to be well focused. If the WD is less, it means that the sample is at a higher position and close to the objective lens. Therefore, greater force is needed to deflect the electron beam by objective lens. The shortest WD generates beam with the smallest diameter and gives the poorest depth of field thus getting an image with the best resolution [9–12].

4.7.6 Stigmator Coils

The stigmator coils are utilized to correct irregularities in the x and y deflection of the beam and thus to obtain a perfectly round-shaped beam. When the beam is not circular, but ellipsoidal, the image looks blurred and stretched [9–12].

4.7.7 Apertures

For refinement of the beam, different size apertures are utilized. The aperture with small size produces a very fine beam. Small objective aperture sizes will produce better resolution, good depth of field and minimal charging. The selection of correct aperture size depends on the requirement of sample and user. The choice and selection of accurate aperture size is the responsibility of the user. Apertures are circular holes in metal discs on the micron scale. The net effect of the aperture is to reduce the effects of spherical aberration. Highest working distance (which is the distance between the sample surface and the objective lens) and small aperture produces images that look in focus over a big change in Z-axis [9–12] (Fig. 4.9).

4.7.8 Specimen Chamber

SEM has a specific sample holder where the stub should be fixed containing the sample on the surface. Generally, carbon tape, silver paste, copper tape, etc. are used for sticking the sample to the stub. If the sample is electrically conductive,

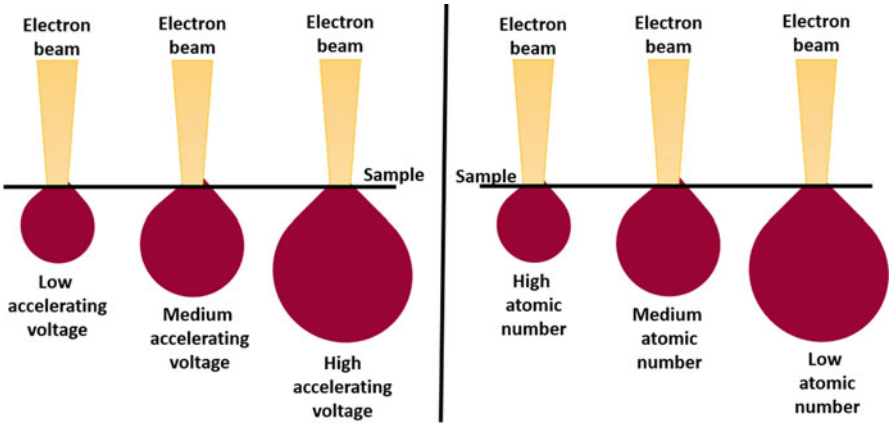

Fig. 4.9 Schematic dependency of interaction volume and penetration depth on the accelerating voltage of the beam and atomic number of the sample

then it can avoid overcharging on the surface. This overcharging may introduce extreme brightness and poor images. Thus, non-conductive samples like polymers are usually sputter coated with a thin layer of carbon or metal that readily reflects electrons and provides a conductive surface for electrons, e.g. gold and platinum. The non-conductive materials must be sputtered in order to reduce the charging problem. After that the sample-covering stub will be fixed in the sample holder and should be put in the sample-holding chamber or specimen chamber. Then vacuum should be generated and ensure that FESEM is at good vacuum level, and proper vacuum level is attained. The sample can be moved in horizontal and vertical directions in FESEM. The position of the specimen can easily be adjusted by using a joy stick that steers in the left-right axis, or forward and backward. Similarly, the sample can be tilted, rotated and moved in *Z*-direction. By this movement, the sample can bring close or keep away from the objective lens. The "secondary electron emission" detector is located at the rear of the object holder in the chamber.

4.8 FESEM Operation

The instrument should be properly checked before systematic operation. Gun vacuum, filament current, emission current and voltage should be checked. If all the things are in order, then prepare the sample. The sample should be dry and free of excessive outgassing. SEM has a specific sample holder where the stub should be fixed containing the sample on the surface. Generally, carbon tape, silver paste, copper tape, etc. are used for sticking the sample to the stub. First two-sided carbon tape should be fixed on the stub, and then a thin layer or a small amount of material will be placed on the carbon tape because the thin layer properly sticks with the carbon tape which reduces the charging problem and helps in getting a good image. Some requirements are needed when operating SEM analysis. Additionally, when using SEM, the samples have to be electrically conductive to avoid overcharging on the surface. This overcharging may introduce extreme brightness and poor images. Thus, non-conductive samples like polymers are usually sputter coated [4] with a thin layer of carbon [1] or metal that readily reflects electrons and provides a conductive surface for electrons, e.g. gold [2] and platinum [8]. The non-conductive materials must be sputtered in order to reduce the charging problem. After that the sample-covering stub will be fixed in the sample holder and should be put in the sample-holding chamber or specimen chamber. The stage height which is working distance and specimen surface offset must be properly adjusted to avoid the contact of the specimen with lens column and thus avoid specimen and stage damage. For the correct stage height estimation, the sample height must be correctly estimated, which is the distance between the top surface of the sample holder and surface of the specimen. Gun valve should be closed during sample exchange. The gun valve separates the upper column from the rest of the microscope [9]. Then vacuum should be generated and ensure that *microscope is at good vacuum level* and *proper vacuum level is attained*.

Once pressure in the main chamber reaches to 9.6×10^{-5} Pa (JEOL JSm-7600F), then set the accelerating voltage (0.5–30 kV) while keeping in mind that high voltage can give better resolution, but at the same time, it also causes charging problems for non-conductive materials. Thus, it will be better to select high accelerating voltage for conductive materials, but lower voltage should be selected for non-conductive materials in order to avoid charging issues. Also select better working distance (WD) which is the distance between the sample surface and the objective lens. The stage height (Z) will also be set and the stage will rise to the set Z depending on the specimen surface offset. A better resolution will be achieved through smaller WD, but keep in mind that very small WD may cause accident of the sample with the lens column, and therefore WD between 6 and 8 mm are usually suggested. After setting all these things, switch on the gun and the focused beam is rastered across the surface of the sample with the help of deflector coils which is controlled by the scan generator. The size of the rastering pattern is under magnification control. Once the beam is focused on the surface of the sample, the magnification should be changed in order to change the size of the rastered area on the sample. The size of the monitor raster pattern is constant. Magnification will increase if we reduce the size of the area scanned on the specimen [9], which can be represented as:

$$\text{Magnification} = \text{area scanned on the monitor}/\text{area scanned on the specimen}$$

Electron gun alignment is important in all the electronic microscopes, which must be aligned in SEM. The image should remain stationary during changing focus. If the object is moving during focusing, this indicates that the beam (electron gun) is not aligned. Similarly, astigmatism correction is important which is caused by different focal lengths for rays of various orientations, resulting in a directional image blur.

During SEM analysis, one has to keep a suitable probe current (i_p) (the applied current to specimen which produce numerous imaging signals) in a small probe diameter (d_p) (the diameter of the final beam at the surface of the specimen) which would increase the probe convergence angle (α_p) (the half-angle of the cone of electrons converging onto the specimen). But this is not the case due to aberrations in the optic system (more details are given later). A small probe diameter always comes with a decrease in probe current. These parameters are interrelated in other ways. For example, a decrease in accelerating voltage (kV) (the voltage with which the electrons are accelerated down the column) will result in a decrease in probe current as well as an increase in probe size [9].

Electromagnetic lenses, i.e. condenser lenses, are involved in demagnification; the objective lens focuses on the specimen as well as demagnifies. A smaller probe diameter will enable better resolution. The source size of the FEG is comparatively small so that the amount of demagnification necessary to produce small probe sizes is less than that of other electron sources. The objective lens is used to focus the beam on the specimen. Coarse focusing of the specimen is done by choosing the

working distance (WD = distance between the bottom of the objective lens and the specimen), focusing the objective lens to coincide with this value and then changing the physical height of the specimen to bring it into focus [9]. Fine focusing is subsequently done solely with the objective lens.

A: Specimen in focus.
B: Working distance needs to be decreased for specimen to be in focus.

4.9 Operator Control

4.9.1 Accelerating Voltage

The sample can be checked at different accelerating voltages (1–30 kV) depending on its nature. The high accelerating voltage causes reduction in lens aberrations which result in a smaller probe diameter and enhance resolution. The high accelerating voltage enhances the probe current at the sample. For an image of good contrast and high signal-to-noise ratio, a least probe current is required. The high accelerating voltage also causes charging of a sample especially non-conductive and beam-sensitive material. Thus, it is important to control accelerating voltage which can charge up and ultimately damage the material. High accelerating voltage increases the electron penetration more into the sample which ultimately obscures, making the surface features vague [1–12].

4.9.2 Emission Current

Different emission currents can be applied during the checking of materials. The increase in emission current enhances the probe current at the sample which causes charging of a sample, especially of non-conductive and beam-sensitive material. Thus, it is important to control the emission current which can charge up and ultimately damage the material [1–12].

4.9.3 Probe Diameter

The probe diameter or spot size could be varied by altering the current to the condenser lens. The decrease in probe diameter will cause increase in resolution while a decrease in lens aberration and probe current. The image with large spot size will be less sharp but look smooth, while lower probe size will result in sharp but coarser image appearance because of lower signal-to-noise ratios related to a lower beam current. In all types of guns, the smaller probe diameter can be obtained

with higher accelerating voltage. In the case of a tungsten thermionic gun, the source size of the gun is larger and thus has a larger minimum probe diameter. Similarly, in the case of a tungsten thermionic gun, there is a dramatic increase of spot size with increasing probe current, while it is relatively small in FEGs. The spot size is small at high accelerating voltages while it starts to enhance as the accelerating voltage decreases. The probe diameter can determine the sizes of the sample area from which the signal is produced [1–12].

4.9.4 Objective Aperture Size

The objective apertures have a range of sizes that can be selected. Reducing the diameter of the aperture causes decrease in lens aberrations and thus increases the resolution. The decrease in the diameter of the aperture causes

- Decrease in probe current
- Decrease in the convergence angle of the beam and thus increase the depth of focus

The larger diameter of the aperture results in a larger beam convergence angle and thus a reduced depth of focus. However, when using the same working distance but with a narrower diameter aperture, an increased depth of focus results [1–12].

4.9.5 Working Distance

Working distance (WD) which is the distance between the sample surface and the objective lens is adjustable. The enhancement of working distance causes increase in depth of focus and probe size and thus decreases the resolution [1–12].

4.9.6 Focus and Alignment

For better result, the focus and alignment are important, and for the alignment of the microscope, the apertures must be centred. If the microscope is not aligned and trying to focus the beam on the material in order to take image, the image will move because the objective aperture is not centred. For correcting of this, one needs to wobble the current to the objective lens and align the aperture to minimize movement in both the X and Y plane. This adjustment can be done consecutively at higher magnifications [1–12].

4.9.7 Astigmatism

Adjustment of objective lens astigmatism is also crucial which can be done at higher magnifications. In case of high astigmatism, the image is streaking on either side of focus. When extreme, astigmatism displays itself as a streaking of the image even if streaking is not clear, astigmatism should be fine-tuned to acquire quality images [1–12]. An operator turns for objective lens astigmatism by using current differentially to a ring of stigmator coils surrounding the objective lens. The compensating field in the image is responsible for a more circular (symmetric) form of the beam. The objective lens is used primarily to focus and initially magnify the image. It is needed to do fine focusing at high magnifications because increase in magnification relates to a smaller rastered area on the specimen. When the magnification decreases, the focus gets better. During experiment, first estimate the highest magnification for obtaining images and then double that magnification value and conduct final aperture alignment and astigmatism correction, and focus there to get your required images. Alignment must be done upon any change in accelerating voltage, spot size, etc. [1–12].

4.9.8 Tilt

After tilting the sample, the incident beam electrons move along greater distances in the region near the surface. Due to this occurrence, more SEs are produced in this area as compared to areas which are normal to the beam, and these SE signal-produced images reveal the so-called edge effect. Edges and ridges of the sample due to emission of more SEs look brighter in the image [1–12].

4.9.9 High-Resolution Imaging

The resolution means minimum space at which two specimen features can be distinguished as distinct or separate. To obtain high-resolution images, the probe diameter should be adjusted to the scale of interest and make sure that a minimum level of contrast occurs between the appropriate probe current and scan rate settings. SEs give a high-resolution signal and the interaction volume will be quite large even with small probe diameters, and thus at very small magnifications, the pixel overlap will take place. The high resolution can be achieved at low and high voltage, but at low voltage, contamination will be a serious problem which results from the interaction of the electron beam with residual gases and hydrocarbons on the specimen surface [1–12].

For low atomic number samples, it is difficult to get high-resolution images because it produces low SEs and thus poor signal-to-noise ratio. In such a case,

ultrathin metal coating can increase the SE yield while thicker coatings can also produce high SE yield, but in case of thicker coating, the metal particles may appear in the image at high magnification. The uncoated sample image is quite blurry, having no defined edges. Considering the coated sample, the rapid change in metal thickness changes as the beam strikes on the sample which leads to SE signal maxima that allows the size and shape of the feature to be clearly resolved. The coating process acts as a remedy for the charging under the beam considering non-conductive samples [1–12].

4.9.10 Charging

Charging is one of the most important problems in SEM analysis. During charging process, when the electron beam hits the sample surface, it (sample) cannot conduct the beam energy. The possible reason is that the electrons lose all initial energy and are held by the specimen. If a specimen is a conductor, then this charge flows to ground in case of suitable connection. If the ground path is broken, in such a case the conductive specimen collects charge, thus raising its surface potential. Non-conductive specimens will evidently amass charge. The subsequent image will "glow" or show general distortion in the image with enhancement in electron production [1–12].

Conductive tapes or paints bind both conductive and non-conductive samples to their holders. Non-conductive samples contain the thin conductive films (carbon, gold, platinum, etc.) to make the electron flow easy [1–12].

4.9.11 Scan-Square Method of Testing the Conductivity of a Specimen

(i) Focus should be on an area at a high magnification.
(ii) Wait for a few seconds, allowing the beam to irradiate the particular area.
(iii) The magnification should be reduced, and then observe the sample.
(iv) If a bright square is shown, it means negative charging is probable. To avoid it, lower the voltage.
(v) Positive charging is probable only when the dark square appears then rapidly disappears. So, raise the voltage. Note: if the dark square is still there, contamination is most likely responsible for it.
(vi) The effect of charging is intensified at higher magnifications, so make sure to clear these conditions at levels near or at the highest magnification you wish to use.
(vii) To reduce charging in thin metal coatings, the following approaches can be utilized to reduce charging: (a) the probe current should be reduced; (b) the

accelerating voltage should be lowered; (c) the specimen should be tilted to discover a balanced point between the amount of incident electrons and the electrons that escape out of the specimen; (d) imaging should be done with BSEs; (e) rapid scan rates and frame integration should be used; (f) insulator's E2 value should be determined.

E2 Value While calculating the sum of the BSE and SE coefficient at very low kV, an energy range is found where this sum is positive. The presence of this positive form of charging shows that more electrons are emitted from the sample as compared to a primary electron beam. Apart from glowing, a dark box (from the scan footprint) will appear as secondary electrons are discharged. E1 and E2 are the charge balance achieved at voltages near the area of positive charging. Considering each material, E1 and E2 are constants. E2 is obtained at a higher accelerating voltage for uncoated observation, thus using a higher resolution condition of the SEM [1–12].

4.9.12 Specimen Damage by Electron Beam

Mostly the loss of electron beam energy takes place at the irradiated point in the form of heat generation. Polymer materials and biological specimens due to their low heat conductivity are easily damaged using the electron beam [1–12].

The following approaches can be applied to avoid this damage:

(i) The electron beam intensity should be decreased.
(ii) The exposure time should be shortened.
(iii) Low magnifications should be used for imaging large scanning areas.
(iv) The thickness of coating metal should be controlled on the specimen surface.

4.10 Development in SEM

Over the past years, SEM has been developed and equipped with several electron emitters, detectors and systems to increase the microscope liability and overcome some of its disadvantages. For example, SEMs have been frequently equipped with an energy-dispersive X-ray (EDX) analysis system to perform the elemental analysis of certain materials [1–12]. The electron emitter of the microscope has also passed through several improvements, from traditional tungsten and carbon wire to higher performance lanthanum hexaboride (LaB_6) to field emission (FE) gun. Field emission scanning electron microscope (FESEM) has been further developed into cold gun FESEM and Schottky in-lens thermal FESEM [5]. In addition, the invention of environmental SEM enables many natural samples such as polymers, food, drugs and biological and forensic materials to be studied at ambient conditions and without any pretreatment. Thus, the need of pretreating the samples to obtain

a solid, dry and electrically conductive material became no longer a requirement. Furthermore, Hitachi was able to substitute the traditional backscattered and secondary electron detectors by producing a new detector, environmental secondary electron detector (ESED), which is able to detect ions in addition to electrons and provide better surface information [2]. Additionally, we can conduct SEM-based scanning transmission electron microscope (STEM) imaging, that is, STEM can be carried out in a SEM by adding different detectors. A fine, highly focused beam of electrons is scanned over a thin specimen, and the electrons that pass through the thin sample are collected on a detector placed beneath the sample, yielding the desired bright-field images. The bright-field image in the STEM looks quite similar to that observed from the same specimen in the normal TEM measurements. FESTEM measurements have become important for some reasons, for example, suitability for the observations of carbon-based nanomaterials where high beam energy is not always required, since light atom-based material is easily penetrated by less energetic electrons. The FE source reasonably combines with scanning electron microscopes (SEMs) whose development has been supported by advances in secondary electron detector technology [1–12].

4.11 Difference Between SEM and FESEM

(i) Emitter type is the main difference between the SEM and FESEM. SEM uses tungsten filament and crystal of LaB_6 as electron guns which produce or generate electrons by "heating", while in the case of FESEM, no heating but a so-called "cold" source is employed. Field emission is the emission of electrons from the surface of a conductor caused by a strong electric field. Thermionic emitters use electrical current to heat up a filament; the two most common materials used for filaments are tungsten (W) and lanthanum hexaboride (LaB_6). When the heat is enough to overcome the work function of the filament material, the electrons can escape from the material itself. Thermionic sources have relatively low brightness, evaporation of cathode material and thermal drift during operation. Field emission is one way of generating electrons that avoids these problems. A field emission gun (FEG), also called a cold cathode field emitter, does not heat the filament. The emission is reached by placing the filament in a huge electrical potential gradient. The FEG is usually a wire of tungsten (W) fashioned into a sharp point.
(ii) FESEM needs high vacuum as compared to SEM.
(iii) FESEM needs high acceleration voltage as compared to SEM.
(iv) The electron beam produced by the FE source is about 1000 times smaller than that in a standard microscope with a thermal electron gun.
(v) FESEM is high-resolution surface-imaging tool as compared to SEM.
(vi) Clear and well-focused images of particles/surfaces are possible by FESEM at higher magnifications as compared to SEM.

(vii) The resolution of a SEM is basically given by the minimal spot size which can be formed and then rastered over your sample. This probe is formed by demagnifying the image of your gun. A field emission gun emits the electrons from a much smaller area than a thermionic gun. Therefore, the probe will principally be smaller for a FEG instrument compared to a W or a LaB_6 instrument. Additionally, the coherency is much higher and the energy spread smaller. This again allows to more perfectly focus the beam. FESEM has more intensive and at SEM.
(viii) FE gun has the following advantages over the others (W or LaB_6). Crossover diameter is less. Spot diameter is also less compared to thermionic emission. It is more coherent and energy spread is very low.
(ix) The brightness will be very high compared to other thermionic source.
(x) All these will make FESEM give better resolution than SEM.
(xi) Crossover diameter – the point at which the electrons are focused when leaving the electron gun, virtual electron source. For SEM a smaller crossover gives smaller final electron spot, i.e. higher resolution.
(xii) Crossover-free beam pathway of forming beam without crossover is implemented by some manufacturers. It theoretically eliminates some aberrations caused by electron-electron interactions in a crossover spot. Since it is not supported by all manufacturers, we can assume that other ways of increasing resolution are at least as good as that one.

4.12 Applications of SEM

SEM can measure and analyse the following parameters:

(i) Thickness of films and thin coatings
(ii) Surface morphology and appearance
(iii) Size and size distribution
(iv) Shape and dispersion of particles, fibres, nanomaterials or any other additives in composites and blends
(v) Height and lateral dimensions of nanometre-sized materials
(vi) Cell size and size distribution in foam materials
(vii) Chemical composition and elemental analysis of nano- and micro-materials
(viii) Fracture and structural defects analysis

4.13 Application of SEM in Nanomaterials Characterization

SEM is a multipurpose, non-destructive tool which tells the comprehensive information about the morphology, arrangement and composition of nanomaterials. Especially, FESEM has the ability to supply clear and high-quality images and

information about the composition of nanomaterials which is required for various demanding applications in the field of nanotechnology. SEM has been utilized to study the surface morphology of nanomaterials and nanoparticles. Nanotechnology has intensely motivated the development and improvement of recent electron microscopy with many demands, especially for increasing resolution and to achieve more information about nanomaterials. Generally, the nanomaterials have size in the range typically from hundreds of nanometres down to the atomic level (approximately 0.2 nm), and the properties of nanomaterials largely depend on their size. Nanomaterials can have diverse or higher chemical/physical properties as compared to the bulk size of the same material [13–17]. High relative surface area and dominant quantum effects are the main reason and key origins for these features and size. Chemical reactivity of nanomaterials is highly dependent on the surface area of nanomaterials, and thus rise in specific surface area increases chemical reactivity, thus making nanomaterials suitable for many demanding applications.

The high reactivity of nanomaterials makes them useful catalyst in photocatalysis as well as electrocatalysis. Quantum effects play an important role in improving various properties of nanomaterials, and it starts to play role as the size of matter is reduced to tens of nanometres or less. Quantum effects significantly alter the optical, magnetic or electrical properties of materials [15]. For example, gold nanoparticles can appear blue, red or yellow in colour as a function of their size. The main problem in nanoscience is the uniform growth of nanomaterials especially nanoparticles of the same size and size distribution. The growth of nanoparticles with same size is important for specific intended applications. Thus, the growth of nanoparticles with uniform size is one of the crucial challenges [14]. Another challenge is to control the shape of nanomaterials and grow nanomaterials with uniform shape [14]. Shape control of nanomaterials has been emphasized because specific shapes of nanomaterial tune the properties with a greater versatility than can be achieved otherwise [18–20]. In face-centred cubic (fcc) metal particles, for example, the crystallographic {111} and {100} surfaces are different not only in the surface atom densities but also in surface energies, so that single-crystalline silver or gold nanoparticles with sizes smaller than ∼10 nm show intriguing particle shapes such as truncated octahedron or cuboctahedron [21, 22]. In addition, twinned metal particles are found [21, 22]. Twinning is the result of two subgrains sharing a common crystallographic plane, and thus multiple twinning on alternate coplanar planes produces cyclic twinned polyhedron (decahedron and icosahedron) where the twinned tetrahedral subunits are arranged around a fivefold axes [23].

Furthermore, construction of superstructures (ordered assemblies or super lattices) of nanomaterials is of recent key interest not only in future electronics applications but also in fundamental nanoscience [24–29]. Metal (gold and/or silver) nanoparticles are ideal "building blocks" for two- and three-dimensional super lattice structures. Preparation of ordered assemblies often requires surface passivation of the building blocks to protect against modifications of their properties by their environment, as well as to inhibit sintering. The organic surface protection of nanoparticles enables to self-assemble into their super lattices, so that controlling the chemical functionality of the organic monolayer allows the collective properties

of the nanoparticle super lattices to be engineered [24]. Since FESEM utilizes a beam of very energetic electrons to scrutinize materials on an extremely fine scale [9], therefore, FESEM is the highest resolution instrument and extremely useful tool to analyse surface morphology, shape, features, size, composition and crystalline structure with high-resolution surface imaging in the area of nanoscience.

FESEM has been used to identify the surface morphologies of a variety of materials. Here, we explain some of the images of various materials such as metal oxide, polymer and metal oxide-based polymer materials. In an embodiment, the co-doped CuO/ZnO nanomaterials were examined through high-resolution FESEM indicating a nanostructure ingredient with nanorods shape for the chemical sensor application. However, the rod morphology was due to zinc oxide, and the aggregated rod shapes were displayed by copper oxide. The average morphology of ZnO rods was 530 nm, and the aggregated rod shape due to CuO was 8 μm; however, these aggregated rods also consist of other sub-nanorods whose morphologies were 183 nm [13]. ZnO nanoparticles were grown in the form of dense particles with smooth surface for the environmental remediation and methanol sensor [20]. In one of our recent works, we supported the ZnO nanomaterials onto the cellulose acetate polymer for the synthesis of coumarin where it displayed the flower shape morphology under the FESEM imaging. A close look showed that these nanomaterials have flower shape morphologies; however, on aggregation it displayed sheet morphology [14].

The Co_3O_4-based nanomaterials were synthesized for the electrochemical water splitting, where the CeO_2/Co_3O_4 and calcined CeO_2/Co_3O_4 as well as TiO_2/Co_3O_4 and Fe_2O_3/Co_3O_4 were grown in the form of particle morphologies [15]. Other Co-based nanomaterials Co-Al and Co-Ni were grown in the form of spherical particles; however, the Co-NiAl have sheet-like morphology after the FESEM imaging. Other Co-based materials were evaluated for the electrochemical water splitting, such Co_3O_4, $Co_3O_4@SiO_2$, $ZnO@SiO_2$ and Fe_2O_3/Co_3O_4, which were grown in the form of spherical particles; only Fe_2O_3/Co_3O_4 were grown in mixed particle and fibre morphologies. The $Co_3O_4@SiO_2$ showed the mesoporous morphology with an unprecedented surface area. The Zn-Al/C and Zn-Cr/C nanocatalyst were grown in layered double hydroxide morphologies and applied for the photocatalytic reduction of various cationic and anionic dyes. The FESEM images showed the sheet-like shape and morphology for both the catalysts; however, these sheets were made of small particles; therefore, it can suggest that the aggregation of the particle makes sheet-like shape of the corresponding catalysts [17]. Another sheet morphology was examined under the FESEM for the Cd-based materials (Cd-Al/C and Cd-Sb/C), where the Cd-Al/C was grown in the form of layered double hydroxide and the Cd-Sn/C in the form of nanomaterials, although both displayed the sheet morphology. The Cd-AL/C was indicating strong catalytic performance in the decolouration of organic dyes as compared to Cd-Sb/C due to its layered double hydroxide morphologies [18]. The uniform morphology particles were observed for $CoSb_2O_6$ under the FESEM for the chemical sensor and environmental remediation [19]. Similarly, aggregated nanosheets were observed for $CuO\text{-}TiO_2$ [21]. Ag_2O were synthesized in the form of spherical particle with uniform size for 4-nitrophenol

sensing [22]. Cage-like mesoporous core-shell composites with H-type ZSM-5 are synthesized and then encapsulated Pt nanoparticles for the toluene oxidation [23].

FESEM is an extremely important tool for the determination and investigation of inorganic-organic interaction or dispersion. The dispersion of inorganic materials inside the polymer host materials is important, because it controls many characteristics of the synthesized materials. The FESEM are largely used for the polymer and composite materials characterization. The FESEM images of poly(propylene carbonate)/ZnO composite materials displayed spots of ZnO in the polymer host materials. No aggregation was observed below 5% of ZnO content; however, on increasing the agglomeration, it was observed in the polymer host materials. These composite materials are used for the packaging application [24]. Similarly, poly(urethane acrylate) (PUA) and tetrapod ZnO whisker (TZnO-W) composite films displayed homogenous dispersion of TZnO [25]. In our group an efficient adsorbent material $Co_3O_4@SiO_2$ embedded in the chitosan polymer host materials was synthesized for the adsorption of organic dyes. The white spot in the FESEM images indicates the $Co_3O_4@SiO_2$ materials in the polymer host materials. These films were extremely active for the adsorption of organic dyes and indicate an extremely high antibacterial activity [26]. Similarly, in another embodiment, the Ni/Al nanostructured materials were incorporated to the chitosan material in the form of sphere and sheets, indicating high antibacterial and high adsorption performance [27]. Polyethersulfone-based spherical materials were synthesized and incorporated different materials such as SiO_2, carbon black and cellulose acetate-CB. All these spherical materials displayed antibacterial activity and adsorption of nitrophenols. The FESEM displayed the rough nature of the PES polymer with about 2.26–2.45 mm and incorporation of SiO_2, cellulose acetate and carbon black. Then Cu^0 nanoparticles were grown on the surface of PES-cellulose acetate-carbon black materials because of its high catalytic activity. The Cu^0 nanoparticles show strong performance for the reduction of 4-nitrophenol [28]. Similarly, PES-CA-Ag_2O membrane was synthesized and evaluated for their water permeability, mechanical strength, and porosity and contact angle. Cu^0 nanoparticles were grown on the surface of these membranes and then applied for the reduction of 4-nitrophenols. All the membranes and Cu nanoparticle-supported membranes indicated good antibacterial activity. The FESEM images of the Ag_2O indicated the agglomerate morphology of the particles, while the pure PES and PES-CA displayed a dense rough porous nature; while with the addition of Ag_2O nanoparticles to the PES and PES-CA, a well-dispersed nature of the membrane was observed. The Cu nanoparticles are supported on the PES-CA and PES-CA-Ag_2O indicating uniform particles [29]. Besides the aforementioned description, FESEM is used to investigate the particle size, morphology and textural characteristics of a number of materials.

4.14 Summary

FESEM is a useful and leading machine that is capable of achieving a detailed visual image of a particle with high-quality and spatial resolution. It can provide information about the morphology, composition and structure of the materials, especially nanomaterials. A special care is needed during the operation and material analysis. This chapter discussed briefly about SEM techniques, their utilization, principle, their advancement, operation, samples preparation and applications in materials science.

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